

Doctoral Thesis

Catalytic and Sorption Measurements Using Flux Response Technology

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Abstract

Advancements in characterisation techniques in the field of heterogeneous catalysis have been explored, in particular the powerful *in situ* perturbation method, Flux Response Technology (FRT). The adaptation of FRT as a novel *in situ* perturbation technique in gas sorption measurements continues to yield consistent results with literature values. This is made possible because FRT measures miniscule changes in transient flows in the order of $10^{-2} \mu\text{l}/\text{min}$ for gaseous processes involving a change in volume (dV/dt). These changes are measured directly by a very sensitive differential pressure transducer (DPT) in a pneumatic system analogous to an electrical Wheatstone bridge assembly, whereby gas molecules replace electrons and capillaries function as resistors. By showing the successful incorporation of the measurements of adsorption capacities and diffusivity coefficients in the same experimental window, FRT's use as a bolt-on technology for the rapid screening of catalyst material has been highlighted. The technique possesses a distinct advantage in requiring no prior calibrations to the system, enabling the analysis of a broad spectrum of materials and gases. The FRT technique also features a unique ability in being able to act as a dual flowrate and composition detector through the use of carefully calculated delay lines to separate changes in flowrate caused by perturbations of concentration and changes in composition. The FRT technique provides a quick, simple, accurate, and inexpensive method of characterising material properties *in situ* in heterogeneous catalysis.

Several studies into the dynamics of gas sorption processes utilising FRT measurements on adsorbents were undertaken in the completion of this PhD. The diffusivity parameters of propane in varying alumina/ CeZrO_x washcoats of Cordierite monoliths were investigated under isothermal conditions. A novel method of analysing FRT derived response profiles with the Zero Length Column (ZLC) model was established and reported on. The diffusion coefficients obtained were consistent with previously reported macroscopic data and compared well when evaluating the structural differences of the washcoats of each sample (Granato *et al.*, 2010). The

dynamics of ammonia sorption on commercially available zeolites with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios was analysed to investigate the total acidity of these zeolites. The dynamics of carbon dioxide sorption were also investigated to analyse the total basicity of the same zeolite samples. Process optimisations were conducted to obtain an ultra fast isotherm measurement technique for the analysis of nitrogen sorption on aluminium oxides with varying surface areas at 77 K. Finally, insights into the development of a dynamic parallel performance testing (DPPT) FRT setup were undertaken to directly compare the activities of catalytic material operating side by side.

To my dad

Deeshash

Author Declaration

I, Ayodeji Oladipo Sasegbon, declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institute of tertiary education. Information derived from the published and unpublished work of others has been acknowledged in the text.

The work was carried out between October 2009 and June 2014 at Imperial College London under the supervision of Professor Klaus Hellgardt.

Ayodeji Sasegbon

June 2014

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List of Publications

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- Maguire, N., **Sasegbon, A.**, Abdelkader, A., Goguet, A., Hardacre, C., Hellgardt, K., Shekhtman, S. O. (2013). Using temporal analysis of products and flux response technology to determine diffusion coefficients in catalytic monoliths. *Chemical Engineering Science*, 87, 224–233.
- Sasegbon, A.**, & Hellgardt, K. (2012). Flux response technology applied in zero length column diffusivity measurements. *Adsorption*, 18, 5–6, 403–415.
- Palmer, C. A., **Sasegbon, A.**, & Hellgardt, K. (2011). In situ measurement of gas adsorption processes using Flux Response Technology. *Adsorption*, 17(5), 783–794.

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Chapter 1

Introduction

1.1. Background

On the 29th of March 2014, the Intergovernmental Panel on Climate Change (IPCC) published a damning report on the serious impacts and future risks of climate change on human and natural systems that have occurred over the course of the 21st century (Field *et al.*, 2014). The report gathered worldwide press coverage and once again highlighted the dangers and jeopardies that currently exist with food security, temperature rises, and adverse weather effects being witnessed throughout global communities. Seven years earlier the United Nations Population Fund's executive director, Thoraya Ahmed Obaid, issued a stark warning in a report generated to assess the world's growing population. With a projected rise in the world population from 7.1 billion today to 9.2 billion by 2050, the general public were left to chew on her bleak conclusion, "we are not ready for them," a resoundingly macabre thought of grave concern to the rest of the world (UNFPA, 2007). The consequences we face of not being able to provide the basic needs and freedoms of food, housing, education, and employment to surging demographics in itself would fund extremist behaviour, civil unrest, and ultimately violence – unfortunate acts that we witness in shock and horror in the world today. The former vice president for eco-responsibility at Sun Microsystems, David Douglas, shared a profound thought relating to the next billion inhabitants of earth with the famous author Thomas Friedman, in his book – *Hot, Flat, and Crowded*. If these billion people were supplied with a sixty-watt incandescent light bulb to light up their homes, we would be faced with having to provide 10,000 megawatts (assuming the bulbs are used four hours per day), the equivalent of up to twenty new 500-megawatt coal-burning power plants – just so these billion can switch a light on! (Friedman, 2008).

Sobering conclusions, yet, scientists and engineers have been tasked with solving such problems for many centuries. The incentive for innovation could not be made

clearer and the future of climate resilience will depend on a variety of factors ranging from areas to do with new technologies, adaptation of familiar techniques, and the development of sustainable practises. One such area that has helped to significantly improve the livelihood of mankind and will continue to play a key role in the future prospects of planet earth can be found in the field of catalytic research.

Catalysis dates back to the dawn of civilization and without realizing its impact, early man first pioneered processes of producing alcohol (fermentation), sulphuric acid, cheese, soap, and ether. Ever since then, advancements in the field of catalysis continue to aid in the quest of meeting the increasing demands of living necessary for the survival of the human race. The successes of research in the field of catalysis have a direct effect on solving many fundamental technological, environmental, and social problems that face humanity. The term “catalysis” was coined by the famous Swedish chemist Jöns Jacob Berzelius in 1835 when he was able to systematically record and correlate the observations made by other chemists of the same era of a new entity capable of promoting the occurrence of a chemical reaction by a “catalytic contact” (Farnetti *et al.*, 2009; Lindström & Pettersson, 2003). Many innovations have included the efficient utilisation of raw materials, the formation of new sources of raw materials, and the invention of new materials and substances with predetermined intrinsic properties. The development of efficient systems for environmental protection, the mastering of new sources of energy, and the improvement of existing ones hold precedent in policies issued and campaigned for by leading scientific societies throughout the world. Furthermore, the development of new processes and technologies in chemistry and biology have all played monumental parts in shaping mankind’s existence up to the 21st century and will continue to govern the life of human beings in centuries to come.

By the end of the 18th century, the evolution of industrial catalysis brought forth processes such as the catalytic production of sulphuric acid through the lead chamber process where the oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) was performed in the presence of a nitric oxide catalyst mixture (NO/NO_2). This heralded the production of other basic inorganic chemicals such as nitric acid (HNO_3) and ammonia (NH_3) production through the Haber process. Propelled by the need for NH_3

as a key ingredient for agricultural fertilizer and later for the bulk chemical needs required for the explosives in World War I, the beginning of the 20th century marked the start of catalysis playing a major role in the chemical industry. This is shown in Table 1.1, detailing a summary of some of the important industrial catalytic processes produced through the decades of the 20th century.

Table 1.1: Development of key industrial catalytic processes (Bartholomew & Farrauto, 2005)

Year of First Commercialisation	Process	Catalyst	Area of Industry
1875	Sulphuric acid mfg.	Pt, V ₂ O ₅	Chemicals
1903	Nitric acid mfg.	Pt gauze	Chemicals
1913	Ammonia synthesis	Fe/Al ₂ O ₃ /K ₂ O	Chemicals Fertilizers
1923	Methanol synthesis	CuZnO	Chemicals
1930	Fischer-Tropsch synthesis	Fe/K/CuO, Co/Kieselguhr	Petroleum
1920-40	Hydrogenation reactions	Ni/Kieselguhr	Petrochemicals
1936-42	Catalytic Cracking	SiO ₂ -Al ₂ O ₃	Petroleum
1937	Ethylene oxidation	Ag/Al ₂ O ₃	Chemicals
1942	Paraffin alkylation	H ₂ SO ₄ , HF	Petroleum
1950	Catalytic Naphtha Reforming	Pt/Al ₂ O ₃	Petroleum
1955	Stereospecific Polymerisation	TiCl ₃ /Al(R) ₃	Chemicals
1960	Wacker Process	PdCl ₂ (homogeneous)	Chemicals
1964-8	Zeolitic catalytic cracking Hydrocracking	Exchanged X, Y zeolites	Petroleum
1976, 1981	Auto Emissions Control	Pt, Pd/Al ₂ O ₃ , Rh/Al ₂ O ₃	Automotive Environmental Control
1980-95	Selective catalytic reduction of NO	VO _x TiO ₂ , zeolites	Environmental Control
1980-95	Shape selective reactions e.g. mfg. of ethylbenzene	New zeolites, e.g. ZSM-5	Petrochemicals

In the early 20th century, basic organic chemicals were largely based on a primary feedstock of coal through liquefaction, distillation of coal tar, acetylene (from coke), and coal gas (CO/H₂). It was not until Houdry's catalytic cracking of petroleum in 1930 that a shift away from coal feedstocks was observed, even though the first oil well was drilled in 1859. Once again a world at war facilitated the fluid catalytic cracking process by the Allied Forces for the invaluable supply of high-octane aviation fuel for jet fighters in World War II. The rapid growth in catalytic processes after the 1940s was spearheaded by the petrochemical industry in its challenge to meet the demands of the new automotive and expanding airline travel industry. Coupled with various catalytic processes for the manufacture of synthetic polymers, these new drivers brought about a renewed need for refined petroleum that could be used as a cheap source of fuel and products that could be used to generate petrochemicals to enhance our quality of life (Armor 2011).

As a result of the explosive growth in the fuel demanded for industrial activity, mainly by the transportation industry of Europe and North America, the world was made to reflect on the detrimental and hazardous effects of severe increases in air-born pollutants that the surge in cheap fuel had brought about. The impacts that the industry had on the environment became apparent in the early 1970s, which in turn instigated new laws controlling emissions regulation and the research into environmental catalysis (Armor, 1995; Bartholomew & Farrauto, 2005). The prevailing work carried out into environmental catalysis during that period produced significant mitigating steps towards controlling the airborne pollutants. Work such as the hydrodesulfurization method of removing sulphur from fuels thereby reducing global emissions of sulphur oxides (SO_x), the auto emission control catalysts used in reducing the emissions of hydrocarbons, nitrogen oxides (NO_x), and carbon monoxide (CO), and the selective catalytic reduction (SCR) of NO_x from power plants, large ships, as well as heavy-duty trucks (Heck & Farrauto 2009). Furthermore, the discovery of zeolite molecular sieves in the 1960s also propagated an increased industrial awareness into their abilities as phosphate substitutes, as the detergent industry had been made aware of the environmentally damaging effects of phosphates used in laundry detergents. The interest in the zeolite chemistry during the 60s would heighten still, paving the way for the creation of new industries as large

petrochemical companies continued to make interesting discoveries of the “unexpected intrinsic catalytic activities on synthetic crystalline inorganic zeolite salts.” Discoveries that would dramatically alter the course of petroleum refining and significantly reduce the reliance on liquid acid catalysts which produced vast quantities of industrial pollution as residue (Masters & Maschmeyer, 2011).

Looking forward to the present day, international forecasts continue to place catalysis among the most promising fields of research. More than 90% of the production of the chemical industry is based on catalysis and the industry is currently valued at \$14.7 billion. With world demand for catalysts set to rise by 5.8 per cent per year, market projections set the value of the industry to rise to \$19.5 billion by 2016 (Freedonia 2013; Armor 2011). Moving forward in this new century, the importance of the often novel catalytic properties of zeolites continues to create new commercial applications to meet the growing market pull towards energy, sustainability, and emissions control. Born out of environmental legislations that have since been put in place, zeolite catalysts are estimated to constitute approximately 35% of the \$14.7 billion global catalyst market (Xu *et al.*, 2007). To be able to address the concerns about renewables, carbon dioxide (CO₂) levels, and the sustainable delivery of a secure energy future for the global population is the biggest challenge facing the science and engineering community to date. These 21st century drivers require technological innovation and development of catalysts for cleaner fuels, efficient renewables, higher quality lubricants, biomass feedstock integration, food processing, water purification, and biodiversity to name but a few.

The many reasons that underlie the development of the science and technology of catalysis as stated above have been made possible by the effective application of existing catalysts and the development of new types. The need for precise and fast information concerning the catalytic activity, selectivity, and lifetime of an industrial catalysts for a specific catalytic process is difficult, expensive, and time-consuming (Derouane *et al.*, 2002). For this reason, advancements in the knowledge of material characterisation have been critical in the fundamental understanding of the quantitative and qualitative properties of material based catalysts. By understanding the changes that occur in the structure and composition of a material following

pretreatment, during induction periods, in use under reaction conditions, and during regeneration, improved techniques and more efficient advancements in the use of catalysts can be manipulated spanning the entire industry. The task here, which is of fundamental importance in understanding the physical chemistry of a material, is “characterisation.”

Material characterisation techniques offer an understanding of a material’s structure, how that structure determines its properties, and how that material will subsequently work in technological applications. To date, the techniques employed to investigate this structure-property relationship have done so either optically, electronically, magnetically, or through mechanical means. The golden rule underlying material characterisation has been to apply numerous methods, as only one methodology normally does not paint a full picture of understanding (Roque-Malherbe, 2009).

Although advances have been made in understanding catalytic processes occurring at the atomic level from these varying characterisation techniques, there is still an apparent gap in the level of knowledge required to fully evaluate catalyst action. Researchers have termed the difficulties involved in studying catalysis under reaction conditions as the “materials and pressure gap” due to the difficulty in providing detailed structural insight into the complex nanostructures present in heterogeneous catalysts and the lack of surface-sensitive techniques that provide spectroscopic information at relevant pressures (Topsøe, 2003). The pressure gap is defined as the difference of 13 orders of magnitude between ultra high vacuum (UHV) experiments and typical industrial applications, while the material gap is defined as the difference between the behaviour of single crystal surfaces and catalysts used for industrial processes (Pérez-Ramírez *et al.*, 2010).

To bridge this gap, research has been carried out in *in situ* studies to try and directly relate the dynamic changes in the structure of a heterogeneous catalyst during reaction conditions with the aim of understanding the catalyst in its working state while operating in reproduced conditions that are present in systems found across a wide range of environments (Bron *et al.*, 2005; Leppelt *et al.*, 2007; Maguire *et al.*, 2013).

The explosion in *in situ* studies from the 90s onwards illustrated in Figure 1.1 represents the pivotal role it plays in studying catalytic problems in the world today.

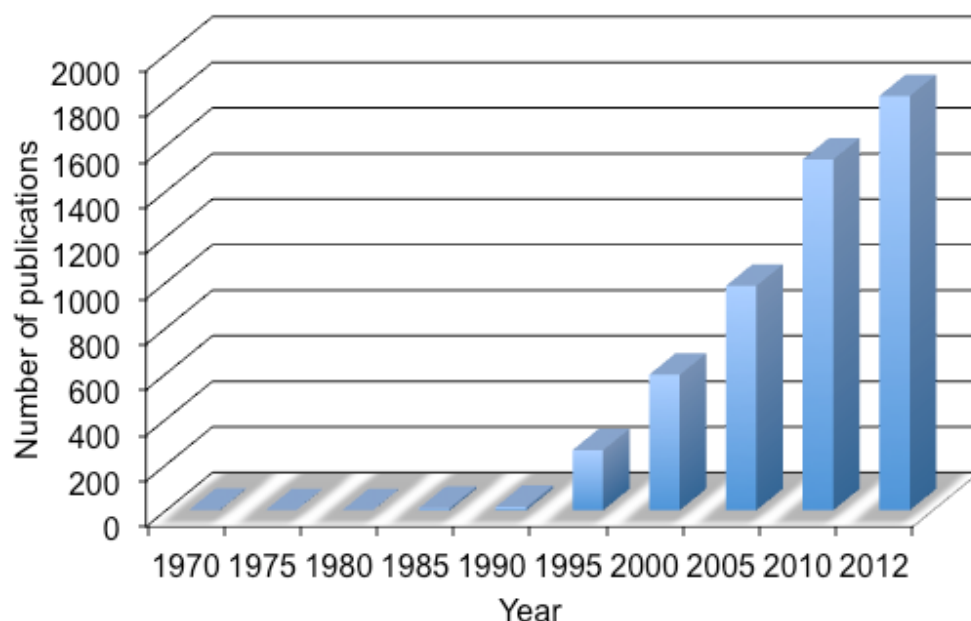


Figure 1.1: Estimated number of publications on '*in situ* characterisation of catalysts' according to Web Of Knowledge literature database.

With over 37,000 independent studies into *in situ* characterisation of catalysts, it is important to recognise the steps being taken towards discovering the detailed knowledge about catalysts. Additionally, these actions offer opportunities for scientists and engineers to design in a more rational way, efficient new catalysts for the sustainable production of bulk and fine chemicals as well as for the removal of harmful compounds in industrial catalytic processes.

For catalyst technology, the major objective of research into heterogeneous catalysis has been the ability to gain an insight into catalytic processes on an atomic scale during catalyst operation. Volumes of work have been published on the characterisation of catalytic processes in model systems dealing with single crystal catalysts which have been convincing, however, problems of reliability have arisen when trying to characterise catalysts of practical interest by comparing them to the kinetic behaviour of model systems. Errors are created through extrapolating speculative surface kinetic parameters based on physicochemical properties of catalysts not operating at reaction conditions. This is due to the fact that several

phenomena are only well understood in the case of single catalyst crystals operating *ex situ* (Somorjai & Borodko, 2001).

The most sensitive probe of catalysts will continue to be the rate and selectivity of a chemical reaction. On a macroscopic level, observations of catalytic processes are adequate but in order to fully understand the mechanisms involved in these processes, microscopic information concerning the structure and reactivity of the intermediates, the nature of adsorption sites and their number during real time is vital. Table 1.2 displays some of the characterisation techniques used in industry and those techniques that are able to observe catalytic processes during operating conditions. What must be made clear however, is the distinction between the live *in situ* studies and those operated under controlled conditions. Only when such *operando in situ* characterisation techniques exist, will direct links be able to be forged between catalyst activity and their surface structure.

Table 1.2: Techniques for investigating catalyst characteristics

Characteristic	Method of Investigation	<i>In Situ</i> Method
<i>Physical Properties</i>		
Surface area	adsorption of N ₂ or CO ₂ , microscopy, computer-controlled scanning electron microscopy (CCSEM)	
Pore size, size distribution	extended N ₂ and CO ₂ adsorptions, Hg porosimetry, nuclear magnetic resonance (NMR) spin relaxation of H ₂ O	NMR
Density	He displacement, pycnometry, Hg displacement, magnetic suspension balance (MSB)	MSB
Catalyst particle size and size distribution	sieving, electronic counting, laser light scattering, scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical imaging	
<i>Mechanical Properties</i>		
Single pellet crush strength	crushing tests in hydraulic press	
Bulk crushing strength	crushing test in hydraulic system	
Attrition and abrasion resistance	rotating drum, air jet and ultrasonic tests	
<i>Chemical Properties</i>		
Chemical state, bulk	thermogravimetric analysis (TG), temperature-programmed reduction (TPR), Mössbauer absorption spectroscopy (MAbS), Fourier transform infrared spectroscopy (FTIR), electron paramagnetic resonance (EPR), neutron scattering (NS), NMR	MAbS, FTIR, NMR
Chemical state, surface	X-ray photoelectron spectroscopy (XPS), temperature-programmed surface reaction (TPSR), extended X-ray absorption fine structure (EXAFS), MAbS, FTIR, NMR	MAbS, FTIR, NMR
Composition, bulk	elemental analysis, atomic absorption spectroscopy (AAS), inductive coupled plasma (ICP), X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), SEM, TEM, TG, FTIR, NMR	XRD, FTIR, NMR
Composition, surface	Auger electron spectroscopy (AES), XPS, secondary ion mass spectrometry (SIMS), EXAFS, ion scattering spectroscopy (ISS), chemisorption, TEM, XRD	XRD
Dispersion or percentage exposed		XRD
Surface reactivity, active site concentration	chemisorption, TPD, TPSR, calorimetry, transient kinetic methods	transient kinetic methods
Surface acidity	adsorption and TPD of bases, infrared spectroscopy (IR), NMR	IR, NMR
Morphology/structure	XRD, SEM, TEM, scanning transmission electron microscopy (STEM), MAbS, low-energy electron diffraction (LEED), EXAFS, TEM, scanning tunnelling microscopy (STM), field emission microscopy (FEM)	XRD, MAbS

Considering the requirements and gaps in technology in the catalysis industry, expert scientists and engineers have built many of the most advanced tools in consolidated user laboratories in order to provide the desirable qualities needed for improved material characterisation. Some of these qualities are summarised below:

- **Realistic operating environment:** Technologies capable of operating across a wide range of extreme temperatures and pressures, similar to industrial process conditions.
- **Real time measurement:** Technologies operating in an *in situ* regime, ridding the need for erroneous extrapolations from compromised model systems.
- **Informative content:** Technologies with the capacity to give manifold information (multipurpose techniques).
- **High-resolution:** Technologies able to generate highly sensitive and precise measurements without affecting accuracy.
- **Speed:** Technologies built on speed of material throughput in order to provide rapid screening turnovers of characterised materials.
- **Lack of calibration:** Technologies that offer minimal calibration and user simplicity.
- **Excellent reproducibility:** Technologies that provide highly reproducible results, which would support the analysis of minuscule changes in material properties.
- **Operational ease:** Technologies that provide easy operation for end-users, offering process automation and remote control.
- **Minimal sample mass limitations:** Technologies that are able to measure bulk samples, decreasing the reliance on single crystal analysis.

- **Ease of data interpretation:** Technologies that rely on simple data interpretation methods to ensure accuracy by minimising the possibilities of human errors.
- **Easy access:** Technologies with minimal purchase and accessibility costs.

Rising to the challenge of creating a characterisation method equipped with these desirable attributes is a tremendous three-fold academic, intellectual, and pragmatic challenge of extensive proportions. The need for the continuous development of *in situ* characterisation methods that operate within industrial process conditions has been highlighted thus far, and is the principal driver behind this PhD. The development of the *in situ* perturbation characterisation technique known as Flux response technology (FRT) shall be the core focus, with apparatus improvements and the measurement and analysis of the technique applied to previously unreported materials.

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Chapter 2

Literature Review of Catalyst Characterisation Techniques used for Gas Sorption and Diffusion Processes

The drastic change in the catalysis industry from the 1950s can be traced back to the development of characterisation techniques. The large growth in the industry has been directly influenced by vital methods of understanding materials and processes used in chemical engineering science. With the tremendous variety of characterisation techniques, it is impossible to review all gas sorption and diffusion methods. What shall be discussed are some of the key static and dynamic measurement methods to provide a comprehensive overview of the technical developments in this field of study. Attaining this list was done so by focusing on recognised techniques used in the physicochemical measurements of surface acidity, basicity, intracrystalline diffusion, and surface area of adsorbent materials.

Solid catalysts used in heterogeneous catalysis are very complex as they are able to possess many different potential active sites dependent on their composition, structure, and morphology. Rational catalyst design and optimisation of catalytic reactions are reliant on *in situ* characterisation techniques that allow studying of the working catalysts and elucidation of the reaction mechanisms under real reaction conditions (Bentrup, 2010). Flux response technology (FRT) is a true *in situ* technique that is able to monitor the processes happening at the catalyst surface in real time without delay. The focus of the literature review shall be to highlight and analytically evaluate characterisation techniques used in adsorbent sorption and diffusion, displaying their respective strengths and weaknesses, and comparing these to those of FRT. The other characterisation techniques that will be reviewed include, the Rubotherm magnetic suspension balance, Cahn microbalance, tapered element

oscillating microbalance, temperature programmed analysis, adsorption microcalorimetry, and temporal analysis of products.

2.1. Gas sorption theories

The phenomenon involved with gas sorption on solid surfaces has been used to modify the product yields of chemical reactions through heterogeneous catalysis in industry. The ability to detect and determine the surface area, kinetic parameters, intrinsic values and site chemistry of catalyst materials have been developed through adsorption studies and are extremely important in evaluating potential catalytic materials (Farra *et al.*, 2013; Kondo *et al.*, 2012; Zhao *et al.*, 2013).

The adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). Physisorption studies are used to characterise similar catalysts according to total surface area and pore volume. Chemisorption analysis techniques are used to evaluate catalyst activity, usually defined as the amounts and types of different reactive gases adsorbed on the surface of the catalyst material which gives rise to parameters such as per cent dispersion, active metal area, crystallite size and surface acidity.

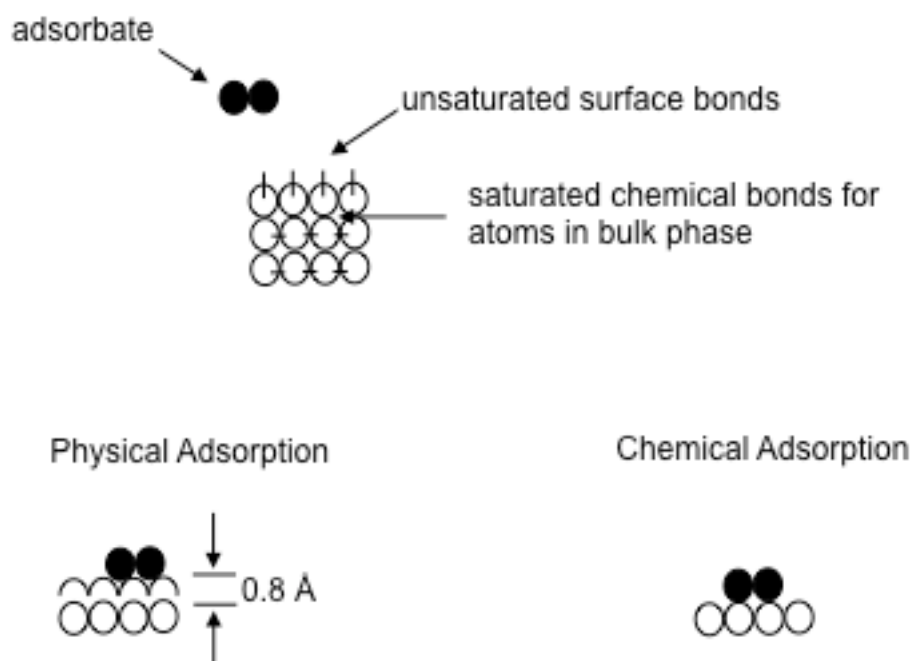


Figure 2.1: Schematic of adsorption on a surface

2.1.1. Physisorption

The basic principle involved in physisorption is the interaction of molecules in the gas phase (adsorptive) with the surface of the solid phase (adsorbent). A film of adsorbed molecules (adsorbate) forms on the surface of the solid upon incremental increases in the partial pressure of the gas. This film of adsorbed molecules is the result of the van der Waals forces that exist between the solid and the gaseous molecules and the accompanying heat of adsorption is comparable in magnitude to the heat of evaporation of the adsorbate. The adsorption isotherm is the measurement of the amount adsorbed versus adsorptive pressure at constant temperature. Measurements of gas adsorption isotherms are widely used for determining the surface area and pore size distribution of solids. Adsorption isotherms can be classified into five fundamental types following the Brunauer-Deming-Deming-Teller (BDDT) classification methodology (W. Wang, 2012).

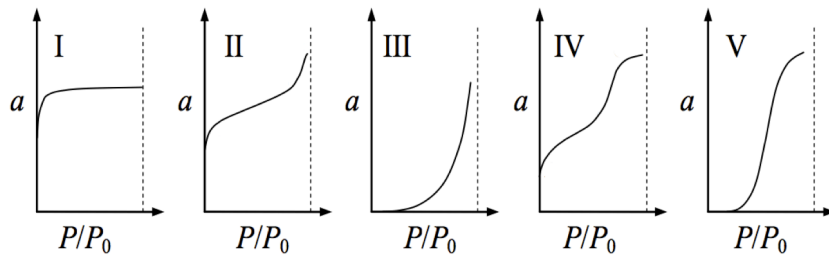


Figure 2.2: Adsorption isotherm categories (BDDT) with the amount adsorbed (a) as a function of the partial pressure (P/P_0) of the adsorbate in the gas phase (W. Wang, 2012)

Type I is called single-molecule adsorption and is often referred to as a Langmuir type of isotherm. It is characterised by a steep and continuous increase in the surface coverage with increasing pressure at low partial pressures. After this surpasses a certain value, the isotherm starts to level off towards a saturation limit, indicative of a completely filled pore system. Microporous materials usually show type I isotherms. Type II isotherms exhibit a slow increase in the convex curve in the first half followed by a sharp increase in the second half of the isotherm because of multilayered adsorption, capillary filling, and capillary condensation. Type IV isotherms are typical for porous materials containing mesopores with capillary condensation occurring in the mesopores. Types III and V are rare and occur in systems with relatively weak forces of adsorption.

2.1.2. Chemisorption

Unlike physisorption, chemisorption is the relatively strong selective adsorption of chemically reactive gases on available sites of metals or metal oxide surfaces. The resulting surface molecules are much more reactive than free adsorbate molecules, and the heats of adsorption are comparable in magnitude to heats of chemical reactions. The difference in the way the adsorbate bonds to the solid surface of the adsorbent in chemisorption makes the selectivity of the process particularly useful as an analytical technique in catalyst characterisation.

Chemisorption analysis techniques provide essential information necessary to evaluate the activity of catalyst materials in the design, production and post-production phases. Because the adsorbate adsorbs only on surfaces having particular chemical properties and does so only under certain thermal conditions, it is possible to probe a surface for specific molecular species.

Table 2.1: Comparing the differences between physisorption & chemisorption

	Physisorption	Chemisorption
Cause	van der Waals forces, no electron transfer	covalent/electrostatic forces, electron transfer
Adsorbents	all solids	some solids
Adsorbates	all gases below the critical point, intact molecules	some chemically reactive gases, dissociation into atoms, ions, radicals
Temperature range	low temperatures low, $\approx$ heat of fusion	generally high temperatures high, $\approx$ heat of reaction
Heat of adsorption	(ca. 10 kJ/mol), always exothermic	($80 - 200 \text{ kJ/mol}$), usually exothermic
Rate	very fast	strongly temperature dependent
Activation energy	low	generally high (unactivated: low)
Surface coverage	multilayer	monolayer
Reversibility	highly reversible	often reversible
Applications	determination of surface area and pore size	determination of surface concentrations and kinetics, rates of adsorption and desorption, determination of active centres

2.1.3. Adsorption equilibria

The dynamic relationship between the rate of adsorption of an adsorbate onto a surface and the rate of desorption is known as the adsorption equilibrium. Typically, the mathematical correlation is depicted by graphically expressing the solid-phase against its residual concentration. These graphs provide the principal data used in modelling analysis, operational design, and application of the adsorption systems (Yaneva *et al.*, 2013). Over the years, a plethora of adsorption equilibrium theories and isotherm models (Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory-Huggins, and Radke-Prausnitz isotherm) have been developed to help explain sorption phenomena. Consequently, there is no single isotherm that can be used to describe all sorption phenomena.

Three fundamental approaches exist in the formulation of equilibrium isotherms, namely, the kinetic approach, the thermodynamic approach, and the potential theory approach. Considering the kinetic approach, the adsorption equilibrium is defined as being in a state of dynamic equilibrium, where both adsorption and desorption rates are equal. The thermodynamic approach provides a framework of deriving numerous forms of adsorption isotherm models. Also referred to as the Gibbs approach, the behaviour of the adsorbed layers, with a two-dimensional equation of state, act as liquid films with the freedom to move over the surface. Potential theory on the other hand conveys the idea of the generation of characteristic curves by assuming that a relationship exists between the sorption potential, the saturation pressure for liquefaction, and the volume of the amount adsorbed, thereby causing a gradual concentration of gas molecules toward the solid surface. This relationship is temperature independent, allowing the formation of an isotherm (De Boer, 1968; Dubinin, 1960; Langmuir, 1916; Myers & Prausnitz, 1965). For the sake of brevity, only the Langmuir, BET, Freundlich, Dubinin-Radushkevich, and Temkin models will be further expanded on.

2.1.3.1. Langmuir isotherm

Methods of extracting information about the surface characteristics of the sample material from their adsorption isotherms have been developed from as early as 1916 when Irving Langmuir pioneered research into deriving an expression for the equilibrium fraction of a solid surface covered by an adsorbed substance as a function of the concentration of the substance in the gaseous phase. Langmuir theory was formulated on the basis of a dynamic equilibrium between the adsorbed phase and the gaseous phase. The implicit assumptions are:

- No lateral interaction between adsorbed molecules
- Each adsorbate molecule occupies only one site
- The adsorbed molecule remains at the site of adsorption until it desorbs (localised adsorption).

The Langmuir isotherm is derived below where A is the adsorbed species (adsorbate), S is an active site on the surface of the solid, θ_A is the fraction of the surface covered by A , $1 - \theta_A$ is the fraction of the surface not covered by A , P_A is the pressure of gas A , k_a is the rate constant for adsorption and k_d is the rate constant for desorption (Bartholomew & Farrauto, 2005). The elementary equilibrium reaction is written as,



where $A - S$ is a surface site covered with adsorbate A . The overall rate of adsorption is the sum of forward and reverse rates. In terms of coverage,

$$r = k_a P_A (1 - \theta_A) - k_d \theta_A \quad 2.2$$

since the rate of adsorption is directly proportional to the gas phase pressure of A (P_A) and the fraction of available sites ($1 - \theta_A$), while the rate of desorption is proportional to the coverage of A (θ_A). At equilibrium, $r = 0$ therefore equation 2.2 can be rewritten as

$$(k_a/k_d)P_A(1 - \theta_A) = \theta_A \quad 2.3$$

Defining K as the equilibrium constant and writing the rate constants in terms of frequency factors and activation energies from the Arrhenius law,

$$K = (k_a/k_d) = (A_a/A_d) e^{-\Delta H_a/RT} \quad 2.4$$

where $\Delta H_a = E_a - E_d$, R represents the gas constant, and T absolute temperature. Assuming $\Delta H_a \neq f(\theta_A)$

$$KP_A(1 - \theta_A) = \theta_A$$

Solving for θ_A

$$\theta_A = KP_A/(1 + KP_A) \quad 2.5$$

At low partial pressures of the adsorbate, there will be a low surface coverage and the adsorbed molecules may be referred to as being isolated from their neighbours. Assuming the surface is homogeneous, the relationship between the partial pressure and the amount adsorbed on the surface will be linear (Bottani & Tascon, 2011; Majer *et al.*, 2008). This relationship is often referred to as Henry's law because of the similarity to the limiting behaviour of gases dissolved in liquids and is shown in equation 2.6.

$$q = K_H P \quad 2.6$$

where, q is the adsorbate loading, K_H is Henry's constant and P is the partial pressure of the adsorbate in the gas phase. At higher partial pressures, the surface will begin to reach monolayer coverage and as the loading increases, molecules can no longer be regarded as isolated from their neighbours. With the adsorbed molecules at adjoining sites interacting with each other, the linear relationship between the partial pressure and the surface coverage according to equation 2.6 is no longer valid.

The drawbacks involved in Langmuir theory are that few physical and chemical adsorption systems conform to the Langmuir equation over the entire range of θ . This has been attributed to the phenomena involved in surface heterogeneity and the interaction of adsorbed species on surface sites. A major advance in adsorption theory generalised the treatment of Langmuir and incorporated the concept of multimolecular layer adsorption, known as BET.

2.1.3.2. BET isotherm

The model of Brunauer, Emmett and Teller in 1938 was the first successful attempt to model multilayer adsorption. BET theory is based on the following important assumptions: (1) the same starting assumptions as Langmuir; (2) adsorbed species in the first layer serve as sites of adsorption for the second layer; (3) the rate of adsorption (r_a) on the i th layer is equal to the rate of desorption (r_d) of the $(i + 1)$ layer; and (4) ΔH_{ads} is the same for the second and succeeding layers and equal to the heat of condensation of the gas (i.e. $\Delta H_{a2} = \Delta H_{a3} = \dots \Delta H_c$). A representation of these assumptions leads to the following derivation of the BET isotherm:

$$\theta = \frac{V}{V_m} = \frac{cx}{(1-x)[1+(c-1)x]} \quad 2.7$$

where $x = P/P_o$, P_o is the vapour pressure of the adsorbing gas at a given temperature, V_m is the volume of gas required to provide a complete monolayer and

$$c = c_o \exp \left[\frac{\Delta H_{a1} - \Delta H_c}{RT} \right] \quad 2.8$$

where ΔH_{a1} is the heat of adsorption on the first layer, ΔH_c is the heat of condensation of gas, and $c_o = \frac{a_1 b_2}{a_2 b_1}$ where a_1 , b_1 , a_2 and b_2 are the preexponentials for condensation to and evaporation from the first and second layers respectively.

Rearranging the BET model into a linear form shown in equation 2.9, allows for the determination of surface area of adsorbent materials. When using the BET model for

surface area determination, partial pressures must range from 0.05 to 0.35 (Sing, 1985a).

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m c} + \frac{c - 1}{V_m c} \left(\frac{P}{P_o} \right) \quad 2.9$$

2.1.3.3. Freundlich isotherm

The Freundlich isotherm model is recorded as having shown the earliest relationship describing non-ideal and reversible adsorption, not restricted to monolayer formation. The Freundlich isotherm shown in equation 2.10, has been applied to materials exhibiting multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Adamson, 1982),

$$q_e = K_F P^{1/m} \quad 2.10$$

where q_e is the equilibrium adsorption capacity, K_F is a constant dependent on temperature, and $m \gg 1$. Presently, the isotherm is widely applied in heterogeneous systems with organic compounds or highly interactive species on molecular sieves, although it has been criticised for lacking a fundamental thermodynamic basis with the isotherm not approaching Henry's law at diminishing concentrations (Ho *et al.*, 2002).

2.1.3.4. Dubinin-Radushkevich isotherm

The adsorption of subcritical vapours onto micropore solids following a pore filling mechanism was initially developed and described using the Dubinin-Radushkevich isotherm. It is generally used in expressing adsorption mechanisms with a Gaussian energy distribution onto a heterogeneous surface (Dąbrowski, 2001; Günay *et al.*, 2007).

$$q_e = (q_s) \exp(-k_{ad} \varepsilon^2) \quad 2.11$$

The Dubinin-Radushkevich isotherm model is shown in equation 2.11 with the theoretical isotherm saturation capacity (q_s), the Dubinin-Radushkevich isotherm constant (k_{ad}), and the isotherm parameter (ε) expressed as:

$$\varepsilon = RT \ln \left[1 + \frac{1}{c_e} \right] \quad 2.12$$

where c_e represents the adsorbate equilibrium concentration. The model does not predict Henry's law at low pressures but has a unique feature in that it is temperature dependent. This allows for the suitable adsorption data at different temperatures (plotted as a function of the log of the amount adsorbed versus the square of potential energy) to be situated on the same characteristic curve (Altın *et al.*, 1998; Foo & Hameed, 2010).

2.1.3.5. Temkin isotherm

The Temkin isotherm has been successfully used to predict gas phase equilibrium by taking adsorbent-adsorbate interactions into account. The model assumes that the heat of adsorption of all molecules in the layer decreases linearly as opposed to logarithmically with coverage (Dada *et al.*, 2012; Foo & Hameed, 2010).

$$q_e = \frac{RT}{b_T} \ln A_T c_e \quad 2.13$$

The derivation of the equation is characterised by a uniform distribution of energy sites, where b_T is the Temkin isotherm constant and A_T is the Temkin isotherm equilibrium binding constant.

2.1.4. Acid-base concept in heterogeneous catalysis

In general, understanding the science of acid and base catalysis follows dealing with a paired concept; a vast number of important chemical reactions exist through these acid-base interactions. Acid catalysed reactions occur through reactants that act as bases which interact with catalysts acting as acids. For base catalysed reactions the

opposite is true, where reactants acts as acids and interact with catalysts that behave as bases. The importance of solid acid catalysts in industry today dates back to the 50s, when the proliferation of heterogeneous acidic catalysts used in the cracking process for petroleum refining was in its infancy. The cracking process is the largest process among industrial chemical processes, responsible for the significant contributions towards the amount of attention placed towards the study of heterogeneous acid catalysis (Armor, 2011; Hattori, 1995; Heck & Farrauto, 2009; Lindström & Pettersson, 2003; Martínez *et al.*, 2013; Pugach & Dorogochinskii, 1969; Smit & Maesen, 2008a). In contrast to this, fewer studies have been dedicated towards understanding heterogeneous basic catalysts, due in part to the severe pretreatment requirement conditions for active basic catalysts (Alsawalha, 2005; Ratton, 1998).

The two fundamental theories designed to describe the acid-base surface interactions in heterogeneous catalysis are based on the works of Brønsted, Lowry, and Lewis. From the point of view of the Brønsted-Lowry definition, a solid is acidic if it is able to donate (or partially transfer) a proton to a basic probe molecule to which the proton bonds (or becomes partially associated). Conversely, a Brønsted-Lowry base is a proton acceptor. In the Lewis definition, a solid is said to be acidic if it is able to accept an electron pair from a basic molecule while also forming a coordinative bond with it. The opposite is true for a base, where it donates an electron pair i.e. Lewis Bases are nucleophilic and “attack” a positive charge with their lone pair.



Equations 2.14 and 2.15 illustrate Brønsted-Lowry and Lewis acid-base interactions respectively. The acid-base interactions in equation 2.14 consist of the equilibrium exchange of a proton from the acid HA to the base B , giving rise to the conjugated base of HA , A^- , plus the conjugated acid of B , HB^+ . In terms of Lewis acid-base interactions, the Brønsted-Lowry type acid HA is as of a result of the interaction with the Lewis-type acid specie H^+ with the base A^- . According to these definitions,

Brønsted-Lowry type acids do not correspond to Lewis-type acids, however, Brønsted-Lowry basic species are also Lewis bases. Acid-base properties of solids are mostly discussed in terms of Lewis and Brønsted definitions of acidity and basicity.

2.1.5. Diffusion

During heterogeneous catalysis, a number of different steps are usually needed in order to convert reactants into desired products. Depicted in Figure 2.3 are the steps generally involved in a heterogeneous reaction. In the case of a gaseous feed stream interacting with a solid sorbent, adsorption onto the surface of the sorbent is the first process to take place. The molecules are then transported to the reactive sites within the pores of the sorbent for a reaction to take place. This transport process is called diffusion. Having reached the catalytically active sites, the gas molecules are free to react and the conversion into desired products takes place. Transport of the products away from the active site occurs after completion of the reaction in order to facilitate the next reaction. Once again, the newly formed product species diffuse out through the pores of the sorbent before desorbing from the surface of the sorbent completely. Through the advancements in the field of heterogeneous catalysis, researchers have been able to improve conversion rates and product yields of a vast number of industrial processes by being able to manipulate adsorption and diffusion rates, which, as one could imagine, have the ability to adversely affect and determine the catalytic behaviour of a system.

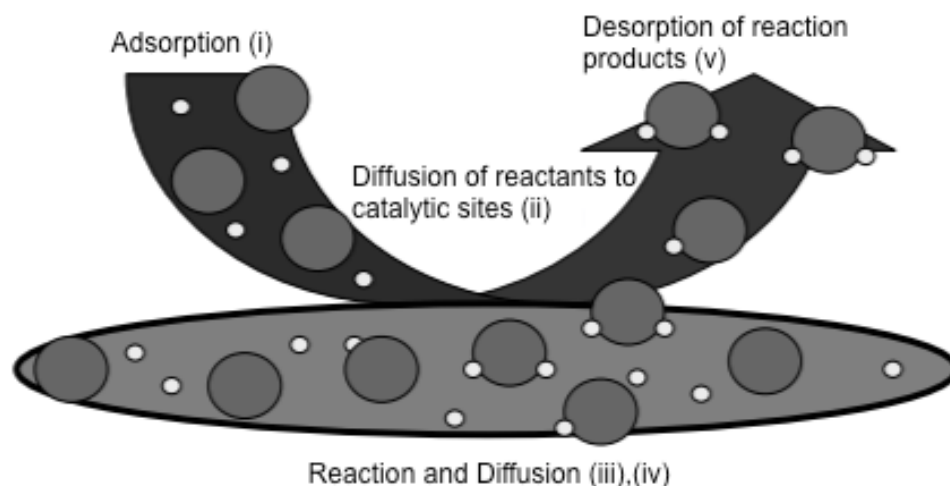


Figure 2.3: Generalised schematic of the catalytic cycle in porous sorbents (Satterfield, 1996)

Diffusion in microporous materials such as zeolites differs from ordinary diffusion due to the fact that adsorbate molecules are in constant interaction with the channels within the framework of the zeolite. As a result, the molecular motion is strongly influenced by parameters such as the size and shape of the channels. These affect the rate of diffusion alongside other parameters such as temperature, pressure, and concentration. Consequently, diffusion of the molecules through a membrane can proceed in a variety of ways depending on the nature of the interactions between the diffusing gas molecules and the membrane. Various gas diffusion processes can be found in the literature, which for the sake of brevity have been narrowed down to focus on the following four diffusion mechanisms, namely, Fickian diffusion, Self-diffusion, The Darken relation, and Knudsen diffusion (Burggraaf, 1999).

2.1.5.1. Fickian diffusion

During the 19th century, Adolf Fick postulated the foundations of the theory of diffusion. In this, he laid down the assumption that the flow of a certain species can be related to the gradient of the concentration according to Fick's first law (Fick, 1855):

$$J = -D_t \left(\frac{\partial C}{\partial x} \right) \quad 2.16$$

where C is the concentration, x is the spatial coordinate, and D_t is the (transport) diffusion coefficient. As a starting point, this brought about the definition of diffusion to be proportionally constant between the rate of flow and the concentration gradient. However, this was not reflective of the true driving force of diffusion, the chemical potential μ , as diffusion is nothing more than the macroscopic manifestation of the tendency of a system to approach equilibrium. The Onsager relation was derived using irreversible thermodynamics to express for the chemical potential and is useful when trying to relate transport diffusion to self-diffusion:

$$J = -L \left(\frac{\partial \mu}{\partial x} \right) \quad 2.17$$

where L is the phenomenological Onsager coefficient.

Exploring Fick's second law brought about an equation relating the change of concentration in a finite volume element with time:

$$\frac{\partial C}{\partial t} = -D_t \left(\frac{\partial^2 C}{\partial x^2} \right) \quad 2.18$$

Through the pioneering work of Barrer and Jost in zeolitic diffusion, Fick's second law can be readily solved for radial coordinates in spherical particles by assuming that the diffusivity is isotropic throughout the crystal, as D_t is independent of the direction in which the particles diffuse (Barrer & Jost, 1949).

2.1.5.2. Self-diffusion

Self-diffusion deals with an equilibrium process unlike transport diffusion where a chemical potential gradient is necessary. In this, the diffusion measurement of labelled molecules within an entity of unlabelled identical molecules occurs and is also referred to as tracer diffusion. Equation 2.19 describes the flow of the labelled molecules:

$$J_i^* = -D_s \left. \frac{\partial C^*}{\partial x_i} \right|_{C=\text{constant}} \quad 2.19$$

where * refers to the labelled molecule and D_s is the self-diffusion coefficient. It should be noted that the self-diffusion coefficient depends on the total molecular concentration i.e. the sum of labelled and unlabelled molecules as the labelling procedure assumes to effect no changes in molecular mobility. An alternate way of introducing the self-diffusion coefficient is via Einstein's equation:

$$\langle r^2(t) \rangle = 6D_s t \quad 2.20$$

where the mean square displacement of the studied molecules ($\langle r^2(t) \rangle$) are related to the observation time (t). It has been shown that both definitions of self-diffusion coefficients in equations 2.19 and 2.20 are equivalent (Kärger & Pfeifer, 1987).

2.1.5.3. The Darken Relation

Having identified the true driving force for diffusion being the gradient of the chemical potential, it was necessary to relate the concentration to the chemical potential by considering the equilibrium vapour phase:

$$\mu = \mu^0 + R_g T \ln p \quad 2.21$$

with p being equal to the partial pressure of the component. The formation of the Darken equation relating the constants D_t and L with each other could then be derived using equation 2.21:

$$D_t = R_g T L \left(\frac{\partial \ln p}{\partial \ln C} \right) = D_0 \left(\frac{\partial \ln p}{\partial \ln C} \right) = D_0 \cdot \Gamma \quad 2.22$$

where D_0 relates to the corrected or Maxwell-Stefan diffusivity and Γ is the thermodynamic correction factor that corrects for the non-linearity between the pressure and the concentration of the adsorbent. A similar expression can now be used to relate transport and self-diffusion to each other according to equation 2.23:

$$D_t(q) = D_s(0) \left(\frac{\partial \ln p}{\partial \ln q} \right) \quad 2.23$$

in which q is the concentration of the adsorbed species in the pores. Although the assumption is that the diffusive process in the two completely different experimental setups can be described in a similar and trivial fashion allowing, generally speaking this is not always the case and deviations from the expression above can be expected (Karger & Ruthven, 1992; Skoulidas & Sholl, 2001, 2003). The work by Paschek and Krishna postulated the use of an extra relation needed to link the Maxwell-Stefan diffusivity and self-diffusivity according to equation 2.24:

$$D_s = \frac{D_0}{1 + \theta} \quad 2.24$$

where θ relates to the coverage inside the pores of the zeolite (Paschek & Krishna, 2001).

2.1.5.4. Knudsen Diffusion

The theory of Knudsen diffusion that aims to describe the phenomenon of gas transport through narrow pores originated in the early 19th century with the extensive work of Knudsen and Fisher in trying to shed light on the problems that exist in characterising diffusion in porous media due to their chemical, physical, and geometrical complexities (Knudsen & Fisher, 1910; Knudsen, 1909). In small pores or at low loading pressures, the mean free path may become comparable or at times greater than the pore diameter, resulting in collisions between the molecules and the pore wall occurring more frequently than intermolecular collisions. The low occurrence of intermolecular collisions means the normal Brownian diffusion does not play a significant role in the diffusive gas transport. With the velocity of the molecule leaving the surface bearing no relation to the velocity of the incident molecule and its direction being purely random, a Fickian expression for the flux in which the diffusivity depends only on the geometric parameters associated with the membrane and the mean molecular velocity of the gas is obtained and is known as Knudsen diffusion (Shi *et al.*, 2012).

$$J = -D_K \left(\frac{\partial C}{\partial z} \right) \quad 2.25$$

where D_K is the Knudsen diffusivity, which when considering kinetic theory for the mean velocity gives:

$$D_K = \frac{\varepsilon d_p}{3\tau} \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}} \quad 2.26$$

with ε being the porosity of the membrane, d_p being the pore diameter, τ the tortuosity, R the gas constant, and M the molecular weight of the adsorbed species. The regime of Knudsen diffusion can be defined by the dimensionless Knudsen number:

$$Kn = \frac{\text{mean free path}}{\text{diameter of channel}} = \frac{\lambda}{d} \quad 2.27$$

If the Knudsen number is much larger than unity, transport is said to occur through a Knudsen flow and no longer through a viscous flow. With numbers less than unity, viscosity is applicable and transport occurs through the Poiseuille flow.

2.1.6. Surface area of porous materials

The standard tool used in characterising the surface area and pore size distribution of highly dispersed or compact porous solids and nanomaterials is gas adsorption. The adsorption measurements at the gas/solid interface form essential parts of a variety of fundamental investigations of the nature and behaviour of solid surfaces. Due to the fact that solid surfaces are rarely smooth on an atomic scale, it has often been useful to distinguish between the external and internal surfaces regarded respectively as the envelope surrounding discrete particles and the deep conduits consisting of pores, cavities, and cracks.

The BET gas adsorption method is the most widely used standard procedure for surface area determination of porous materials and is calculated by evaluating the adsorbate monolayer capacity.

$$A_s = V_m L a_m \quad 2.28$$

$$a_s = A_s / m \quad 2.29$$

In equation 2.28 and 2.29, A_s is the total surface area, V_m is the monolayer capacity, L is the Avogadro constant, a_m is the average molecular cross-sectional area, and a_s is the specific surface area corresponding to an adsorbent of mass m .

2.2. Characterisation techniques used for gas adsorption processes

Chemical catalytic probes are by definition the most sensitive probes of catalytic sites but do not necessarily provide the detailed site structural information that is sought. Characterisation of catalysts should always involve complementary physical and chemical techniques of characterisation and even with this, need to be able to study the catalyst during operation, that is, while the reaction is occurring *in situ*. What is lacking from current physisorption and chemisorption techniques is the ability to measure with the highest sensitivity possible, regardless of the inhomogeneity among catalyst particles and the possibility of structural changes occurring during reactions.

The characterisation techniques to be discussed can be grouped into four categories namely, static-volumetric, gravimetric, oscillometric, and dynamic:

2.2.1. Static-volumetric techniques

Measurements of the amount of gas adsorbed on the surface of solids through volumetric techniques are one of, if not the most pivotal of fundamental data required in material characterisation. The systematic research into gas adsorption dates all the way back to 1773 when Carl Scheele was able to observe the adsorption of air by charcoal with the use of a volumetric apparatus (Robens, 1994). By considering

pressure change within a constant volume, the method has been developed and applied in the analysis of specific surface area, porosity, density, and chemisorption over the years.

The technique today involves the use of a vacuum system comprising of two sections, a dosing section and a sample section. The dosing section allows the introduction of accurately measured quantities of the adsorbate while the sample section contains the material being investigated. The accuracy and precision of the technique depends on a measure of high sensitivity adopted for the calibration of volumes, including the dead space in the sample section, the control of the temperature within the dosing and sample sections, and the pressure measurement. A typical static-volumetric adsorption experiment shown in Figure 2.4 consists of a thermostated sorption chamber, a calibrated storage vessel, vacuum pump, and an expansion valve.

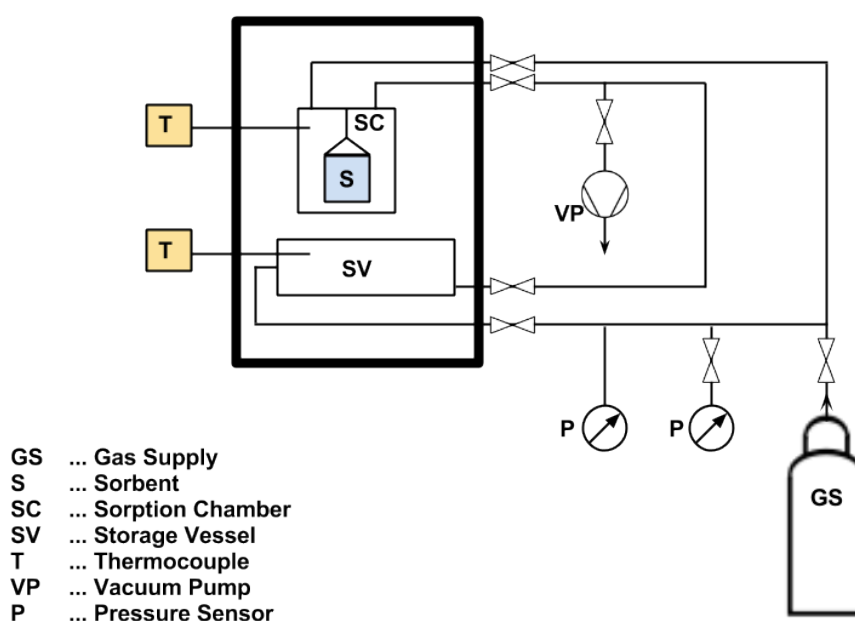


Figure 2.4: Schematic of the experimental setup for volumetric sorption experiments

To investigate the adsorption on the surface of a particular sorbent, a predetermined amount of gas present in the storage vessel is expanded into the previously evacuated sorption chamber. There the gas is partially adsorbed till a consistent measure of pressure and temperature is reached i.e. till thermodynamic equilibrium is obtained. Once this has been realised, the mass of the gas adsorbed on the sorbent can be measured.

2.2.1.1. BET volumetric technique

The determination of specific surface areas by means of the BET theory is derived from the physical adsorption of gases on the external and internal surfaces of porous materials. The amount of adsorbed gas is dependent on the relative vapour pressure and is proportional to the external and internal surface of the materials. This relationship between the relative vapour pressure and the quantity of adsorbed gas at constant temperature gives rise to the adsorption isotherms previously elucidated.

The analysis of nitrogen adsorption isotherms at 77 K for the determination of surface area and pore characteristics has been established as a ubiquitous characterisation tool with its widespread commercial use. The International Union for Pure and Applied Chemistry (IUPAC) recommendations of 1985 and 1991 provide the standard operating procedure used in BET surface area calculations (Haber, 1991; ISO, 2010; Sing, 1985b) – known amounts of nitrogen are pulsed in a stepwise fashion into the sample cell containing the sorbent material. The material would have been previously dried and outgassed by heating under vacuum, prior to the introduction of nitrogen into the cell. Consequently, the amount of gas adsorbed is the difference of gas admitted and the amount of gas filling the dead volume.

From this, the surface area can be determined by extracting the BET parameters from the adsorption isotherm plot of the amount of gas adsorbed against the relative pressure to find the monolayer capacity according to equations 2.9 and 2.28.

2.2.1.2. Critical review and recommendations

The primary advantages of static-volumetric methods lay within the level of simplicity involved with performing gas adsorption measurements and with the application of BET theory. This allows for a high degree of automation, which in turn eases the amount of supervision required during experimental runs. The technique also profits from being able to operate within a wide range of adverse operating conditions, such as corrosive environments (Condon, 2006; Gauden *et al.*, 2010; Keller, 2005). However, several disadvantages exist in the use of static-volumetric techniques. One such example relates to the high amount of sorbent material needed for considerable changes in the gas pressure due to adsorption to be recorded. Another involves the approach to equilibrium, which for certain processes may last hours or – worse still – even days.

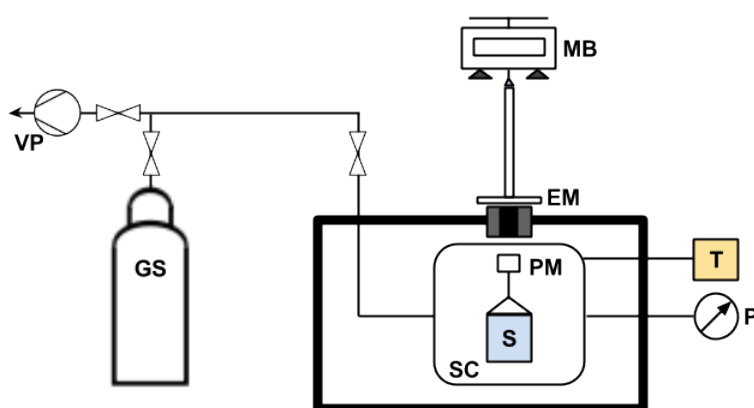
Uncertainties have also been acknowledged in the experimental procedure, where upon expansion from the storage vessel, the sorbate gas may not only be adsorbed on the surface of the sorbent but also on the walls of the sorption chamber. In addition to this, researchers have often concluded that BET surface area measurements for sorbent materials containing mesopores are inherently overestimated due to the fact that pore filling is observed at pressures very close to the pressure range where monolayer-multilayer formation on the pore walls occurs, which inadvertently leads to a significant overestimation of the monolayer capacity (Cejka *et al.*, 2007; Lowell, 2004; Seki, 2002). Static-volumetric techniques are also unable to evaluate the kinetics of the experimental process and also bear a significant cost (Condon, 2006; Fadoni & Lucarelli, 1999; Keller, 2005).

2.2.2. Gravimetric techniques

The gravimetric technique is similar to the volumetric, except that the quantity of adsorbed gas is determined by the weight increase of the sorbent sample. In this way, the principle of the gravimetric method is much simpler than the volumetric. Even though the method of comparing masses by weighing them in earth's gravity field dates back through the ages to biblical times, gravimetry is a relatively new process of investigating sorption phenomena of gases in porous materials (Keller, 2005). This

was due to a lack of highly sensitive balances able to measure infinitesimally small weight changes in sorbent samples but this quickly changed by the end of the 19th century with the introduction of micro and magnetic suspension balances. Measurements today are used to characterise porous media by measuring adsorption equilibria and exploring adsorption kinetics. Illustrated in Figure 2.5 is a typical setup for gravimetric sorption experiments.

Experimental investigations routinely consist of mounting the sorbent sample on the microbalance then activating by evacuation and calcining with helium. At the end of the calcination, the balance is evacuated again to get an initial measure of the sorbent. The start of the experiment is initiated by the introduction of the sorbate gas from which point the change in the balance's recording due to surface adsorption on the sorbent and buoyancy effects of the sample in the surrounding gas is measured. The isotherm is then simply constructed as the mass gain of the sample versus pressure.



- GS ... Gas Supply
- S ... Sorbent
- SC ... Sorption Chamber
- T ... Thermocouple
- VP ... Vacuum Pump
- P ... Pressure Sensor
- MB ... Microbalance
- EM ... Electromagnet
- PM ... Permanent Magnet

Figure 2.5: Schematic of the experimental setup for gravimetric sorption experiments

2.2.2.1. Rubotherm magnetic suspension balance

The Rubotherm magnetic suspension balance (MSB) has been developed to measure gravimetrically, the adsorption equilibria of binary gas or vapour mixtures. The MSB allows samples to be weighed in closed vessels without contact, thereby keeping all the components in contact with the adsorbate at the experimental conditions. The principle behind the technology is as follows: A sample is weighed by means of a highly developed magnetic suspension from the outside and the suspension force is transmitted through this contactless technology from the pressured measuring cell to a microbalance at ambient atmosphere. Instead of hanging directly at the balance, the sample to be investigated is linked to a so-called suspension magnet consisting of a permanent magnet, a sensor core, and a device for decoupling the measuring load (sample). This increases the usefulness of the technology in that it can be used to measure mass changes in a sample even under extreme conditions such as corrosive and toxic gases as well as severe atmospheric conditions ($\text{UHV} < p < 200 \text{ MPa}$, $77 \text{ K} < T < 2200 \text{ K}$) with the utmost accuracy (Dreisbach & Seif, 2003).

In this also lies the advantage the Rubotherm MSB has over other ‘conventional’ gravimetric systems. Magnetic suspension balances allow gravimetric sorption measurements to be performed in a range of pressure and temperature using adsorbates inaccessible for almost all other (gravimetric and volumetric) instruments. The vast range of applicability in pressure and temperature as well as the variety of useable adsorbates distinguish the MSB from other commercially available adsorption measuring apparatus (Dreisbach, 2006). By means of these measurements it is possible to determine transport quantities and state quantities very easily and accurately (sorption, diffusion, surface tension, density). The three main areas of application are sorption measurements, thermo gravimetrics, and density measurements, dealing with material transport, investigation of chemical reactions, and state quantities of fluids/density of porous materials respectively.

The MSB has been used to evaluate high-temperature and high-pressure gas isotherms of nitrogen and butane on activated carbon to a high degree of accuracy (Jadot & Weireld, 1999); used to evaluate the adsorption equilibria of binary gas mixtures (Dreisbach & Seif, 2003); used to determine the hydrogen storage capacity of carbon

nanotubes (Lan & Mukasyan, 2005); as well as being used to determine the diffusion and sorption data of methanol and toluene in the ternary system methanol-toluene-poly(vinylacetate) (pvac) (Schabel *et al.*, 2007).

2.2.2.2. Critical review and recommendations

Although the MSB has been shown to provide a wide range of applicability in catalyst characterisation, work by Jadot and Weireld was able to show certain major problems that are not typical of the gravimetric method. Analysis of the gas density provided a degree of uncertainty. In order to measure the density accurately, the pressure and temperature within the measuring cell must be equal. Fluctuations in either parameter compromise the accuracy of the technique (Jadot & Weireld, 1999). Pini *et al.* commented on similar problems with the MSB. Although pressure homogenization is fast and easy, temperature gradients inside the measuring cell need to be kept as small as possible and require an intricate heating system (Pini *et al.*, 2006).

2.2.2.3. Cahn microbalance

The Cahn microbalance is a highly sensitive technique capable of measuring relatively small changes in sample masses and is sensitive to changes as small as 10^{-6} g (Bohn *et al.*, 2005). The mode of operation is based on the “balance beam” principle in which the weight to be measured is applied to the sample side of the beam which applies a force about the axis of rotation. An equal and opposite force is produced in the same axis by the electric current flowing in the torque motor if the beam is at the beam reference position. A greater force from the system side will require a greater opposite force from the torque motor to keep the beam at the reference position. Hence, a direct measure of the force on the beam is attributed to the current required to produce the torque motor force and can be calibrated to measure in units of weight.

A host of researchers have utilised the Cahn microbalance in gravimetric applications. The work by Vestbø *et al.* led to the development of a high pressure microbalance to evaluate pressure-composition isotherms for hydrogen storage materials (Vestbø *et al.*, 2007). Lin *et al.* continued along the same vein and were able to evaluate the

hydrogen storage performance of carbon nanotube composites using a Cahn microbalance (Lin *et al.*, 2010). Anderson *et al.* measured the adsorption isotherms of CO₂, N₂, and CH₄ on nanoporous carbon at elevated temperatures and high pressures (Anderson *et al.*, 2010).

2.2.2.4. Critical review and recommendations

The Cahn microbalance suffers from specific problems associated with temperature and relative humidity effects that affect the accuracy of the measured results. Temperature and relative humidity fluctuations around the sample cause uncertainties in the measurement of the sample's moisture content. The Cahn microbalance is highly sensitive to changes in moisture throughout the sample cell, thus, is directly compromised by such fluctuations (Bohn *et al.*, 2005). Another problem with this gravimetric technique is that the sample is momentarily exposed to air when transferring to the system, often causing unwanted changes such as oxidation and reaction with the moisture in air (Vestbø *et al.*, 2007). It is of critical importance to guard against such effects that compromise the accuracy of the technique.

2.2.3. Oscillometric methods

Oscillometric techniques used today in gas adsorption measurements were developed through the work of Kestin and others in the 80s, when they used the torsional pendulum of a dense disk moving in a viscous medium to measure the density and viscosity of the fluid (Keller, 1995; Kestin *et al.*, 1980). Here, gas adsorption measurements are conducted through the slow oscillations of a rotational pendulum or, likewise, the relaxational motion of a freely floating rotator. From this, the inertia of mass against acceleration can be compared with the standardized mass of the sample under investigation. The instrument setup for oscillometric measurements of gas adsorption equilibria is shown in Figure 2.6.

The sorbent sample being investigated is homogeneously distributed in a disk fixed to a torsional wire and stabilized by a stem bearing a small mirror. Two diodes fixed at known angles are able to observe the motion of the pendulum from the reflected laser

beam. From this, researchers are able to calculate the respective angular frequency and logarithmic decrement by a Gaussian minimisation procedure.

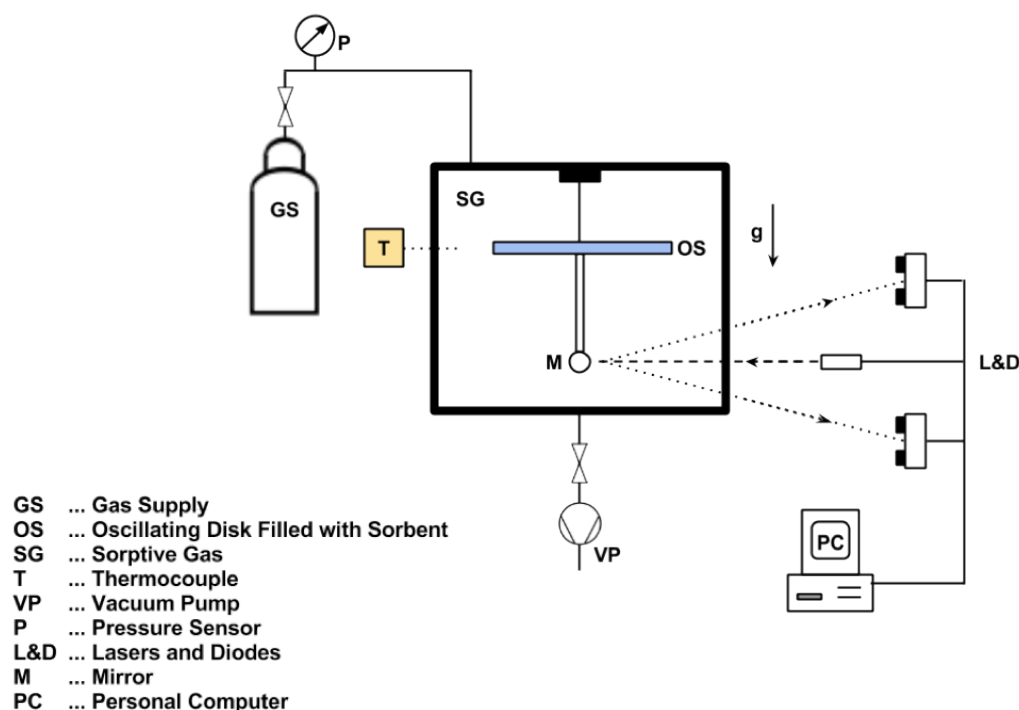


Figure 2.6: Schematic of the experimental setup for oscillometric gas adsorption measurements

2.2.3.1. Tapered element oscillating microbalance

Since its introduction in 1980, the tapered element oscillating microbalance (TEOM) has established itself as a highly suitable tool in detecting coking, adsorption, and diffusion effects in the field of heterogeneous catalysis. It was originally developed by Patashnick *et al.* as a tool for the accurate real-time monitoring of the amount of particulate matter in the effluent streams of combustion systems but has subsequently proven itself to be an invaluable tool in the research into heterogeneous catalysis (Patachnick & Rupprecht, 1977).

The TEOM offers a method of measuring mass changes in a fixed bed reactor while reaction gases are passed through a sample. In this gravimetric technique, the mass of the sample is determined by monitoring the frequency changes of the tapered oscillating element (Eigenmann, 2000). The main feature involved in the TEOM

technique is the use of an oscillating element that is based on inertial forces, instead of weight, to measure the amount adsorbed. The TEOM technique has several distinct advantages for measurement of adsorption in microporous materials, namely (Zhu *et al.*, 1998):

- The ability to provide a well-defined gas phase due to the high gas flow of feed with carrier gas through the adsorbent bed.
- The ability to provide a high mass resolution across the entire range of operation.
- The ability to operate at variable conditions over a wide range of pressure and temperature.

A disadvantage of conventional microbalances used in catalyst characterisation is that a large part of the feeds used in the respective experiments bypass the basket containing the catalyst. This makes it difficult to obtain differential operation in the conventional systems. Being able to measure the catalytic activity of a sample by utilising gradientless operation is a highly advantageous aspect of the TEOM technique. The inertial microbalance eliminates the problems of bypassing and allows for such measurements (Gates & Knoezinger, 2007).

The theory behind TEOM is based on the relationship between the natural frequency of the oscillating tapered element and its mass. Based on the operating principle, the total mass change detected consists of the amount adsorbed by the sample and the mass change caused by the variation in densities between the different gases used in the experiment. If the TEOM is oscillating at the start of the experiment with frequency f_0 and exhibits the frequency f_1 after a mass uptake, the total mass uptake can be obtained as a function of f_0 , f_1 and the spring constant K_0 (Zhu *et al.*, 1998).

$$\Delta M = \Delta M_a + \Delta M_g = K_0 \left(\frac{1}{f_1^2} - \frac{1}{f_0^2} \right) \quad 2.30$$

where ΔM_a is the adsorbed mass and ΔM_g is the change in the gas density determined by measuring the mass change during a blank run under the same conditions.

The TEOM technique has been successfully used in many aspects of catalysis research. Examples include, monitoring the amount of carbon deposition *in situ* on nickel catalysts (Pan & Song, 2009), analysing the effect of coke deposition on transport and adsorption in zeolites (Chen, 1996), and measuring the adsorption and diffusion of hydrocarbons on zeolites (Smit & Maesen, 2008b). Research carried out by Chen *et al.* showed that numerical values could be derived for the diffusional time constant during transient uptake measurements using TEOM, while Zhu *et al.* were able to demonstrate the use of TEOM in transient uptake and desorption experiments as well as for steady state and equilibrium experiments (Smit & Maesen, 2008a).

2.2.3.2. Critical review and recommendations

The TEOM process has been shown to possess certain advantages over conventional gravimetric techniques in sorption studies over heterogeneous catalysts; however, there are some limitations in its use. The TEOM cannot be used for volatile or fragile samples because they may alter the natural oscillating frequency of the test bed (Jalani *et al.*, 2005). The sample cell of the TEOM cannot be connected directly to a gas chromatograph or mass spectrometer for online analysis because the tapered element must be free to vibrate without restraint. Inaccuracies also exist in measuring the adsorptive properties of catalysts following gas perturbations within the sample element due to the vibrations caused by the perturbations (Chen *et al.*, 2007).

2.2.3.3. Quartz Crystal Microbalance

The development of the Quartz Crystal Microbalance (QCM) stemmed from the early work of Jacques and Pierre Currie in the eighteenth century with their discovery of the piezoelectric effect; the application of pressure in certain crystallographic directions to crystals of Rochelle salt was found to produce electricity (Duck, 2009). When it was later discovered that quartz crystals could be used as transducers and receivers of ultrasound in water, its application in items of everyday interest such as microphones and loudspeakers rose significantly. By 1921 the first quartz controlled oscillator was demonstrated. Over ten years later in 1934 heralded the dominance of quartz crystals used in a variety of frequency control applications. The discovery and

use of the AT-cut quartz crystal had the distinct advantage of having a near zero frequency drift with temperatures around room temperature. It was not until 1959 with the breakthrough work of Günter Sauerbrey that the QCM stood the chance of being used as a quantitative tool to measure very small masses as it is used today. Sauerbrey published results showing that an added mass was directly proportional to the frequency changes of a quartz crystal resonator (Sauerbrey, 1959). The Sauerbrey equation is depicted below:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta M \quad 2.31$$

in which Δf is the frequency change, f_0 is the resonant frequency, ΔM is the mass change, A is the active crystal area, ρ_q is the quartz density, and μ_q is the shear modulus of quartz for AT-cut crystals.

As an ultra-sensitive mass sensor, the QCM consists of a thin piezoelectric AT-cut quartz crystal with a diameter of 0.25 – 1.0 *inches*, sandwiched between a pair of electrodes connected to an oscillator. The technique has the ability to perform *in situ* measurements of adsorption phenomena on material surfaces and is sensitive to mass changes between the orders of 10^{-9} – 10^{-12} g. The use of QCMs has progressed subsequently over the years and is used in multiple scientific disciplines, such as chemistry, biology, material science, medicine, and environmental monitoring. The QCM is also particularly suited to measuring low sorbate concentrations on non-rigid or swelling sorbent materials such as polymers. The apparatus also profits from its ease of operation and relatively inexpensive cost (Chiang & Mintz, 2008; Marx, 2003, 2007).

2.2.3.4. Critical review and recommendations

Although QCMs were employed initially in applied physics to study metals in vacuum, the technique has since been extended across scientific fields to investigate different phenomena such as adsorption, desorption, corrosion, and moisture accumulation. The QCM-based sensing procedure is simple, non-hazardous, operates

in situ, and is cost effective. Recent developments have also highlighted the quartz crystal microbalance with dissipation (QCM-D) technology that allows for real-time, label-free measurements of molecular adsorption and/or interactions on various surfaces with a dissipation parameter providing novel insights regarding structural (viscoelastic) properties of adsorbed layers (Vashist & Vashist, 2011).

Limitations of the technology have shown that electrochemical QCM can only be used to study electroplated, evaporated, or sputtered materials. A lack of reproducibility of experimental results, which has been attributed to drifts in sensors has also been commented on (Marx, 2003). With the wide range of demonstrated features, QCM-based sensing techniques still lack critical evaluations to demonstrate their pros and cons when compared to existing technologies (Vashist & Vashist, 2011).

2.2.4. Dynamic techniques

Dynamic techniques operate by manner of feeding a probe gas continuously (saturating) or through pulses (titrating) onto a catalyst sample to determine the monolayer capacity, from which the fundamentally important characteristics such as surface acidity, active metal area, etc., can be determined. Under conditions of dynamic flow, the ability to control heating rates can be used to express individual characteristic reaction rate curves that can be used in categorically classifying various catalysts.

Dynamic techniques for catalyst characterisation are directed at measuring the stage of non-equilibrium adsorption that varies dynamically when gas flows through the catalytic layer. This method is simple compared to the volumetric technique and the characterisation time is significantly reduced. However, since the measurement result is affected by the adsorption property of the catalyst and the operation condition, the method is less accurate when compared with the volumetric technique. Figure 2.7 presents the schematic for a typical dynamic flow experiment comprising of a sample cell stationed within a thermocoupled furnace, a gas selector for directing gas to various parts of the system, and a thermal conductivity detector (TCD) capable of

responding to changes in gas composition and providing the means to control the sample temperature.

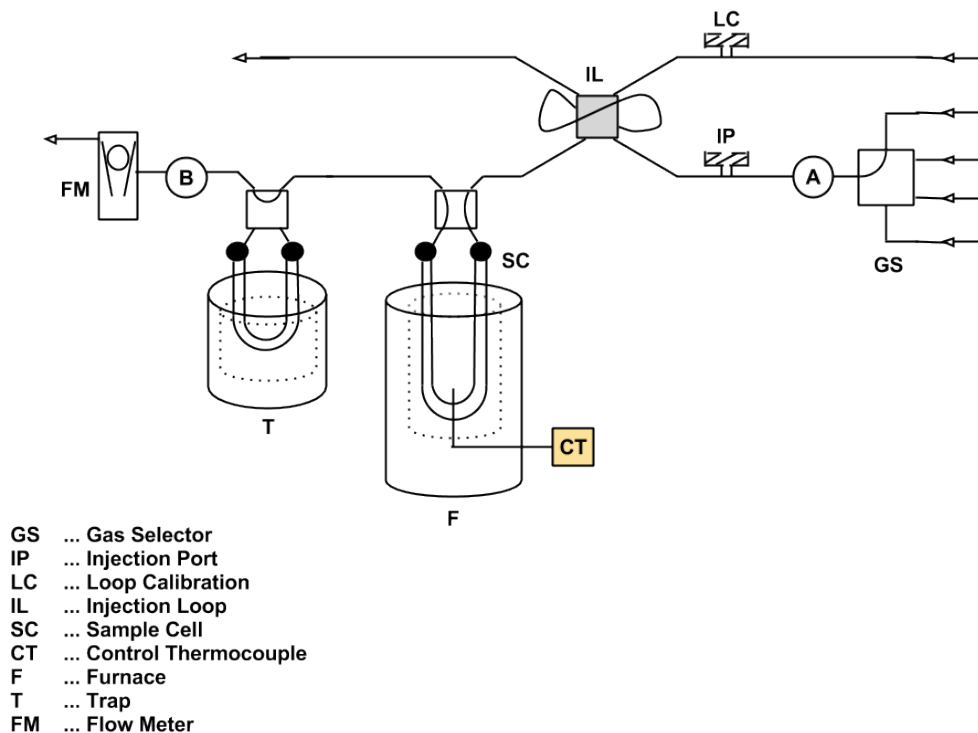


Figure 2.7: Schematic of the experimental setup for dynamic flow measurements with TCD, A and B.

2.2.4.1. Temperature programmed analysis

Temperature programmed (TP) techniques, in which both the temperature and the surface coverage of heterogeneous catalysts vary with time, measure the reactivity of a solid as a function of the temperature under controlled conditions (Boaro *et al.*, 2003). The temperature at which the species react or are desorbed from the surface reflects the bond strength of a particular species. Different chemical species react at different temperatures, displaying distinct maxima in the TP profile. Naturally, the more reactive species react at lower temperatures and *vice versa*.

This technique was first used by Cvetanovic and Amenomiya (H. Wang, 2004) and has been widely applied to characterising heterogeneous catalysts in industry. The most commonly employed techniques are temperature programmed desorption (TPD),

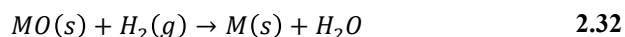
reduction (TPR), surface reaction (TPSR) and oxidation (TPO). Depending on the method in use, a gas reagent (H_2 , H_2/H_2S , or O_2) is pumped over the catalyst to be investigated while the temperature (energy) is increased. During the temperature rise, the reactant consumption and/or product formation are measured by comparing the thermal conductivity of the gas before and after the reactor, using a TCD (Rothenberg, 2008). Further analysis can be carried out by determining the composition of the gas effluent leaving the reactor using gas chromatography, mass spectrometry or other methods (Baker *et al.*, 1999).

1.2.4.1.1. Temperature programmed desorption

This technique was originally developed by surface scientists to quantitatively investigate the kinetics of desorption of molecules from well-defined single crystal surfaces under high vacuum (Bartholomew & Farrauto, 2005). By measuring the rates of desorption of adsorbed molecules as a function of temperature, it is possible to study the adsorption states, binding energies, surface concentration, and desorption kinetics of various catalysts. Modern developments in TPD methods have introduced analytical techniques to characterise the acidic and basic properties of solid catalysts (Tago *et al.*, 2005). The process is carried out by utilising the co-adsorption of CO_2 and NH_3 onto solid catalysts.

1.2.4.1.2. Temperature programmed reduction

TPR is mainly used to study the reducibility of oxidic species such as metal oxides dispersed on a support. To investigate the properties of such catalysts, a stream of diluted hydrogen (or another reducing agent) is flowed over the sample as the sample temperature is increased. From this, a measurement of the hydrogen consumed and the temperature profile under which the reduction took place is plotted. The quantity of hydrogen consumed versus temperature can then be used to reveal the number of reducible species in the sample, the reduction stoichiometry, insights into reduction mechanisms as well as their activation energies. The peaks that appear at various thermal energy levels correspond to a different oxide and the amplitude of each peak is proportional to the reaction rate. The general reduction reaction follows:



where $MO(s)$ is the solid metal oxide and H_2 the reduction gas. The energy equation is:

$$G = G_0 + RT \log \left(\frac{P_{H_2O}}{P_{H_2}} \right) \quad 2.33$$

where G is the free energy, P_{H_2} and P_{H_2O} are the pressures of the hydrogen and water vapour products, and R and T correspond to the gas constant and temperature respectively (Webb *et al.*, 1997).

1.2.4.1.3. Temperature programmed surface reaction

TPSR involves the reaction of a gas-phase species such as H_2 , O_2 , or H_2O with a previously adsorbed species such as CO, surface carbon, or surface coke. The products in the gas-phase are measured as a function of time using mass spectrometry, gas chromatography or other gas analysers. In the resulting spectrum, it is typical to find peaks corresponding to “reaction states,” i.e. temperatures at which the reaction passes through a maximum. Such data can be used to analyse the unsteady-state reaction rates, relative reactivities of surface species, and activation energies for the reaction (Bartholomew & Farrauto, 2005).

1.2.4.1.4. Temperature programmed oxidation

In TPO, the extent to which a catalyst can be re-oxidized is examined. Usually the sample is pretreated and the metal oxides are reduced to the base metal. The sample is heated at a uniform rate as the reactant gas, typically 2% oxygen, is applied to the sample in pulses or as a steady flowing stream. The oxidation reaction occurs at a specific temperature and the resulting uptake of oxygen is quantified. From this, the amount of oxygen consumed during the reaction is related to the amount of reducible species on the surface (Song *et al.*, 2005). Provided the stoichiometry factor for

oxidation is known, the degree of reduction is evaluated and related to the active sites of the catalyst.

2.2.4.2. Critical review and recommendations

Temperature programmed analysis techniques are most often confined to a qualitative level by discussion of peak maxima, number and position of peaks, and total reactant consumption. There has also been an issue with the accuracy of using TPD to estimate the heats of adsorption of reactions due to the non-uniform nature of the assumptions involved in analysing the data (Gorte, 1996). Such assumptions vary from lab to lab and are used to account for the effects of re-adsorption and diffusion which occurs simultaneously during the adsorption process. However, several theoretical models have been developed especially for TPD and TPR analysis (Boaro *et al.*, 2003).

2.2.4.3. Adsorption microcalorimetry

Within this technique lays a very useful method of directly measuring the strength with which molecules interact with solid surfaces. Adsorption microcalorimetry has been widely used to measure the strength with which probe molecules adsorb onto solid catalyst surfaces. It also enables the analysis of the heat of adsorption, the entropy of adsorption, and the heat capacity of the adsorbed phase in gas-solid interactions; qualities that provide important ingredients in understanding the thermodynamics of surface reactions (Ljiljana & Aline, 2008). Advances in the field of adsorption microcalorimetry have also made it possible to measure differential heats of adsorption on metal powders, polycrystalline metal films, and a host of other materials (Spiewak & Dumesic, 1998). This has provided new insights into the interaction of adsorbates with metal surfaces and has advanced the study of metal-based catalyst systems.

Systems employed in adsorption microcalorimetry are designed to measure both the amount of gas adsorbed during a differential gas dose and the heat that is evolved as a result of the adsorption process. The amount of adsorbed gas is computed by determining the difference between measured final pressure and that predicted from

the ideal gas law. The heat released during the adsorption process is measured on the basis of the heat-flow concept. The heat evolved from the adsorption process “flows” out of the reactor chamber and through thermopiles to heat sinks. The thermopiles produce a signal that is proportional to the rate at which heat is flowing and this signal integrated over time, yields the total heat generated (Phillips, 1997).

2.2.4.4. Critical review and recommendations

It is often difficult to determine the nature of adsorbed species, or even to distinguish between the different kinds of adsorbed species from calorimetric data. In many cases, this technique fails to distinguish between cations and protonic sites due to the insufficient selectivity of the adsorption. For example, the differential heats of NH_3 adsorption on strong Lewis centres and strong Brönsted sites are relatively close to each other. This can make it difficult in some cases to discriminate Lewis and Brönsted sites solely by adsorption microcalorimetry of basic probe molecules if no complimentary techniques are used.

Difficulties also lie in finding good correlations between the site strength distribution and the activity or selectivity of a catalyst. In catalysis, only a fraction of the energy spectrum of the surface may actually be involved during the catalytic reaction. The rate of conversion may also be determined by diffusional limitations and not only by the strength of acid sites if the critical size of the reactant molecule is commensurate with the pore dimensions (Ljiljana & Aline, 2008).

2.2.4.5. Temporal analysis of products

Transient measurements in the temporal analysis of products (TAP) were first introduced by Gleaves *et al.* in 1988 and have since played a pivotal role in the research into heterogeneous catalysis (Breitkopf *et al.*, 2009). TAP reactors provide a very fast and convenient way of describing the active surface of catalysts regarding their ability to adsorb and convert reactant molecules. These reactors are designed to operate in the millisecond time regime; thereby creating a much higher time resolution compared to other non-steady state pulse reactor systems (Breitkopf *et al.*,

2009). Possessing this functionality provides the ability to analyse and describe a more detailed view of catalytic reactions in short lived active species and intermediates.

For these measurements, well-defined gas pulses of $10^{13} - 10^{19}$ molecules are emitted (pulse width of 0.1 – 20 ms) over a catalyst bed under high vacuum conditions, and the broadened pulse emerging at the outlet of the reactor is detected and analysed using a mass spectrometer (Leppelt *et al.*, 2007). From this, the pulse shape and the amount of molecules leaving the reactor give an insight into the mechanism and kinetics of the reaction.

The main feature of a TAP pulse experiment is the transport by Knudsen diffusion within the microreactor. Thus, the transport characteristic of any component is constant with respect to the composition of the pulse. For a gas mixture, Knudsen diffusion is highly beneficial because the diffusivities of the individual components are independent of concentration, pressure and composition of the mixture.

One of the main advantages of using a TAP reactor is that, due to the relatively small number of molecules, the catalyst surface is virtually unchanged during single-pulse experiments. A revised version of the TAP reactor design (TAP-2) was published later by the same group of Gleaves *et al.*, exhibiting major modifications, in particular, constructing the pulse valves and the heating system outside the main vacuum chamber, allowing easier catalyst exchange (Gleaves *et al.*, 1997). Further modifications to the process setup of the TAP-2 reactor have been established by researchers from The Institute of Surface Chemistry and Catalysis, Ulm University (Leppelt *et al.*, 2007). The main features of this new reactor are the use of a turbomolecular pump and the use of a differentially pumped gate valve, allowing for fast and simple changes between high-pressure operations with the ability to perform *in situ* catalyst analysis.

2.2.4.6. Critical review and recommendations

Despite the inherent advantages that lay within the theory of temporal analysis of products, current systems suffer from complex and expensive construction. The Multitrack TAP reactor designed by Nijhuis *et al.* comprises of three mass spectrometers in a row to analyse the pulses at the same time and to monitor the reaction educts and products, while the TAP-2 system is designed with an atomic beam deposition system (Leppelt *et al.*, 2007).

2.2.5. Chromatographic Techniques

Among the separative sciences, gas chromatography (GC) is a physicochemical process based on the broadening factors embraced by the van Deemter equation, which enables precise and accurate physicochemical measurements to be made by the application of a simple and inexpensive experimental setup (Cazes, 2005). In GC, the gaseous phase is used to transport the solutes along the column and the residence time of the solutes are affected by the vapour pressure, a parameter also affected by temperature and the intermolecular forces of attraction between the solutes and the stationary phase.

2.2.5.1. Inverse Gas Chromatography

Inverse Gas Chromatography (IGC) was developed in the 1950s and used initially in the characterisation of catalyst support materials such as alumina, activated carbon, and silica (Kiselev & Yashin, 1969). Presently, IGC has been developed as a dynamic sorption technique capable of measuring several properties of porous materials including sorption isotherms, surface heterogeneity, heats of sorption, surface energy, and free energy among others. Inverse Gas Chromatography gets its name from its mode of operation – with IGC, the sample under investigation and of interest is in the stationary phase while the mobile phase acts as the probe molecules, which is in contrast to the common analytical gas chromatographic experiment. This way an empty column can be filled with the (porous) sample adsorbent under investigation and the probe adsorbate molecules in the mobile phase are able to probe the surface of the sample (Thielmann, 2004).

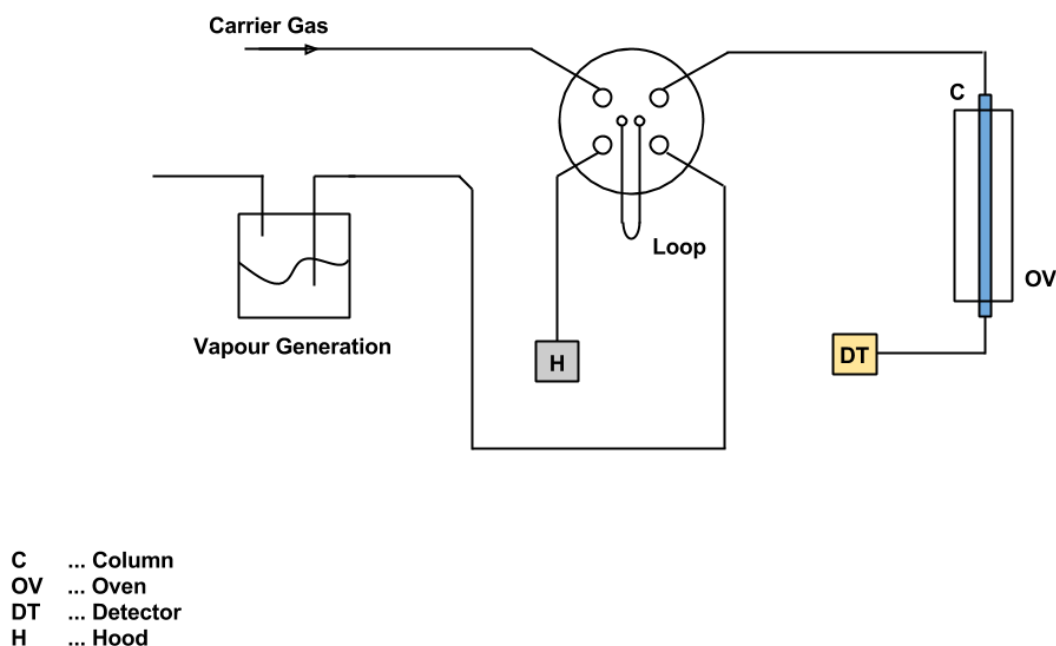


Figure 2.8: Schematic of the experimental setup for a pulse IGC experiment

Two operating techniques exist when carrying out IGC measurements, namely, the pulse or frontal technique. With pulse experiments as the name suggests, only a finite amount of the probe molecule is injected and transported by the mobile phase (carrier gas) to the adsorbent, resulting in a peak in the chromatogram reflective of the sorption on the surface of the sample. In the frontal technique, the probe molecules are added continuously to the mobile phase and the chromatogram displays a breakthrough curve. The frontal technique benefits from an established equilibrium due to its continuous nature while the pulse technique assumes a fast equilibration of the probe molecules adsorbing on the sample surface (Thielmann, 2004). The primary information concluded from IGC experiments is the retention and the dead time of the probe molecules. The retention time can be defined as the amount of time elapsed between the injection of probe molecules and the elution of the peak maximum. The dead time is the amount of time required for the probe molecules to travel through the system without any interaction. Retention times are typically measured using chromatographic detection methods such as flame ionisation (FID) and thermal conductivity (TCD) detectors.

2.2.5.2. Critical review and recommendations

Several advantages exist in the characterisation of porous samples using IGC. In summary, the method allows for the examination of different porous samples where difficulties have been commented on in the analysis of surface activity, e.g. contact angle measurements. Changes in surface properties as a result of surface modifications can be followed using IGC. It is also possible to analyse the influence of the modifier structure on evaluated parameters as well as easily determine the relationship between monolayer and surface characteristics (Voelkel, 2004). Drawbacks of the technique focus on the fact that the classical elution method neglects the mass transfer phenomena as well as the method being influenced by the carrier gas flow (Cazes, 2005). The thermal conductivity detectors used in the systems offer high versatility but are limited in terms of their sensitivity. Flame ionisation detectors on the other hand offer the sought after sensitivity, however are usually limited to use with only organic systems (Thielmann, 2004).

2.3. Summary

A detailed and comprehensive study of the capabilities, limitations, and drawbacks of the key characterisation methods in heterogeneous catalysis (gas-solid) were examined by analysing each individual mode of operation, configuration, and measurement procedure. The literature review was split accordingly to focus on static-volumetric, gravimetric, oscillometric, and dynamic techniques used in gas sorption processes. A quick overview was also conducted beforehand on the governing principles behind gas sorption and diffusion processes.

Deciphering the information gathered on the measurement techniques used in gas sorption and diffusion processes brought to focus the pertinent discussions surrounding current analytical methods. Static-volumetric methods are time-tested and mostly used as the method of choice in measuring surface properties of catalytic properties *ex situ* as measurements are taken prior to or at the end of a given sorption process. Comparing static-volumetric methods with a majority of the other methods discussed highlighted its simplicity, ease of operation, and inexpensive nature; however, major sources of internal errors within the system lie with the need to

calibrate for dead volumes. Powerful *in situ* techniques reviewed included the Rubotherm Magnetic Suspension Balance and the Temporal Analysis of Products reactor. Both methods have shown a great deal of promise in aiding to bridge the pressure and material gap in surface studies as the Rubotherm MSB is able to operate under extreme experimental conditions and at industrial operating conditions. The TAP reactor is suitable for the rapid determination of complex reaction kinetics. The major drawback of both methods and a host of others within the same category is the significant expense required in purchasing the apparatuses. A majority of the techniques also perform under vacuum, limiting the accuracy and suitability of experimental results in their use as industrial modelling data.

It was clear from the review of the literature that an important hurdle still to cross remains in developing and refining an array of measurement techniques capable of operating *in situ*, requiring no prior calibration, able to operate at extreme experimental conditions, and provide users with an inexpensive capital investment. The contribution of such apparatuses to the physicochemical analyses required in materials science would provide much needed data required for optimising industrial processes.

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Chapter 3

History and Materials of Flux Response Technology

Flux response technology (FRT) is a comprehensive *in situ* gas measurement technique centred on a pneumatic Wheatstone bridge assembly. The flux response process uses a differential pressure transducer (DPT) to make differential measurements between two gas streams in a range as precise as $10^{-2} \mu\text{l}/\text{min}$. Analysis of catalytic performance is carried out by measuring between the system side of the bridge, where the given sample is attached, and an inert reference side. The technique is based on capillary viscometry and can be used to measure miniscule changes in flowrate between two gas streams for potentially any gaseous process involving a change in molar hold-up ($\delta N/\delta T$) (Buffham *et al.*, 1986; Mason *et al.*, 1998; Russell *et al.*, 2002; Sasegbon & Hellgardt, 2012).

FRT functions analogous to an electrical Wheatstone bridge assembly whereby gas molecules represent electrons and flow capillaries represent resistors. A schematic of the Wheatstone bridge assembly is illustrated in Figure 3.1.

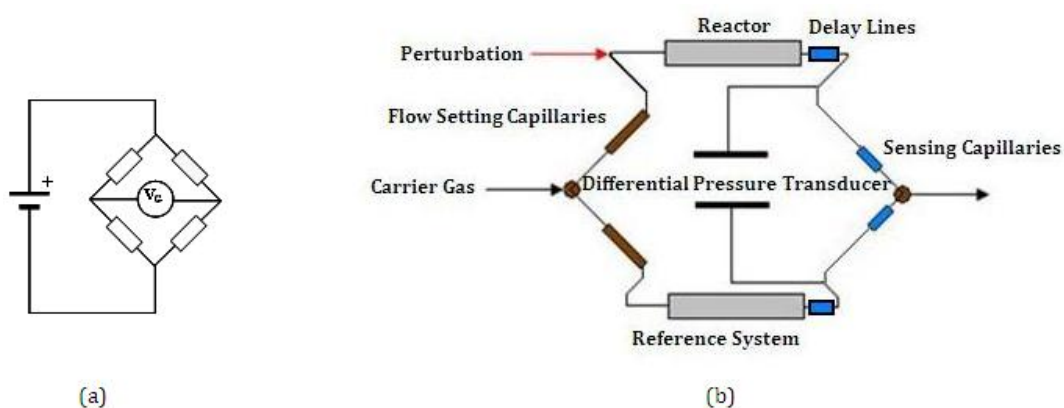


Figure 3.1: Schematic of the experimental configuration for Flux Response Technology (a) Electrical Wheatstone bridge assembly (b) Pneumatic Wheatstone bridge assembly (Sasegbon & Hellgardt, 2012)

One side of the bridge, referred to as the system side, can be perturbed by pressure, concentration, and temperature. The other side of the bridge parallel to the system side is the reference side and is setup to replicate the experimental configuration of the system side. An imbalance in the pneumatic Wheatstone bridge between the system and reference sides caused by a perturbation is measured by a DPT as a voltage difference and can be used to carry out very sensitive differential measurements for a range of processes. FRT has had a hand in replicating and pioneering new research in catalysis from its inception in the 90s till this present day across a broad range of subject areas such as, sorption-effect chromatography, perturbation viscometry, kinetics of heterogeneous reactions, membrane uptake measurements, surface area determination, and acid site quantification.

Professor Bryan Buffham and Professor Geoffrey Mason developed the technology behind FRT in their innovative work on sorption-effect chromatography at Loughborough University. Here, the research professors were able to outline a novel technique of making chromatographic measurements by being able to measure changes in the effluent volumetric flowrate caused by injection, absorption of the sample, and desorption of the resolved bands. The ability to perform these flowrate measurements was developed in order to make simultaneous binary adsorption equilibrium measurements (Buffham *et al.*, 1993) on the basis of model-independent chromatography theory (Buffham, 1978). In addition to this, their work on composition-front scanning of porous media provided another basis for the development of FRT. Here they were able to show how it was possible to deduce the transit time of the front across a small inactive zone in a model adsorptive porous medium from the effluent flowrate change during a scan (Buffham *et al.*, 1996). Upon their retirement, the technology was transferred over to Imperial College London under the principal supervision of Professor Klaus Hellgardt and has continued to advance in its ability as a novel catalyst characterisation tool.

The outline of chapter 3 starts with a discussion of FRT's scope within industrial catalyst characterisation techniques. Following this, an explanation of the basics and theory of FRT, including a critical review and recommendations. An appraisal of the assemblage materials and a literature review of its applications through the years follow

on from the recommendations. Finally, the aims and objectives of the PhD are represented.

3.1. FRT – A universal tool in catalyst characterisation

Over the decades, characterisation methods based on gas adsorption processes have been widely deployed in chemical engineering and chemistry. This phenomenon underlies a number of extremely significant processes that provide technological, environmental, and biological data used in catalyst characterisation. The practical applications that adsorption plays in chemical reaction and separation processes are of paramount importance in industry and for environmental protection. In most catalytic processes, the adsorption of the substrate is the first stage in the chemical reaction. Exploring separation processes of mixtures in both laboratory and industrial scale setups show increasing trends towards utilising the change in concentration of components at the interface. These arms of surface science in chemical engineering have become a well-defined branch of physical science representing an intrinsically interdisciplinary area between, physics, chemistry, biology, and engineering, with adsorption science providing a key backdrop to each discipline.

It is a strongly held view that adsorption science possesses a dominating role in modern industry due to its use and impact in appropriate technologies that reduce the earth's ecological load, that foster the design and introduction of renewable energy sources, that produce new revolutionary solid materials in the search for ecology-friendly materials, and generate economic gains in highly competitive markets. Catalyst characterisation techniques have improved along the way to try to adapt to the challenges incurred in existing in a world where only the technologies and processes that give the possibility of sustainable development of people and society are justified. One of the crucial improvements in characterisation techniques came through the introduction of *in situ* studies. This brought about a breakthrough in atomic-scale data of the catalyst while in operation (during its life so to speak). The “black box” of detailed chemical and structural information that curtailed the enhancement of chemical processes based on single model theories, rather than the various interpretations and speculations on post-mortem analysis of surface science conditions (i.e., ultrahigh vacuum, idealised surfaces of single crystals) where conflicting deductions and models

were made on separate kinetic experiments, proposed for the same reaction over the same catalyst. Today, *in situ* studies are so widely practised that an entire subcommunity of scientists practising in the development of *in situ* catalysis research is flourishing (Jones *et al.*, 2012).

With the need for this complex data came the separation of characterisation techniques into two broad categories – the developing *in situ* methods and the traditional *ex situ* methods of characterisation. In *in situ* studies, the complex knowledge required for the efficient and rationale design of catalytic materials is provided by experimentally analysing through the multi-layered processes of catalyst preparation, activation, action, and regeneration. The term *ex situ* comes from the fact that traditional approaches in material science only probe the catalyst samples under investigation before and after the chemical reaction process, only providing partial answers in understanding the catalyst material. The reoccurrence of these experimental conditions presents itself as the *pressure* and *material* gap in heterogeneous catalysis.

The term has evolved through experimentation often being carried out under ultrahigh vacuum (UHV) using single crystal materials (Morgan, 2007). This has led to errors in surface analysis generated through extrapolating speculative surface kinetic parameters from model systems, based on physicochemical properties of catalysts not operating at reaction conditions (Somorjai & Borodko, 2001). Indeed, a host of researchers have commented and demonstrated on the difficulties that exist and the challenges that must be undertaken to bridge the gap between surface science and catalysis (Bron *et al.*, 2005; Jackson *et al.*, 2003; Oosterbeek, 2007; Pérez-Ramírez *et al.*, 2010; Schlögl, 1993; Topsøe, 2003)

The field of catalysis and catalyst characterisation is hugely complex and filled with a vast array of analytical tools, each possessing their own inherent advantages and disadvantages. FRT places itself within the list of emerging *in situ* techniques alongside other techniques such as the temporal analysis of products (TAP) reactor and the Rubotherm magnetic suspension balance that look to overcome the problems of the pressure and material gap.

3.2. Background of FRT

3.2.1. Fundamentals

Flux response technology (FRT) is a powerful gas *in situ* perturbation technique that can be used to measure minuscule changes in flowrate between two gas streams for potentially any gaseous process involving a change in volume. Based on a pneumatic Wheatstone bridge assembly, the flux response process uses a DPT to make precise differential measurements between two gas streams. By considering the simplified notational flux response system in Figure 3.2 for the adsorption of a single component on the surface of an adsorbent, the behaviour of flux response technology can be explained.

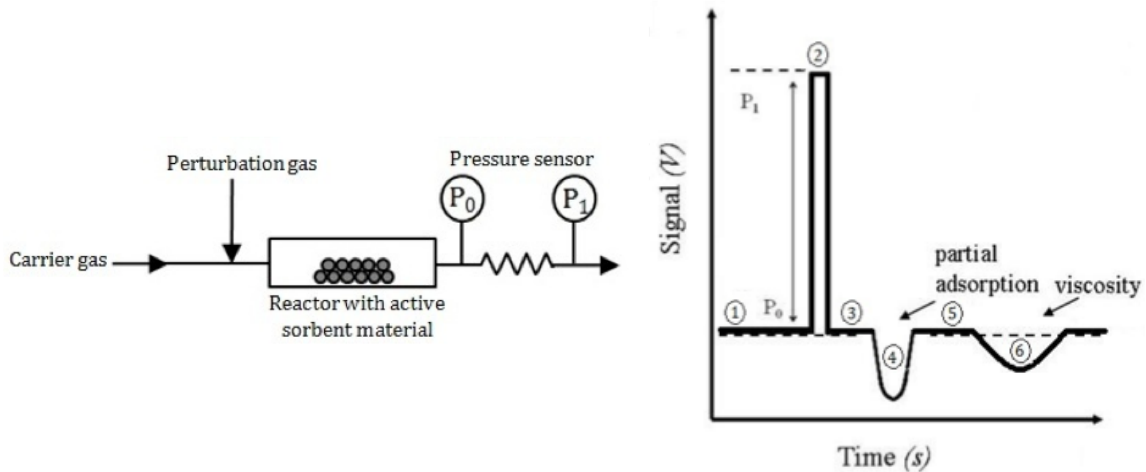


Figure 3.2: Schematic setup of a flux response experiment with complimentary flux profile

The key features of the notational system include the adsorbent material within the reactor, the sensing capillary, and the pressure sensors. Measurement of the pressure difference across the sensing capillary versus time is shown in the flux response profile in Figure 3.2. The numbered points are: (1) the initial baseline signal produced by the constant inert carrier gas flowing through the system; (2) the pulse injection of the perturbation gas used to interrogate the surface of the adsorbent, causing a surge in the signal; (3) the perturbation gas passing through the inactive reactor; (4) the perturbation gas adsorbing onto the surface of the active material causing a flux response; (5) the response returning to the initial baseline; (6) the detection of a viscometric response due to the composition change associated with the gas mixture. Integration of the area

underneath the flux response peak equates to the amount of molecules adsorbed onto the surface. Hence, FRT can be considered as the perfect molar flow meter.

The governing equations used to extract information from the flux response profile are developed by understanding the flow through the sensing capillary. Theoretically, the Hagen-Poiseuille Law for laminar flow is used to describe the flow through the capillary. Assuming the flow through the sensing capillary is laminar, viscous and incompressible, the change in pressure p_z with distance z for the flow of fluid through a section of tube of the sensing capillary is given by,

$$\frac{dp_z}{dz} = -K_c \mu Q \quad 3.1$$

where Q is the volumetric flowrate, μ is the viscosity, and K_c is a constant dependant on the characteristics of the tube. For an ideal gas,

$$Q = \frac{MRT}{p_z} \quad 3.2$$

M is the molar flowrate of gas, T is the absolute temperature, and R is the gas constant. By substituting for Q in equation 3.1 with equation 3.2, the longitudinal pressure gradient can be expressed as,

$$p_z \frac{dp_z}{dz} = -K_c \mu MRT \quad 3.3$$

The viscosity of a gas is dependant primarily on temperature. At low pressure, it is considered to be independent of pressure, which makes μ a constant in equation 3.3. Integrating along the whole length of the capillary tube gives the following equation:

$$p^2 - P_{BPR}^2 = 2K_c \mu MRT \quad 3.4$$

where $K = K_c L$, L is the length of the capillary tube, p is the pressure at the inlet of the capillary, and P_{BPR} is the outlet pressure (Mason *et al.*, 1998).

The development of the flux response system differed from the notational setup shown in Figure 3.2 to mitigate the small environmental disturbances that affected the accuracy of the results. Examples of such effects include the vibration of the work surface and the opening and shutting of the laboratory door. These disturbances were avoided by producing a differential system where the system setup was analogous to a Wheatstone bridge as shown earlier in Figure 3.1. FRT draws from the technology of a Wheatstone bridge in its precise comparison of resistances.

During the operation of the flux response apparatus, the flow setting and flow sensing capillaries cause a fixed pressure difference between the system and the reference side of the Wheatstone bridge, thereby resulting in a constant flowrate through the entire apparatus. The upstream (flow setting) capillaries cause a 99 % pressure drop, which determine the carrier gas flowrate. What is observable in a typical flux response profile as shown in Figure 3.2 is the constant baseline, described as a null system - the flow rates in both legs of the bridge are the same, causing the pressure measured by the DPT to be constant (p_0). Once a perturbation of probe molecules is introduced to the apparatus, the Wheatstone bridge assembly becomes imbalanced by the additional flow and the DPT detects a new pressure (p_1) within milliseconds - a near instantaneous response time due to the low pneumatic resistance of the pneumatic network. The virtually incompressible nature of the gas causes it to behave like a piston and pressure changes travel to the sensing DPT at the speed of sound of the carrier gas. During the course of the process, the probe molecules reach the catalyst where some of the molecules are adsorbed to the active sites within the catalyst. This net molar flow from the gas phase onto the surface of the catalyst produces a tiny reduction in the volumetric flow through the reactor side sensing capillary. The loss in gas molecules from the gas phase is detected by the DPT due to the highly sensitive nature of the bridge.

Because the change in pressure (Δp) caused by the probe molecules perturbation is small compared to the total pressure (P) of the apparatus and, with little error, the gas can be assumed ideal at room temperature and just above atmospheric pressure, the perturbation signal can be linearised. The integral of the pressure response to this tiny volumetric change has been shown to be directly proportional to the amount of probe molecules in the perturbation adsorbed onto the catalyst surface (Richardson *et al.*,

2008). Since the perturbation signal reaches the DPT within some *milliseconds* (based on the length scale of the equipment), a signal is observed well before the perturbation reaches the outlet of the apparatus. Therefore, FRT falls into the category of *in situ* techniques. Ultimately, it is the DPT, which limits the response time of the apparatus to 10 *milliseconds*.

Downstream of the upstream capillary chokes are the delay lines. The delay lines play a vital role in separating out the individual responses/phenomena during an experimental run by extending the path length of the signal to the DPT. These lines are pieces of empty tubing, typically several metres of 1/4 " PFA tubing or a custom-made stainless steel delay box that provide the important and powerful feature of allowing FRT to act as a combined flowrate and composition detector. Elucidating this point further, the addition or removal of a perturbation causes a near instantaneous pressure response, whereas the pressure responses from composition effects can be postponed as these only occur when the composition front reaches the sensing capillaries. Figure 3.3 presents examples of typical FRT profiles for single component adsorption.

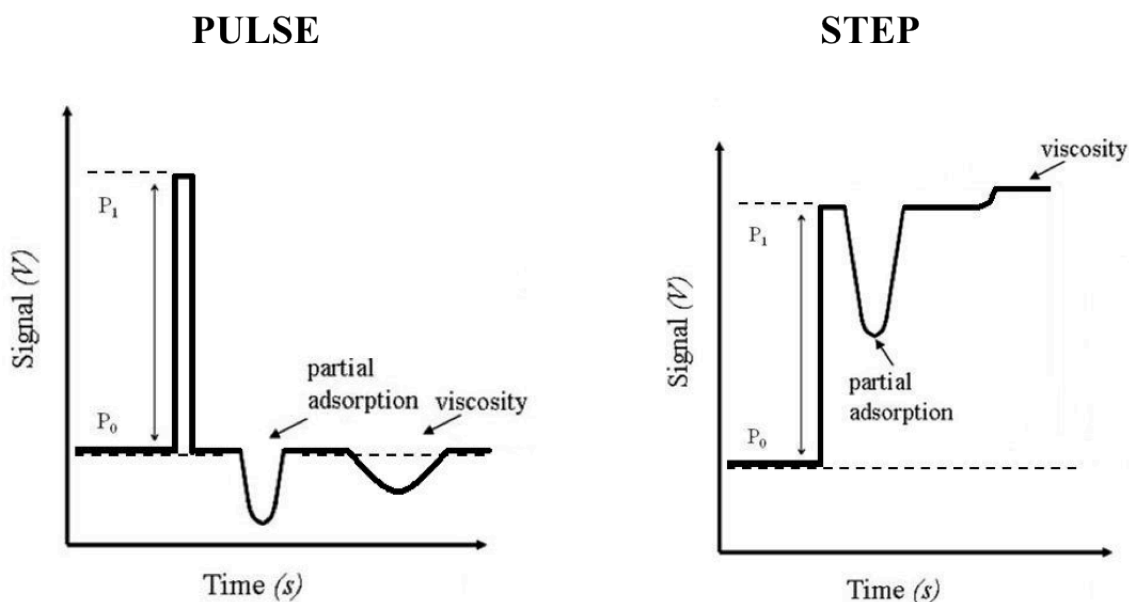


Figure 3.3: Typical flux response profiles for pulse and step experiments

Pulse and step experiments are the two well-established means of carrying out FRT experiments. In the pulse experimental setup, tiny quantities of probe molecules are injected to interrogate the material under investigation for a limited period. This method

of analysis is highly suited towards titration experiments. On the other hand, step experiments are performed through a longer experimental window, where there is a continuous injection of probe molecules until the system achieves a steady state or quasi equilibrium. As a result of this, step experiments can be programmed to study the dynamic cyclic behaviour of a sample. Although both experimental modes are able to divulge similar information, data extraction and analysis from step experiments is less complicated. What is important to note is that regardless of the mode of operation, the quantities of probe molecules injected into the system can be tightly controlled via the concentration and duration of the pulse/step.

3.2.2. Critical review and recommendations

The range of analysis available for catalytic characterisation from FRT contributes to the salient features of the technology. From detecting mass transport phenomena to observing the viscosity of gas mixtures, FRT boasts a clear flexibility in its features. To this extent, the capabilities of FRT include:

- FRT can potentially be used for any gaseous process with a volume change (dV/dt) caused by a perturbation of pressure, concentration or temperature.
- Flux response analysis of sample materials requires no prior calibration before test runs, thereby increasing the accuracy of flux measurements. The theory behind the analysis involves evaluating comparative ratios between both sides of the Wheatstone bridge.
- The construction of the FRT apparatus is relatively inexpensive when compared to other commercially available characterisation apparatus.
- FRT exhibits quick process and throughput times.
- FRT is an *in situ* technique that detects the response of sample materials to external perturbations at dynamic and steady state conditions.

Limitations and weaknesses of FRT are:

- The FRT apparatus must be built to insure internal components and peripheral connections are well insulated. Temperature fluctuations compromise the accuracy of the flux response.

- Analysis can only be undertaken for reactions that involve a net molar change i.e. ($\sum \nu_i \neq 0$).
- Current FRT apparatus operate only at atmospheric pressure.

3.2.3. Theory

In order to explain the workings of flux response, we must draw from the main features of a typical experimental response profile as illustrated in Figure 3.4. Considering the notational flux response system in Figure 3.2, at a time zero a known composition of perturbation gas is added to the carrier gas stream causing a rise in pressure indicated by the jump in the profile from p_0 to p_1 . The amount of time the pressure stays constant at p_1 is dependent on the time it takes for the composition front to traverse the length of the delay line. The increase in flowrate due to the addition of the perturbation gas stream is proportional to $p_1 - p_0$. As the composition front reaches the capillary tube, the change of viscosity as a result of the composition change causes a further response from p_1 to p_2 . This viscosity response may be a rise or fall depending on whether the viscosity of the combined carrier and perturbation gas stream increases or decreases. The viscosity change is proportional to $p_2 - p_1$.

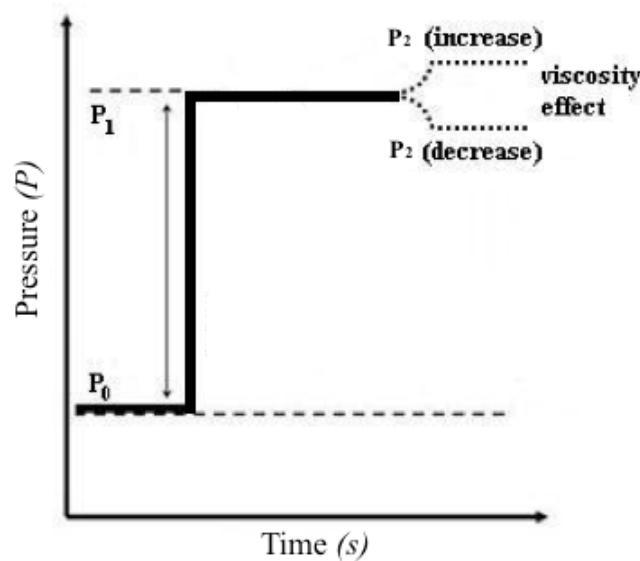


Figure 3.4: Expected flux response profile for perturbation addition

Two main analytical methods exist to extract information from a flux response profile – the differential analysis and the integral analysis. The differential analysis assumes that the perturbation step size is extremely small. The analyses of such perturbation sizes within the flux response apparatuses are impractical as they cannot be measured accurately enough. Integral analysis on the other hand assumes small and finite perturbation sizes, allowing for the accurate measurement of perturbation sizes within the flux response apparatuses.

3.2.3.1. Differential analysis

If a small change in flowrate and viscosity have occurred such that the pressure at the inlet of the capillary tube has risen by δp in response to a change in flowrate (δM) and a change in viscosity ($\delta\mu$), then equation 3.4 becomes

$$p^2 - P_{BPR}^2 = 2K\mu MRT \quad 3.4$$

$$(p + \delta p)^2 - P_{BPR}^2 = 2K(\mu + \delta\mu)(M + \delta M)RT \quad 3.5$$

Expanding equation 3.5 and subtracting equation 3.4 gives

$$2p\delta p + (\delta p)^2 = 2K(\mu\delta M + M\delta\mu + \delta M\delta\mu)RT \quad 3.6$$

For linear behaviour, the second-order terms $(\delta p)^2$ and $\delta M\delta\mu$ are very small, therefore, equation 3.6 is simply put as:

$$p\delta p = K(\mu\delta M + M\delta\mu)RT \quad 3.7$$

Substituting for RT in equation 3.7 with equation 3.4 gives

$$\frac{2p\delta p}{p^2 - P_{BPR}^2} = \frac{\delta M}{M} + \frac{\delta\mu}{\mu} \quad 3.8$$

Equation 3.8 forms the basis used to describe the two steps presented in Figure 3.4; the change in flowrate upon the addition of the perturbation gas (p_0 to p_1), and the pressure change due to the change in viscosity of the gas mixture (p_1 to p_2).

For the first pressure step in Figure 3.4, there is no viscosity change as the composition front has yet to reach the sensing capillaries through the delay lines ($\delta\mu = 0$). Therefore, equation 3.8 can be expressed as

$$\frac{2p_0(p_1 - p_0)}{(p_0^2 - P_{BPR}^2)} = \frac{\delta M}{M} \quad 3.9$$

For the second pressure step in Figure 3.4, there is a change in viscosity but non in the gas flowrate measured at the sensing capillaries as the flowrate change from the addition of the perturbation stream remains constant ($\delta M = 0$). This time, equation 3.8 takes the form

$$\frac{2p_1(p_2 - p_1)}{(p_1^2 - P_{BPR}^2)} = \frac{\delta\mu}{\mu} \quad 3.10$$

The ratio of equation 3.9 to equation 3.10 produces,

$$\frac{p_1(p_2 - p_1)}{p_0(p_1 - p_0)} \frac{p_0^2 - P_{BPR}^2}{p_1^2 - P_{BPR}^2} = \frac{M}{\mu} \frac{\delta\mu}{\delta M} \quad 3.11$$

Estimating the capillary and the pressure step sizes such that $p_0 \approx p_1 \approx p_2$ and $p_0^2 - P_{BPR}^2 \approx p_1^2 - P_{BPR}^2$, then equation 3.11 can be simply expressed as:

$$\frac{p_2 - p_1}{p_1 - p_0} = \frac{M}{\mu} \frac{\delta\mu}{\delta M} \quad 3.12$$

Now, assuming the carrier gas stream is of composition of X_i^0 and the perturbation stream is of composition X_i^{pert} and flowrate δM , by taking a simple mass balance the addition of the perturbation stream will produce a composition change in the carrier gas stream of,

$$\delta X_i = \frac{\delta M}{M + \delta M} (X_i^{pert} - X_i^0) \quad 3.13$$

The subscript i is used to denote any of the components in the mixture. Eliminating δM by combining equations 3.12 and 3.13 produces an equation giving the change in

viscosity (μ) in terms of the change in composition (X_i) and the size of the two changes in pressure (p_0 to p_1 and p_1 to p_2). It must also be noted that δM is negligible relative to M for differential-sized steps. Equation 3.14 shows the final working equation and the second key expression in describing the differential mode of analysis.

$$\frac{1}{\mu} \frac{\delta\mu}{\delta X_i} = \frac{p_2 - p_1}{p_1 - p_0} \frac{1}{(X_i^{pert} - X_i^0)} \quad 3.14$$

In the limit when $\delta\mu$ and δX_i become very small, $\delta\mu/\mu \delta X_i \rightarrow (d\mu/dX)/\mu$ and equation 3.14 becomes a differential,

$$\lim_{\delta X_i \rightarrow 0} \frac{1}{\mu} \frac{\delta\mu}{\delta X_i} = \frac{1}{\mu} \frac{d\mu}{dX_i} = \frac{d \ln \mu}{dX_i} = \frac{p_2 - p_1}{p_1 - p_0} \frac{1}{(X_i^{pert} - X_i^0)} \quad 3.15$$

3.2.3.2. Integral analysis

In the case of small finite perturbations gas, after the perturbation stream has been added, the pressure rises to p_1 and the flowrate to $M + m$. The viscosity remains at μ due to the effect of the delay lines. Applying to equation 3.4,

$$p_0^2 - P_{BPR}^2 = 2K\mu MRT \quad 3.4$$

$$p_1^2 - P_{BPR}^2 = 2K\mu(M + m)RT \quad 3.16$$

Once the composition front has travelled along the delay lines and reached the sensing capillary, the viscosity change ($\mu + \Delta\mu$) of the gas mixture causes a pressure change to p_2 . This second pressure step is expressed as,

$$p_2^2 - P_{BPR}^2 = 2K(\mu + \Delta\mu)(M + m)RT \quad 3.17$$

Subtracting equation 3.4 from equation 3.16 produces

$$p_1^2 - p_0^2 = 2KRT\mu m \quad 3.18$$

which can be factorised to

$$(p_1 - p_0)(p_1 + p_0) = 2KRT\mu m \quad 3.19$$

Repeating the same procedure for equations 3.16 and 3.17,

$$(p_2 - p_1)(p_2 + p_1) = 2KRT\Delta\mu(M + m) \quad 3.20$$

and dividing equation 3.20 by equation 3.19,

$$\frac{p_2 - p_1}{p_1 - p_0} \frac{p_1 + p_2}{p_1 + p_0} = \frac{M + m}{m} \frac{\Delta\mu}{\mu} = R_{add} \quad 3.21$$

gives R_{add} , the ratio of addition of perturbation gas. Bearing in mind that the pressure differences ($p_2 - p_1$ and $p_1 - p_0$) are small relative to the absolute pressure of the system, the ratio $(p_1 + p_2)/(p_1 + p_0)$ can be considered unity and ignored to produce the simplified equation,

$$\frac{p_2 - p_1}{p_1 - p_0} = \frac{M + m}{m} \frac{\Delta\mu}{\mu} = R_{add} \quad 3.22$$

Assuming the carrier gas is absent of species i and the addition of the perturbation stream contains species i , the mole fraction can be written as:

$$X_i = \frac{m}{M + m} \quad 3.23$$

With $\Delta\mu = \mu_1 - \mu_0$ and μ_1 representing the viscosity of the combined carrier and perturbation gas streams, equation 3.23 can be substituted into equation 3.22 to give,

$$\mu_1 = \mu_0(1 + R_{add}X_i) \quad 3.24$$

3.3. Materials

3.3.1. Functions of the Key Components of FRT

Due to the highly sensitive nature of FRT, various technical aspects of the technology have to be addressed before a working machine can be made to obey the theories of the method. Presented in Figure 3.5 is a schematic of one of the FRT apparatuses used during the course of this research. The salient features of the schematic include the DPT, the electronic mass flow controllers and back pressure regulators, the delay lines, the Wheatstone bridge, and the temperature programmable furnace.

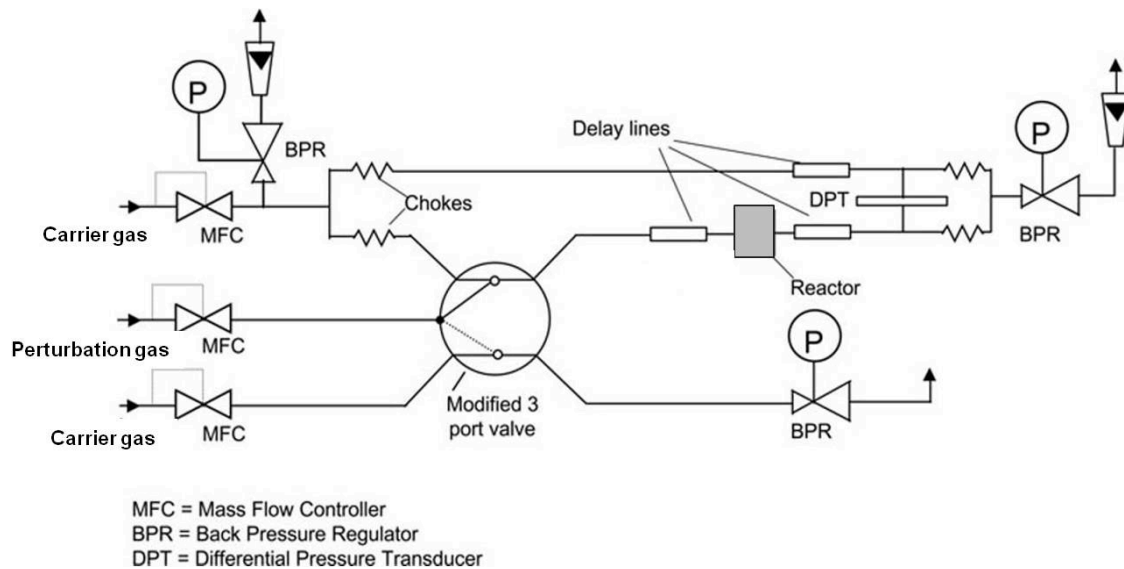


Figure 3.5: Schematic representation of a typical FRT experimental setup (Richardson *et al.*, 2004)

- **Differential Pressure Transducer**

The role that the DPT plays in FRT is crucial to its operation. During a null system, the signal from the DPT is considered as being perfectly balanced i.e. both system and reference legs are subject to equal flows through each side of the apparatus. At this point, the signal from the DPT is 0 volts. Following a perturbation of gas into the system stream, the volumetric flowrate increases. This in turn causes a direct response in the form of a pressure increase within the system to be detected by the DPT. This increase in volumetric flowrate is directly proportional to the signal response from the DPT and is measured as a voltage change (ΔV).

Two main types of differential pressure transducers exist, namely, the variable capacitance pressure transducer and the inductive pressure transducer. The capacitance transducer typically uses a thin diaphragm positioned between two fixed metal plates. Changes in pressure will either widen or narrow the gap between the two plates, therefore varying the measured electric fields. On the other hand, inductive pressure transducers use the principle of inductance to convert the flexing of a diaphragm into the linear movement of a ferromagnetic core. The measured magnetic field is as a result of the movement of the core, which varies the induced current generated by an AC powered primary coil on another secondary pick-up coil. The robustness of the capacitance transducer in testing environments with high-pressure fluctuations as well as its precise sensitivity over a wide range of temperatures lend to the inherent advantages displayed by this pressure sensor. However, moisture and corrosive gases easily damage the transducer. Inductance transducers have high resolutions, excellent linearity, and are inexpensive. The main disadvantage with this transducer is the limited range of the sensor.

The FRT systems make use of the differential capacitance transducer, as it is capable of handling pressure surges that may be caused during the running of the system by accidental leakages, pressure bottlenecks etc. The DPT is manufactured by Furness Controls (Model R.S.N 9411283) and is capable of measuring both positive and negative pressure differences corresponding to ± 1 V for a differential pressure of ± 10 mm of water. When used for experiments containing corrosive gases such as ammonia, the DPT is fixed to the upstream capillaries so that the corrosive gas bypasses the DPT in order to keep the transducer's internal components within a conducive environment.

The analogue signal from the DPT is measured with the use of a DataShuttle/USB 54 data acquisition system manufactured by Adept scientific. This data acquisition system converts the analogue signal to digital from which it can be easily processed with the use of a PC. Benefits of the acquisition system include ease of connection (USB), a fast response time, and a high resolution (22-bit).

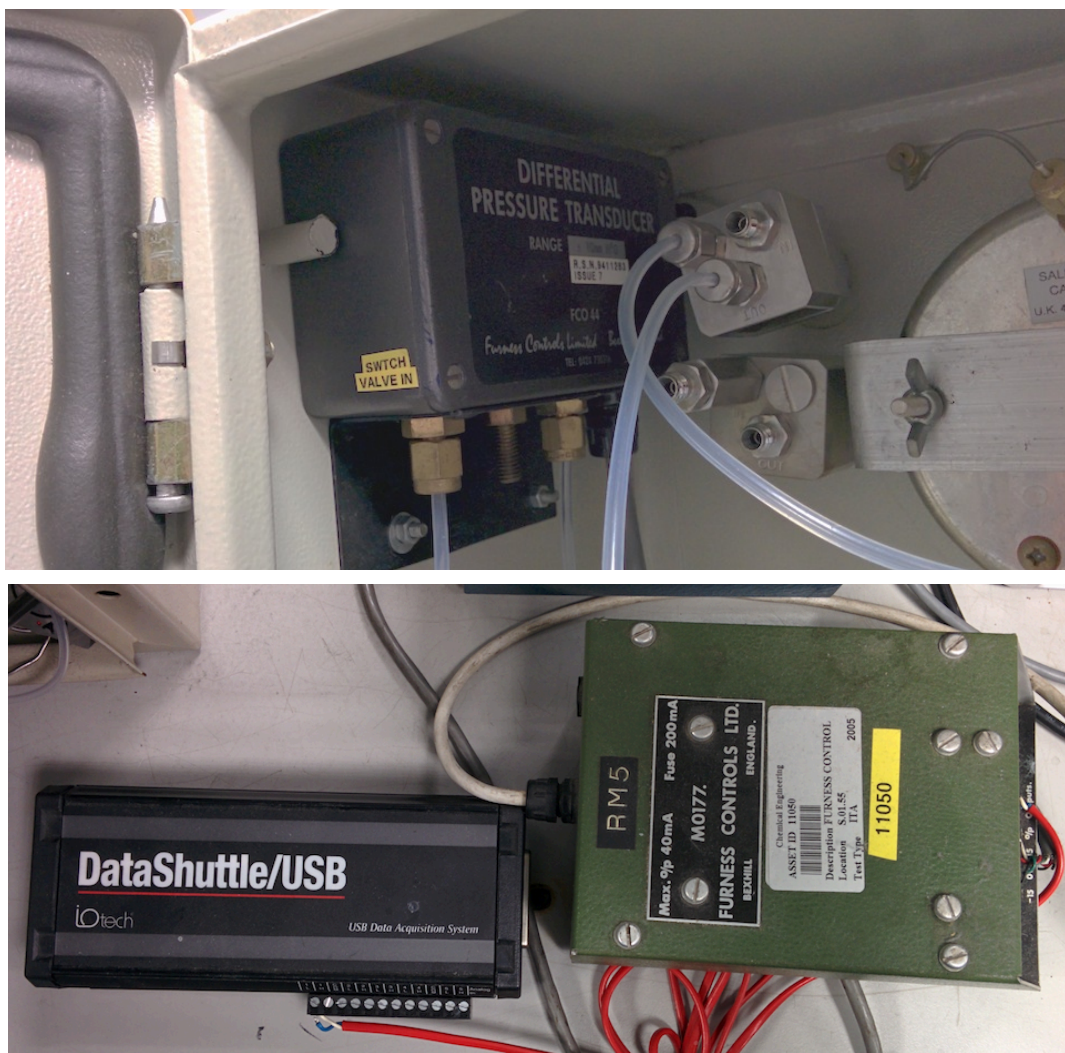


Figure 3.6: DPT with accompanying data acquisition system

- **Electronic Mass Flow Controllers & Back Pressure Regulators**

Balancing the pressure in the apparatus is controlled by both the electronic mass flow controllers (EMFC) and the back-pressure regulators (BPR). The carrier gas EMFC maintains the pressure drop across the Wheatstone bridge, thus acts like a pressure regulator. Attached to the EMFC is a BPR. The BPR keeps the inlet pressure constant and vents the excess gas. The upstream BPR sets the upstream pressure at a constant value while the downstream BPR safeguards the apparatus from atmospheric fluctuations such as sudden temperature changes. During operation, the upstream pressure is usually set just above atmospheric pressure between 1.25 – 1.5 *bar*. At these conditions, a minimal amount of excess flow is vented through the BPR.

The BPRs have also been modified by closing off the spring cavities and connecting them with 1/16-in tubing which enables them to experience the same local pressure, thereby preventing atmospheric pressure fluctuations. Control of the volumetric flowrates of both carrier and perturbation gases entering the apparatus is carried out using the EMFCs.

The EMFCs used in the FRT apparatus are manufactured by Bronkhorst (EL-FLOW Select series) and provide the unique capability of measuring and controlling an extensive range of flowrates between 0.014 – 2000 *ml/min*, thereby allowing for an increased level of data collection in FRT experiments. Advantages of the EMFCs include fast response times, excellent reproducibility, high accuracy, and virtual pressure and temperature independence. The digital features of the device also allow for the implementation of alarms and counter functions to combat flowrate fluctuations that may arise through leaks and disturbances from the gas manifold. Porter Instruments manufacture the BPRs used in the FRT systems.

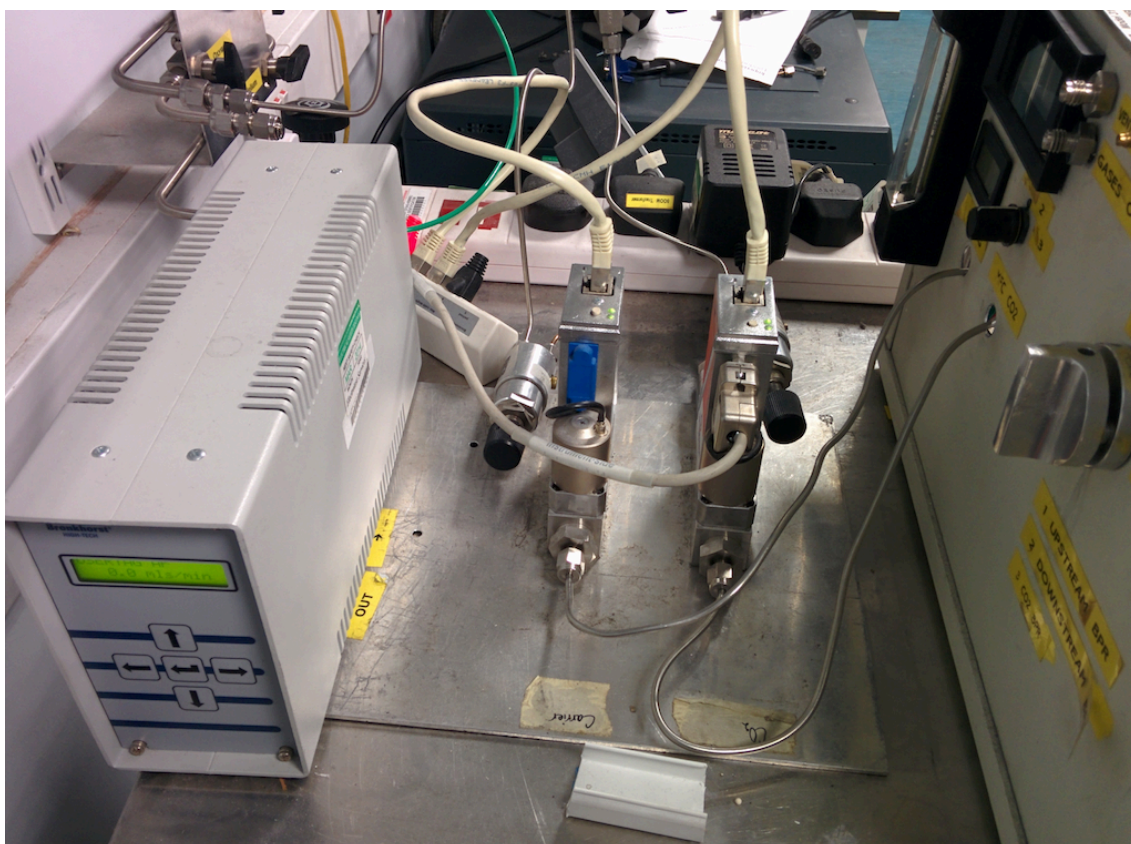


Figure 3.7: EMFCs used in the FRT systems

- **Delay Lines**

Downstream of the upstream capillary chokes are the delay lines. The delay lines play a vital role in separating out the individual responses during an experimental run. They prolong the composition front from the addition of a perturbation gas from reaching the sensing capillaries instantaneously. In this way, effects such as adsorption, desorption, and reaction can be detected individually. The delay lines are typically several metres of 1/4-in nylon, PFA, stainless steel tubing, or a custom-made delay box. The length of the delay lines varies in accordance with the requirements of the experimental configuration.

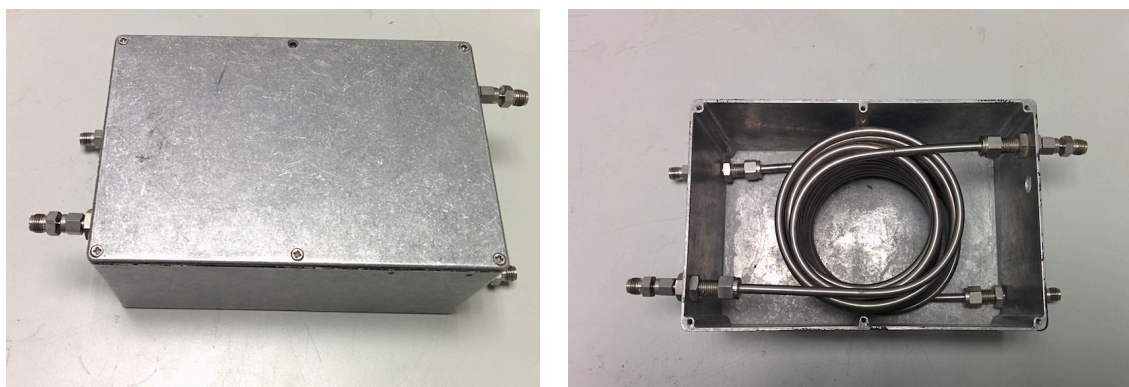


Figure 3.8: Delay lines

- **Wheatstone bridge**

Flow sensing and flow setting capillaries combine to make up the Wheatstone bridge assemblage. The flow setting capillaries act to control the flowrates passing through the system and reference legs of the bridge. During operation, the carrier gas stream makes its way through to the Wheatstone bridge housed in a metal block, where it is split into the closely matched system and reference streams before passing through the flow setting capillaries. The volumetric flowrate of the system and reference legs upstream of the DPT are also controlled using the EMFCs. The carrier gas subsequently passes through the sample under investigation and the delay lines before it re-enters the Wheatstone bridge assembly and the downstream flow sensing capillaries.

Mounting the Wheatstone bridge within the metal block serves the purpose of keeping the local temperature fluctuations between the capillaries to less than $1 \times 10^{-5} \text{ }^{\circ}\text{C}$. Measuring the noise level of the baseline signal is undertaken to ensure that this specification is met. The metal block can be fabricated from either stainless steel or brass. The flow setting capillaries are laminar flow elements manufactured by Porter Instruments. The downstream flow sensing capillaries are filter elements (0.5 to 10 microns) manufactured by Swagelok. Minimisation of the dead volume within the apparatus is also carried out as zero dead volume connections are machined into the block. The older systems built at Loughborough University used stainless steel tubes of 1.5 m length and 0.25 mm internal diameter for the upstream capillaries. The downstream capillaries consisted of 0.5 m length and 0.76 mm internal diameter stainless steel tubes. This is why the porous filter elements in use in the FRT systems today are referred to as capillaries.

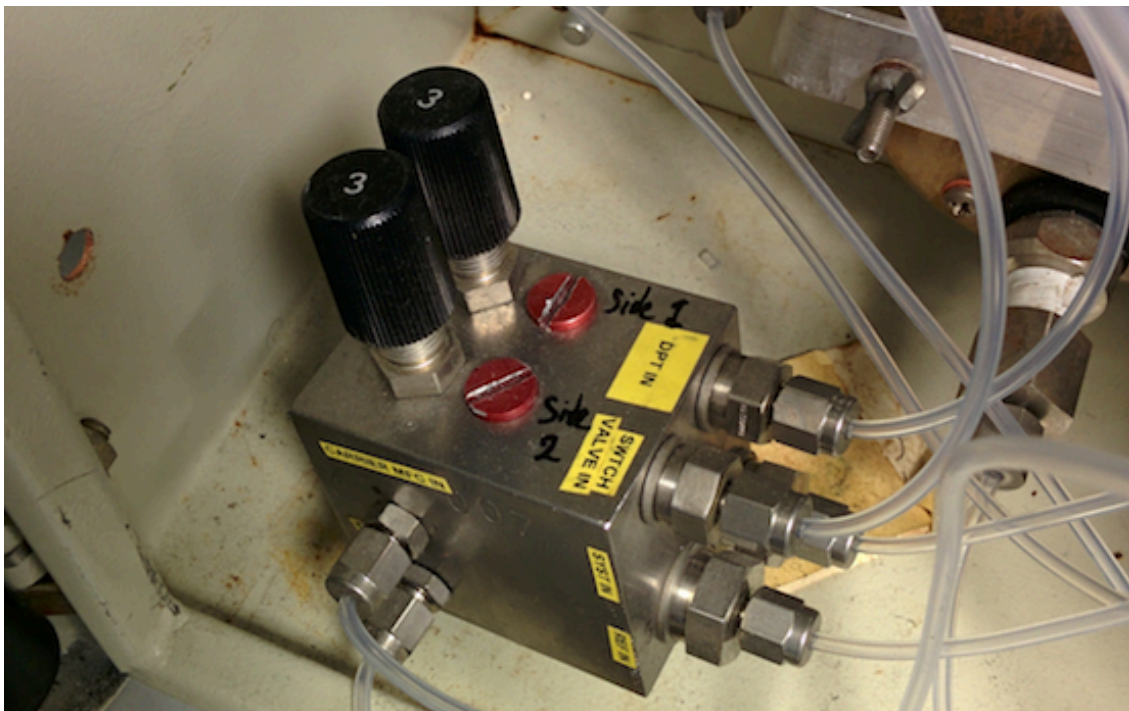


Figure 3.9: Wheatstone bridge used in FRT applications

- **Temperature programmable furnace**

A temperature programmable furnace is integrated into the Wheatstone assembly of the FRT experimental configuration. The furnace houses both the system and reference

reactors made up of 4 mm I.D. quartz tubes. The system reactor contains a fixed bed of the test sample in a well-defined geometry. In order to keep the temperature distribution between the system and reference reactors equal, the furnace was built with a modified aluminium block compartment fixed to two electric heating clamps in the Imperial College Chemical Engineering Student Workshop. The furnace is controlled with a modified heat controller constructed in the Imperial College Chemical Engineering Electrical Workshop and operates up to 1000 °C.

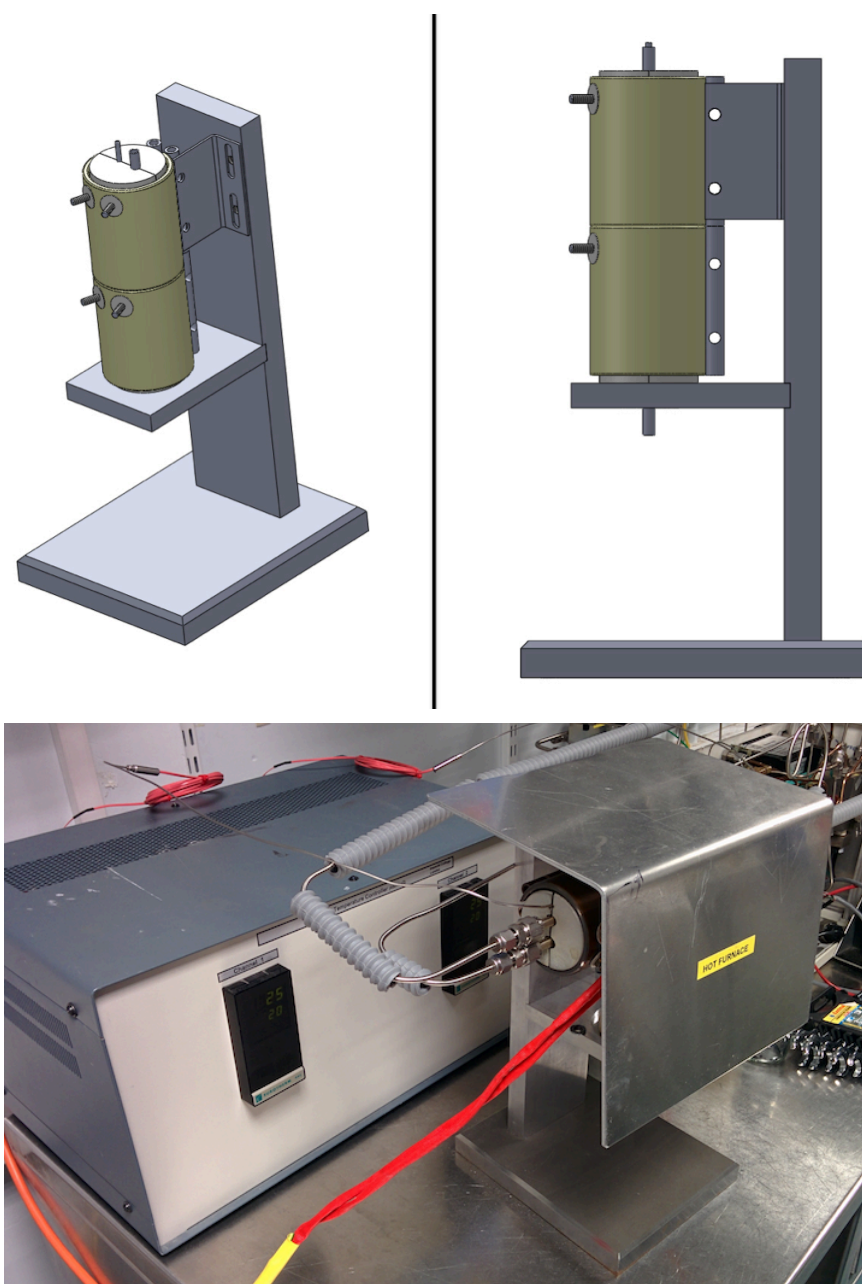


Figure 3.10: CAD model and working construction of the temperature programmable furnace

3.3.2. FRT Systems

Three FRT systems were inherited from the Department of Chemical Engineering, Loughborough University during the transfer of the technology to the Department of Chemical Engineering and Chemical Technology, Imperial College London. Over a six year period, these apparatuses have been continuously modified in order to carry out experimental work and studies in novel fields of catalysis. A detailed description of each system emphasising the type of experimental work tailored to each apparatus is provided below.

3.3.2.1. Downstream FRT System

The downstream FRT system is made up of PFA and stainless steel tubing with separate upstream and downstream brass blocks containing the flow sensing and flow setting capillaries. The Downstream FRT system is characterised by having its DPT situated downstream of the system. In this way, the DPT is susceptible to active degradation if exposed to corrosive gases during experimentation. For this reason, this system is only suitable for the investigation of sample materials where the perturbation gas is not of a corrosive nature. Consequently, the Downstream FRT system has been modified for the investigation of ultra fast surface areas of aluminium oxide at liquid nitrogen temperature, the investigation of the number of basic sites on commercial zeolites using CO₂, and the investigation of the corresponding CO₂ diffusivity coefficients in the commercial zeolites. The Downstream FRT system is shown in Figure 3.11.



Figure 3.11: Downstream FRT System

3.3.2.2. Upstream FRT System

The Upstream FRT system like the name suggests, has its DPT located upstream of the system. This modification allows for the investigation of sample materials using corrosive gases, as the perturbation gas is able to bypass the DPT on its way through the system. In this way, the internal components of the DPT are kept safe during operation. The system is made up of PFA tubing with a single stainless steel block that houses the flow setting and flow sensing capillaries. Combining the capillaries within the same block ensures that both sets of capillaries are exposed to the same local temperature. This way, the errors in accuracy due to fluctuations in temperature are minimised. The modifications to this system were done in line with providing a working apparatus capable of studying acid site quantification on zeolites using ammonia. The Upstream FRT system is presented in Figure 3.12.

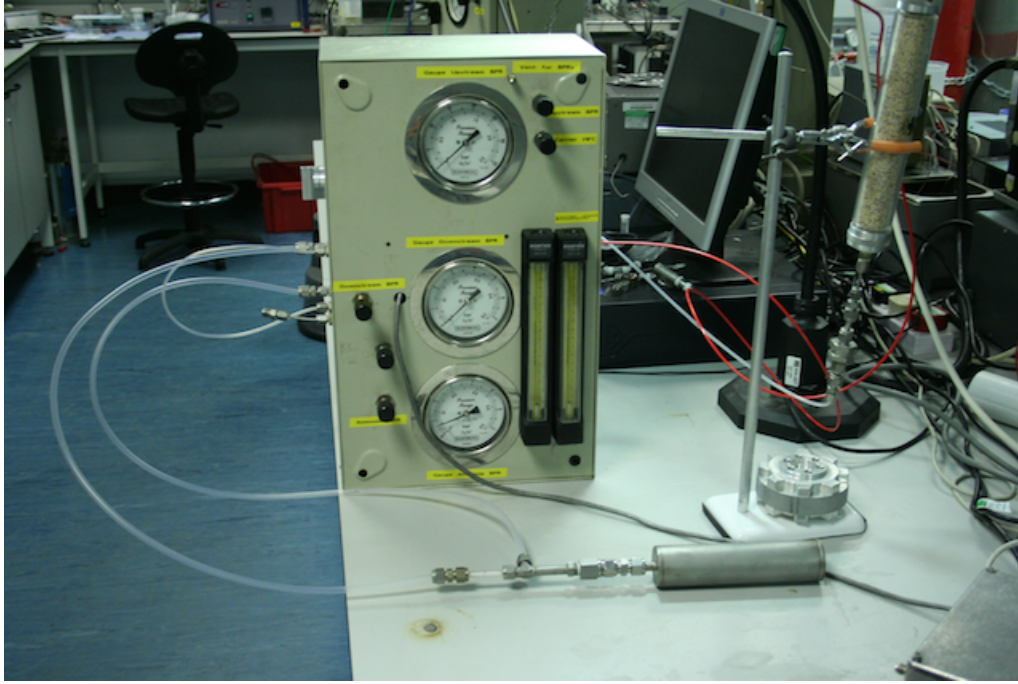


Figure 3.12: Upstream FRT System

3.3.2.3. Upstream Stainless Steel FRT System

The experimental configuration of the Upstream Stainless Steel FRT system is extremely similar to the Upstream FRT system. It too is comprised of a single stainless steel block that houses both the flow setting and flow sensing capillaries. The DPT is also fixed upstream of the system, thereby allowing FRT investigations using corrosive gases. The main difference that will be highlighted clearly in Figure 3.13 is the use of only stainless steel pipework throughout the system. The Upstream Stainless Steel FRT system is also considerably smaller than the other two systems. This system was built with the viewpoint of providing a more user-friendly working apparatus geared towards a compact and robust working setup. The possibility of improving the accuracy of the measured flux response signals was also a key driver as the insulation area of the Upstream Stainless Steel FRT system is considerably less compared to the other two systems.



Figure 3.13: Upstream Stainless Steel FRT System

Modifications to this system allowed for the investigation of propane diffusion coefficients in the washcoats of cordierite monoliths.

3.3.2.4. FRT Component Specifications

The component parts used in the FRT systems are listed in Table 3.1.

Table 3.1: Specification of FRT component parts

Component	Manufacturer	Model Part	Specification
Carrier gas EMFC	Bronkhorst	EL-FLOW Select series	min. 0.16 ... 8 <i>ml/min</i> max. 0.16 ... 25 <i>l/min</i>
Perturbation gas EMFC	Bronkhorst	EL-FLOW Select series	min. 0.16 ... 8 <i>ml/min</i> max. 0.16 ... 25 <i>l/min</i>
DPT	Furness Controls	R.S.N 9411283	± 1 <i>V</i> for 10 <i>mm</i> H ₂ O
Upstream flow setting capillaries	Porter Instruments	Red anodize	60 <i>ml/min</i>
Downstream flow sensing capillaries	Swagelok	SS 2 F K 2	2 micron element pore size
Modified upstream BPR	Porter Instruments	9000 SMVS 60	60 <i>psi</i>
Modified downstream BPR	Porter Instruments	9000 SMVS 15	15 <i>psi</i>
Modified perturbation gas BPR	Porter Instruments	9000 SMVS 30	30 <i>psi</i>

3.4. Literature review

Over the years, FRT has been successfully applied in studying various aspects of catalysis including, sorption-effect chromatography, kinetic effects of heterogeneous reactions, and perturbation viscometry. Most recently, FRT has highlighted novel analytical methods of quantifying acid sites in zeolites, determining gas crossover and permeabilities across a variety of polymeric membranes, and establishing the surface areas of materials at 77 *K*.

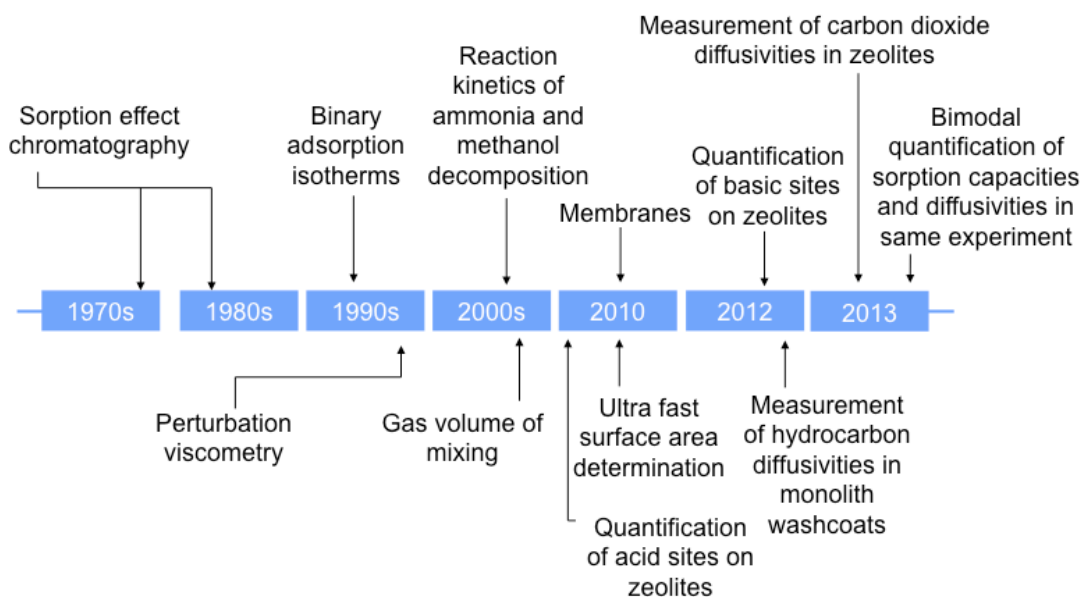


Figure 3.14: Timeline of key innovations in flux response technology

3.4.1. Sorption-Effect Chromatography

Flux response analysis grew out of opportunities presented in sorption-effect chromatography and composition front scanning used to identify the void zones in packed columns (Rathor & Buffham, 1988). Researchers Rathor and Buffham were able to show how a pause in the flow of gas entering the chromatography column when the sorbable material entered the packing, could be used to develop a theory that could measure the void zones in packed chromatographic columns. They were able to identify experimentally through the use of a sensitive differential capillary flowmeter, the fluctuations that existed when the flow of gas was absorbed by the stationary phase. The dip and surge in flow were attributed to the absorption and the complementary band of absorption leaving the packing. Buffham *et al.* were able to develop on this theory and suggested further explanations for the downstream flow rate changes that occurred in a two-column chromatograph (Buffham *et al.*, 2002). In terms of adsorption, they explained the downstream changes were caused by the irregular capture and release of molecules in the internal anomalous zone of the two-column chromatograph.

As a result, this method of FRT is based on the sorption effect technique for measuring gas-solid adsorption isotherms. The change in gas flowrate brought about by the capture and release of the molecules from the solid surface has been termed the sorption effect. In this method of FRT, the sorption effect is analysed and used to measure two

parameters (Buffham *et al.*, 2000). Firstly as a measure of the interaction between the molecules and the surface and secondly as a measure of the change in gas volumes that occurs due to the interaction between the gas and the solid.

3.4.2. Kinetic Effects of Heterogeneous Reactions

Flux response technology has been successfully applied in the determination of reaction kinetics for heterogeneous catalytic reactions in microreactors (Buffham *et al.*, 2000). The concept of flux response is based on the *net flux* of molecules leaving a reactor i.e. the difference in the number of molecules adsorbed and desorbed during the reaction. To explain this concept further, one must understand the details of what is transpiring on the surface of the catalyst.

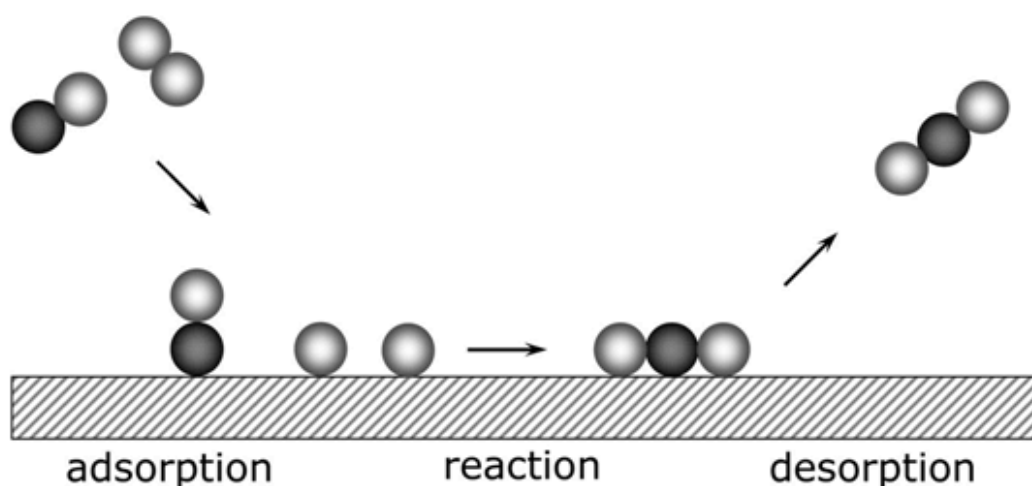


Figure 3.15: Schematic representation of a catalytic reaction cycle

In a typical catalytic reaction as shown in Figure 3.15, two key principles occur on the surface of the catalyst which provide vital information in understanding the workings of the catalyst; adsorption of the reactants and desorption of the products. During a reaction, the number of molecules adsorbed and desorbed from the catalyst surface may differ. This difference is known as the *net flux* and is the principle theory of investigation examined in flux response technology. Buffham *et al.* define the flux response for a continuous flow gas-solid reaction as the net rate at which the molecules leave the reactor when some input, or other variable is changed. The work carried out

by Buffham *et al.* has shown how the analysis of this flux response yields important information regarding the kinetics of the reaction (Buffham *et al.*, 2000).

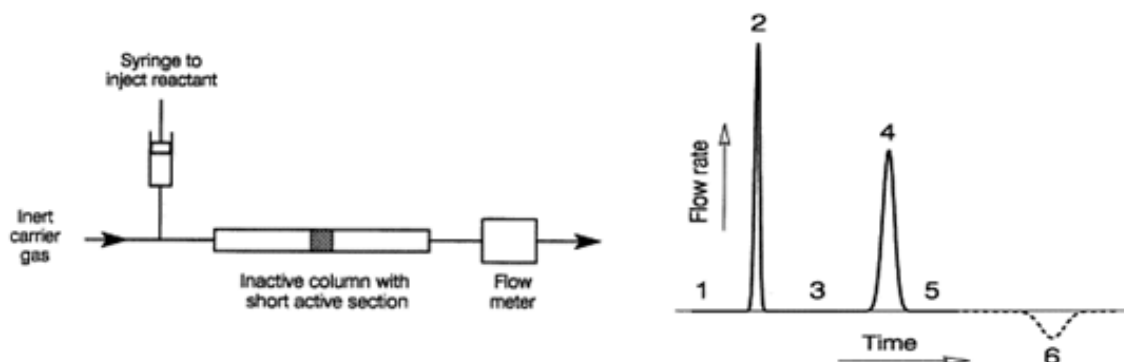


Figure 3.16: Schematic of a typical flux response experiment with the complimentary rate vs. time profile (Buffham *et al.*, 2000)

In a typical flux response experiment, the measurement of the effluent flow rate versus time is illustrated in Figure 3.16. The numbered points are: (1) the initial baseline flowrate (2) the pulse injection of the reactant, causing a surge in the flowrate (3) the reactant passing through the inert packing (4) the change in the number of moles during the reaction causing a flux response (5) the response returning to the initial baseline (6) the detection of a viscometric response due to the formed products. By analysing the resultant flux response peaks, Buffham *et al.* were able to develop the theory required to determine the extent and conversion for a reaction.

In demonstrating this theory, Buffham *et al.* exhibited flux response technology in analysing the rates of heterogeneous catalytic reactions in a continuous-flow gas-solid microreactor. Experiments were carried out using the catalytic decomposition of methanol over platinised alumina in which a perturbation of methanol was injected into a helium carrier gas stream by means of a syringe. To determine whether the reaction had taken place, the effluent gas stream was linked to a mass spectrometer to analyse its composition. By considering a single irreversible reaction, the theory was developed as follows,



where, ν_R and ν_P are the moles of reactant R consumed and product P produced respectively. The argument was that the molar amount of reactant R injected into the microreactor could be determined by considering the integral of the injection peak. By letting the signal measured by the DPT be $S(t)$ and the molar flowrate be $F(t)$, the molar amount of reactant R was given by,

$$R = K \int_{t_1}^{t_3} S(t) dt = \int_{t_1}^{t_3} F(t) dt \quad 3.26$$

where, the time subscripts t_1 and t_3 refer to points 1 and 3 in Figure 3.16. K is the calibration factor that converts the measured signal from the DPT to a molar flowrate. The flux response of the reaction shown between points 3 and 5 gives the net molar amount produced by the reaction:

$$P_{net} = K \int_{t_3}^{t_5} S(t) dt = \int_{t_3}^{t_5} F(t) dt \quad 3.27$$

The extent of reaction if the reaction were to go to completion would be expressed as R/ν_R . In reality, the actual extent of reaction is $P_{net}/(\nu_P - \nu_R)$. The conversion ratio X is defined as the ratio of the actual extent of the reaction to the extent were the reaction to go to completion. Hence, from equations 3.26 and 3.27, the conversion X is given as,

$$X = \frac{\nu_R}{\nu_P - \nu_R} \frac{P_{net}}{R} = \frac{\nu_R}{\nu_P - \nu_R} \frac{\int_{t_3}^{t_5} S(t) dt}{\int_{t_1}^{t_3} S(t) dt} = \frac{1}{(\nu_P/\nu_R) - 1} \frac{\int_{t_3}^{t_5} F(t) dt}{\int_{t_1}^{t_3} F(t) dt} \quad 3.28$$

By adapting known techniques in gas adsorption, Buffham *et al.* were able to successfully apply FRT to methanol decomposition over platinised alumina and as a result, were able to explain the flux response as the cumulative outcome of several interacting and competing effects such as adsorption, desorption, rate of reaction, and heat of reaction.

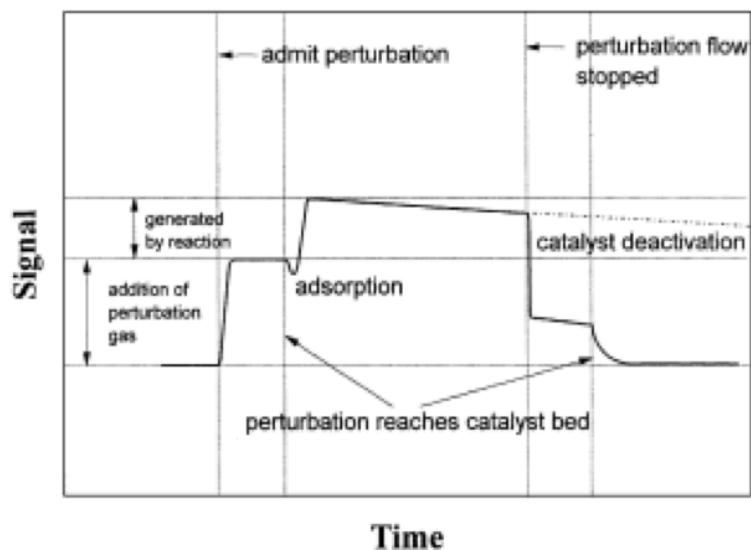


Figure 3.17: Expected results for simultaneous flow and concentration perturbations (Buffham *et al.*, 2000)

A typical flux response profile is shown in Figure 3.17 and details the reasoning behind generated flux response profiles. As the reactant is added at the syringe point, a step change is induced due to the change in the inlet flow rate. Subsequent to this, a flux response is attained. Adsorption is followed by reaction and finally catalyst deactivation. The return of the flow rate to its original baseline following cessation of the perturbation flow is delayed by desorption. Such responses were easily detected and recorded the adsorption of reactants and desorption of products. The results of the experiments clearly showed FRT as a tool that could be applied to micro-catalytic reactions, but also offered an insight into plausible improvements and recommendations for the future development of the technology.

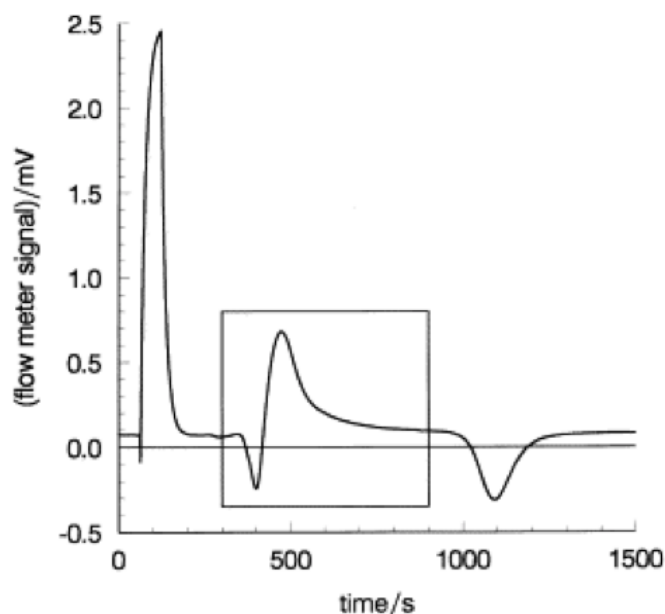


Figure 3.18: Flux response profile for NH_3 decomposition at $600\text{ }^\circ\text{C}$ and 0.1 barg (Buffham *et al.*, 2002)

Subsequent investigative studies were carried out by Buffham *et al.* to further demonstrate the flux response technique. One such experiment involved investigating ammonia decomposition over cylindrical platinised alumina catalyst pellets (Buffham *et al.*, 2002). In this experiment, a pulse of an ammonia (10 mol %)-argon mixture was injected into argon through a microreactor and the flux response profile for this experiment is shown in Figure 3.18. The first peak (positive) depicts the flowmeter response caused by the addition of ammonia. The second peak at about 350 s (negative) is caused by the ammonia being adsorbed, which is then followed by another positive peak as the adsorbed ammonia reacts and desorbs. The final negative peak is a viscometric response to the products and unreacted ammonia reaching the flow meter.

Following on from these experiments, Buffham *et al.* went about developing a mathematical model and simulation of the flux response of a gas-solid microreactor. A combination of the model with a series of flux experiments allowed reaction, adsorption, and mass-transfer rate coefficients to be determined. However, several limitations to this model became apparent during the study. First off, a major difference between the time scales of the experimental data and the simulated results existed. This was due to different reaction parameters, operating variables, physical scales, and the range of validity of the mass transfer correlation. Another limitation was due to the fact that model parameters and kinetic data could not be extracted from the flux response

data. Such limitations were actively considered and proposed solutions consisting of varying operating conditions, catalyst pellet size, and physical conditions were suggested in order to be able to extract more realistic parameters for the simulation (Buffham *et al.*, 2002).

As a novel technique, Buffham *et al.* were able to demonstrate the effectiveness and potentials of FRT in catalytic reactors and also acknowledged the vast scope for growth and development (Buffham *et al.*, 2000, 2002).

3.4.3. Perturbation Viscometry

As studies into FRT continued over the years, further applications were instilled beyond its use in gas solid micro-reactors and gas chromatography. Possessing the capacity to detect infinitesimal changes in flowrates provided an opportunity for the technology to be extended and used as a technique in perturbation viscometry. Being able to distinguish gas viscosities accurately is a pertinent parameter in thermo-physical models because viscosities indicate how different molecules interact with each other (Mason *et al.*, 1998). To this effect, the development of a differential capillary viscometer has been a continuous project undertaken by FRT researchers (Mason *et al.*, 1998, 2000; Russell *et al.*, 2002, 2005, 2004).

The perturbation viscometer technique in FRT originated from the work Mason *et al.* carried out involving a modified capillary viscometer (Mason *et al.*, 1998). Experimental results showed how a small stream of perturbation gas was able to alter the flow rate and composition of a mixture flowing through a capillary tube.

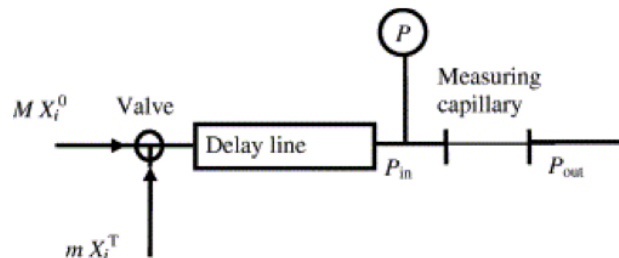


Figure 3.19: Schematic diagram of perturbation viscometer (Russell *et al.*, 2002)

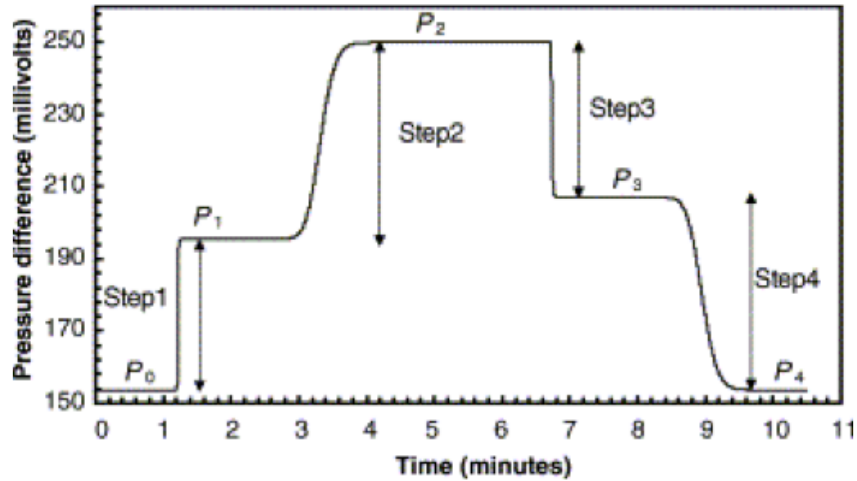


Figure 3.20: Typical pressure profile during perturbation viscometry (Russell *et al.*, 2002)

By taking Figure 3.19 and Figure 3.20 into consideration, the concept behind perturbation viscometry can be explained. A main gas flow (M) of a known composition (X_i^0) flows through the valve followed by a delay line and then the measuring capillary tube. Upon addition of the perturbation gas (m) of composition (X_i^T), the pressure at the inlet of the capillary tube rises proportionally to the change in flowrate (Step 1). A second change in pressure is also detected due to the empty volume between the point where the perturbation gas is added and the capillary tube. This second pressure change is proportional to the change in viscosity (Step 2). Removal of the perturbation causes the pressure change from P_2 to P_3 (Step 3) followed by a decrease in viscosity and a return to the original baseline (Step 4).

The main differences between conventional viscometers and the modified viscometer were key to the development of the FRT technique. The first main difference was the measurement of the gradient of viscosity-composition function as opposed to directly measuring the gas viscosity. The second major difference involved a change in the setup of the apparatus. The capillary tube was used first as a flow meter, then a viscometer. The mathematical division of the two responses results in the viscosity-composition gradient (Mason *et al.*, 1998). By incorporating these two major differences, Mason *et al.* showed that the measurement of differentials followed by integration is more accurate than direct measurements of viscosity.

This capillary viscometer was developed further still and through considerable modifications gained from experience, was able to carry out experiments at higher

temperatures. A fully thermostated apparatus developed by Russell *et al.* (2002) was able to demonstrate this to good effect by investigating a helium-nitrogen gas mixture at 360 °C. Consistent results in these investigations proved the viscometer's suitability in both low and high temperature experiments. Furthermore, results have shown perturbation viscometry can be successfully used to determine viscosity-composition data for both ideal and non-ideal gases at a range of temperatures (Russell *et al.*, 2006). The use of FRT in perturbation viscometry has developed from a basic laboratory technique to an established method that can be used in addition to other conventional measurement techniques.

3.4.4. Gas Permeabilities of Polymeric Membranes

The measurement of gas permeability by FRT has been applied in the investigation of low-level gas permeabilities in proton exchange membrane (PEM) electrolytes used for fuel cell applications and packaging films.

Modifications to the FRT apparatus included the integration of a permeation cell to house the membrane under investigation into the Wheatstone bridge. This experimental modification allowed for both the *in situ permeability* and the *online permeability* modes of analysis to be applied in the investigation of gas permeabilities. The schematics of both methods of permeability analysis using FRT are illustrated in Figure 3.21 and Figure 3.22. In the *online permeability* mode of analysis, the permeation cell is attached to the system side of the Wheatstone bridge via an ON/OFF valve, allowing for the delayed accumulation of the permeate gas used in pulse-type experiments.

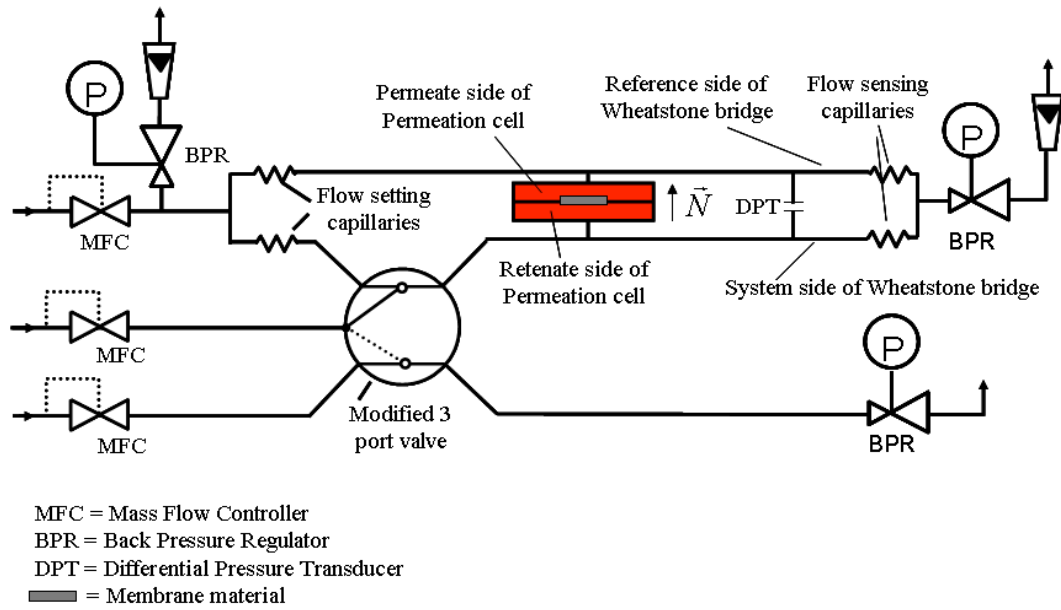


Figure 3.21: Schematic of FRT *in situ* permeability technique (Palmer, 2010)

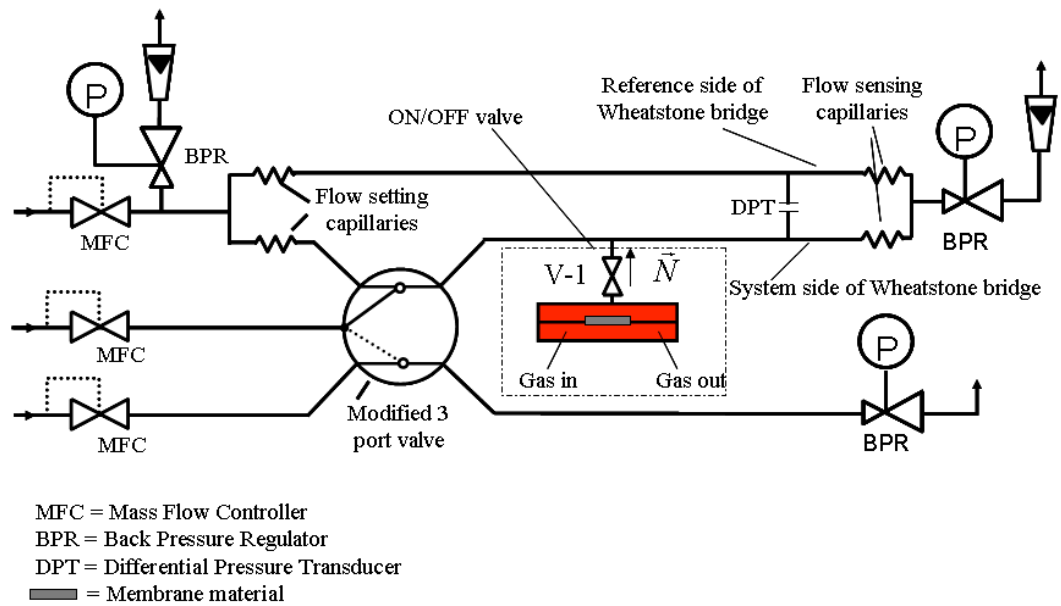


Figure 3.22: Schematic of FRT *online* permeability technique (Palmer, 2010)

The expected flux response profiles of the *in situ* method shown in Figure 3.23 shall be used to explain the theory of the method. Firstly, consider the flux response profile in part (a) of Figure 3.23 that separates the system and reference signal. The system signal represents the addition of perturbation and the loss of permeate gas from the retenate side of the permeation cell. The reference signal represents a steady baseline until the gain of permeate gas is measured. It should be noted here that the DPT measures the system side as a positive voltage and the reference side as a negative voltage. Secondly,

consider part (b) of Figure 3.23 where the flux response profile is a combination of both the system and reference signals. Upon the addition of the perturbation gas to the system side of the Wheatstone bridge, a pressure step change is exhibited (Δp_0). The composition front travels through the length of the apparatus till it reaches the surface of the membrane. At the surface of the membrane, the perturbation gas diffuses through the membrane, causing a reduction in pressure in the FRT apparatus. Following this, the permeate gas enters the reference side of Wheatstone bridge resulting in the flux effect, (Δp_1) representing the difference of the system and reference signals at the interface of the membrane. The viscosity effect from the change in the composition of the carrier gas (p_3) is the third change in pressure.

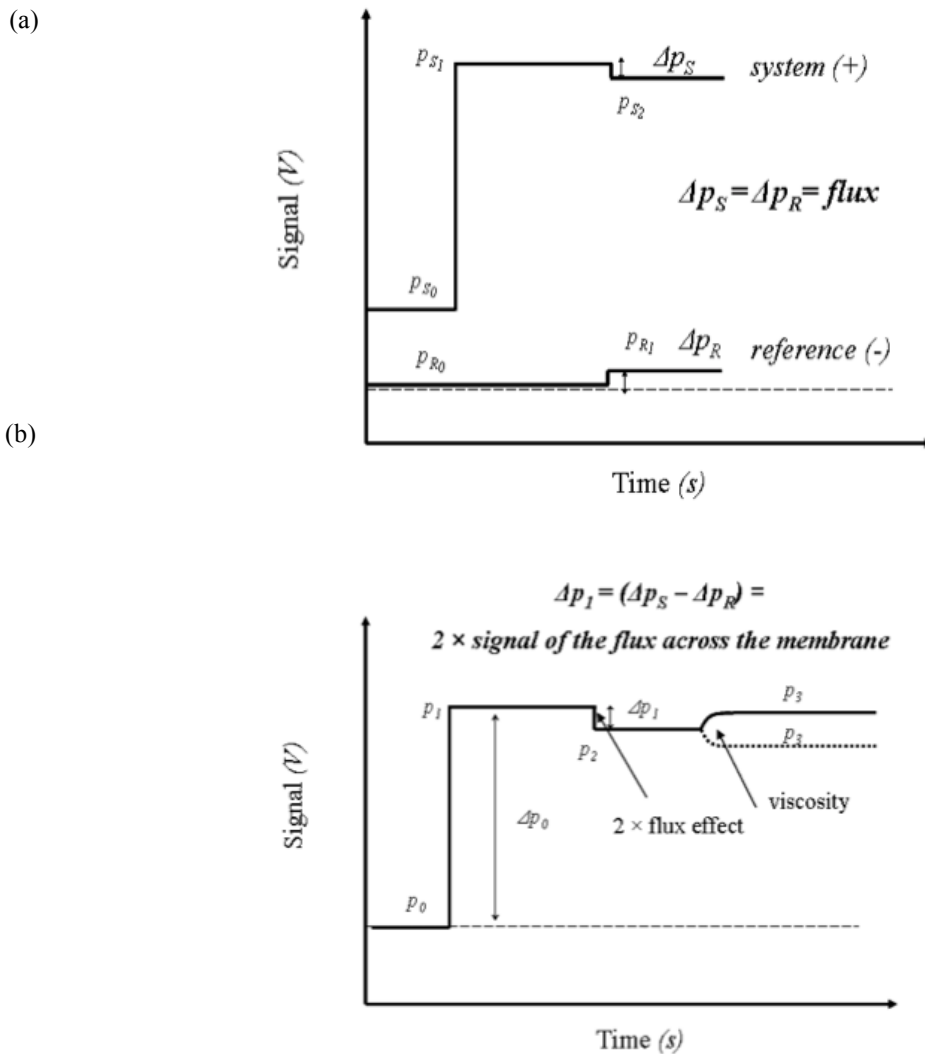


Figure 3.23: (a) Schematic of the expected flux response profile showing the system and reference signals for the *in situ* permeability method (b) Schematic of the expected flux response profile for the *in situ* permeability method (Palmer, 2010)

The fundamental benefit of the *in situ permeability* mode of analysis is the ability to perform dynamic experiments on membrane systems. This allows for the measurement of transient fluxes through the investigated membranes.

The *online permeability* method involves the delayed accumulation of the permeate gas for a given time before making pulse injections into the FRT apparatus. This delayed time is referred to as the accumulation time. Consequently, the experimental setup is less restricted by the specification of the DPT because the accumulation time can be incorporated to suit the permeation rate of the diffusing gas. Figure 3.22 demonstrates the experimental configuration showing the permeation cell attached to the system side of the Wheatstone bridge via an ON/OFF valve (V-1). Gas permeability experiments are carried out by closing the V-1 valve to accumulate the permeate gas for a given accumulation time before being injected into the FRT apparatus. Successive pulses of the permeate gas allows for the determination of the flux of permeate gas across the membrane. Figure 3.24 and Figure 3.25 represent the expected flux profiles for the *online permeability* method.

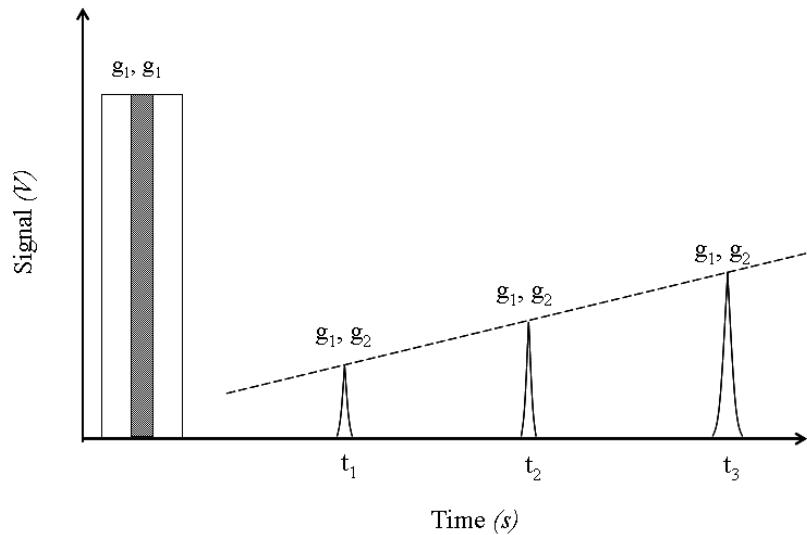


Figure 3.24: Schematic of the accumulation profile (Palmer, 2010)

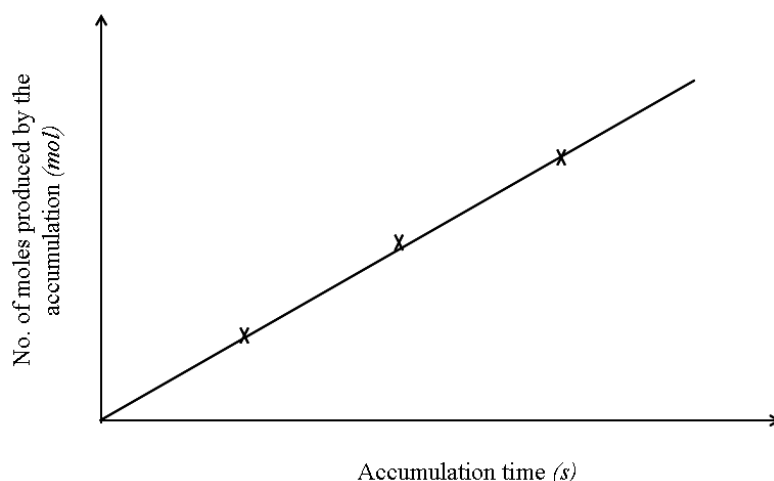


Figure 3.25: Schematic of the online permeability flux profile (Palmer, 2010)

3.5. Summary of *In Situ* Techniques

The remarkable difference in catalyst characterisation over the past fifty years has largely been defined by developments in the field of catalysis that have been sparked by the vast needs of the industry. These growing challenges include, the need to gain an enhanced control of catalysts in order to meet the requirements for increased optimisation of current processes and the realisation of future possibilities; the appearance of new classes of solids with catalytic properties and peculiar characteristics; the need for improvements in technology and computer based development enabling the use of powerful and user-friendly versions of known techniques; and the need to explore and analyse the intrinsic details of catalysts operating in real time under working conditions (Bartholomew & Farrauto, 2005).

Presented in Table 3.2 is a comparative analysis of the *in situ* catalyst characterisation techniques explored in the preceding sections. The analytical summary is structured around evaluating each of the techniques against specified criterion that aim to satisfy both the scientific and practical aspects of the methods previously described. Limiting factors that determine how effective these tools perform include how fast they operate, how much they cost, whether they operate in real time under operating conditions, with minimal calibration, are able to work within a high resolution, and are able to generate highly reproducible results.

Table 3.2: Analysis of the inherent benefits and limitations of various characterisation techniques

		FRT	TAP REACTOR	MAGNETIC SUSPENSION BALANCE	CAHN MICRO BALANCE	TPA	TEOM	ADSORPTION MICROCALORIMETRY
Operating Conditions	<i>Temperature</i>	Limited by the furnace	200 -1200 <i>K</i>	77-2273 <i>K</i>	288-303 <i>K</i>	293-1273 <i>K</i>	293-873 <i>K</i>	100-403 <i>K</i>
	<i>Pressure</i>	Atmospheric to 10 <i>bar</i> currently	Vacuum to 3.33 <i>bar</i>	UHV-2000 <i>bar</i>	Atmospheric	Vacuum (excluding TPD)	50.7 <i>bar</i>	UHV
	<i>Resolution</i>	0.02 μg		0.01mg - 1 μg	0.1 μg	0.5 – 5 <i>g</i>	1 μg	0.5 – 2 <i>g</i>
	<i>Response Time</i>	0.1 <i>s</i>	0.1 <i>s</i>	1 <i>s</i>	10 <i>s</i>	A few seconds	0.1s	Submillisecond
Experimental Considerations	<i>Steady State</i>	YES	YES	YES	YES	YES	YES	YES
	<i>Non-Steady State</i>	YES	YES	YES	YES	YES	YES	YES
	<i>Catalyst Contact</i>	Flow through catalyst bed	Pulsed through catalyst bed	Dosing through closed sample vessel	Diffusion into catalyst heap	Gas flow through catalyst bed	Constant flow through catalyst bed	Gas dose of sample cell
Economics	<i>Purchase Cost</i>	£15,000	≈£65,000	≈£80,000	£6,000	£25,000	£50,000	≈£30,000
Practical Considerations	<i>Versatility</i>	Any reactor, shape and size	Short length tubular reactor			Quartz tube fixed bed (typically 2-6 <i>mm</i>)	Short length tubular reactor	

3.6. Aim

The systematic characterisation of catalytic materials under reaction conditions is desirable in order to accurately understand and evaluate such materials for industrial applications. Having evaluated some of the key catalytic characterisation techniques presented in the Literature Review in Chapter 2, it has been concluded that the desirable attributes still missing from present day studies are crucial in developing an improved understanding of surface and transfer properties (surface area, sorption isotherms, pore diffusion etc.). Such developments would serve to propagate the continuous advances in industrial catalysts and sorbents. The importance of developing powerful and robust *in situ* techniques cannot be understated. Thus, the aim of this project is to address some of the critical limits of the characterisation methods outlined in Chapter 2, namely *in situ* catalyst characterisation and comparison.

3.7. Objectives

The focus of the PhD is in catalyst characterisation and sorption measurements of materials that are under laboratory development as well as those that are commercially available. The studies conducted will be used to develop FRT as a desirable *in situ* method for the characterisation of porous materials. In order to achieve the overall aim delineated above, the following objectives have been identified:

- **Objective I:** *Develop the FRT-Zero Length Column diffusion method and apparatus to investigate the transfer properties of CO₂ and C₃H₈ in zeolites and synthetic materials for green house gas storage and abatement.*

The development of the FRT-ZLC technique shall be discussed in Chapters 5 and 7. To demonstrate the viability of the procedure, experimentation geared towards the study of diffusivity coefficients in cordierite monolith washcoats and commercially available zeolites is reported upon. This novel method of analysing diffusion coefficients is compared with several other macro and microscopic techniques.

- **Objective II:** *Demonstrate FRT's capability in exploring the acidic and basic properties of commercial zeolites using NH_3 and CO_2 respectively.*

The total acidic and basic properties of commercially available zeolites are explored in Chapters 6 and 7. A new feature discussed in Chapter 7 is the bimodal operation of FRT whereby both sorption capacities and diffusion coefficients can be measured in the same experimental window.

- **Objective III:** *Improve the design of the flux response system to incorporate the ultra fast measurements of catalyst surface areas.*

Several modifications to the FRT systems are explored in Chapter 8. The FRT surface area determination system is studied to incorporate process upgrades to increase the turnaround times of characterised samples as well as improve on the system's accuracy. Further process optimisations are explored to increase the range of applications available to FRT.

- **Objective IV:** *Compare experimental results obtained from commercial (industrial) catalysts using flux response technique with published data as well as other well-known characterisation techniques.*

All the results derived through the FRT studies have been compared and contrasted all the way through Chapters 5 till 8. Peer-reviewed journal papers of the various FRT systems and characterisation studies are shown in the List of Publications.

3.8. Summary

Chapter 3 pieced together the theoretical principles, analytical fundamentals, methods, and materials of construction required for the FRT technique. An in-depth literature review was conducted, focusing on the development of the technique from the earlier studies on sorption-effect chromatography all the way up until the most recent work carried out in the determination of gas permeabilities of polymeric membranes. A critical review of the technique was carried out and compared with previously analysed characterisation techniques in Chapter 2.

It has regularly been shown that FRT is a powerful and capable *in situ* measurement technique able to analysis virtually any gaseous process in which a change in pressure occurs. Several advantages exist with the method, namely; its ability to act as a dual flowrate and composition detector due to the inclusion of delay lines in the system that are able to extend the path length of the concentration front; the lack of calibration required to run experiments due to the use of differential measurements between two gas lines, the excellent sensitivity of the technique brought about through the pneumatic Wheatstone bridge system configuration, making use of a very sensitive differential pressure transducer; the fast process turnaround times; and the inexpensive capital cost.

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Chapter 4

Experimental Methods

4.1. FRT Ammonia Sorption

A series of high temperature experiments were carried out using FRT to measure the surface acidities of zeolites with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. These experiments were performed isothermally and involved measuring the sorption values of identical gas mixtures of ammonia in an argon carrier flow on different zeolites across various temperatures. In this setup, the upstream FRT system was fitted with a temperature programmable furnace, which housed the system reactor. The system reactor used for the test runs was a 4 mm quartz microreactor of length 0.3 m. The use of a dummy reactor for the reference side of the Wheatstone bridge was not vital in operating this specific FRT system. Because only a few milligrams of test sample was used in the system reactor, a negligible pressure drop across the bridge was observed.

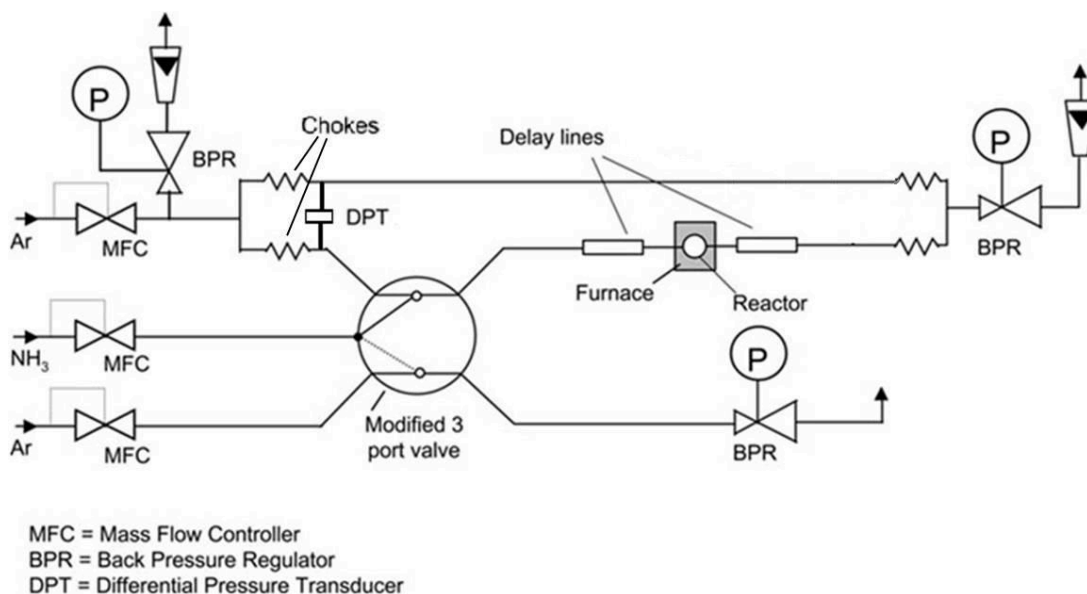


Figure 4.1: Schematic of the upstream FRT system

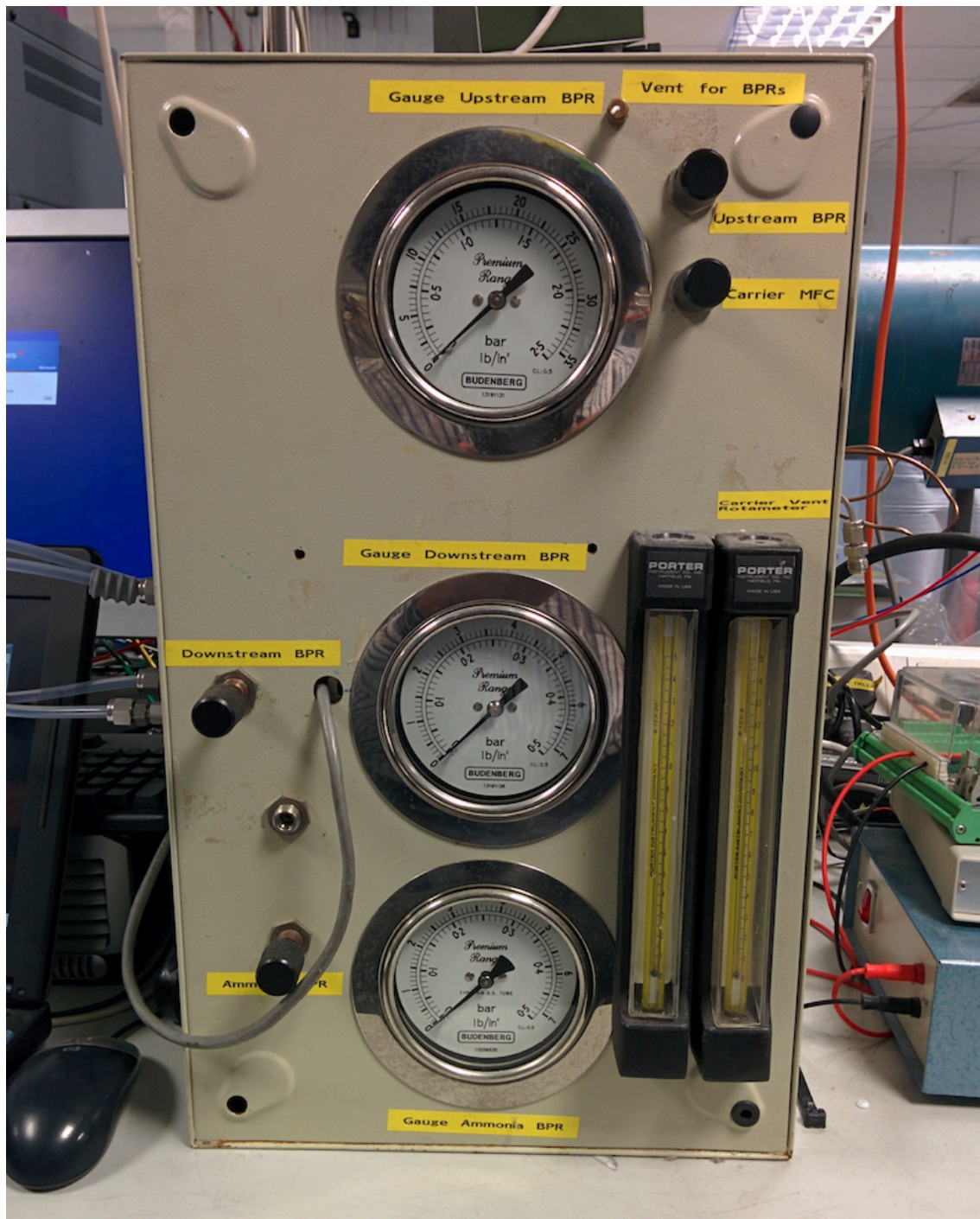


Figure 4.2: Experimental setup for NH_3 sorption experiments

Figure 4.1 and Figure 4.2 represent the schematic and the experimental setup of the upstream FRT system. One of the most important features of this flux response system was the positioning of the DPT. To protect the internal components of the DPT, it was positioned upstream to shield against the corrosive properties of the ammonia gas. Figure 4.3 shows the expected flux response profile for this experiment.

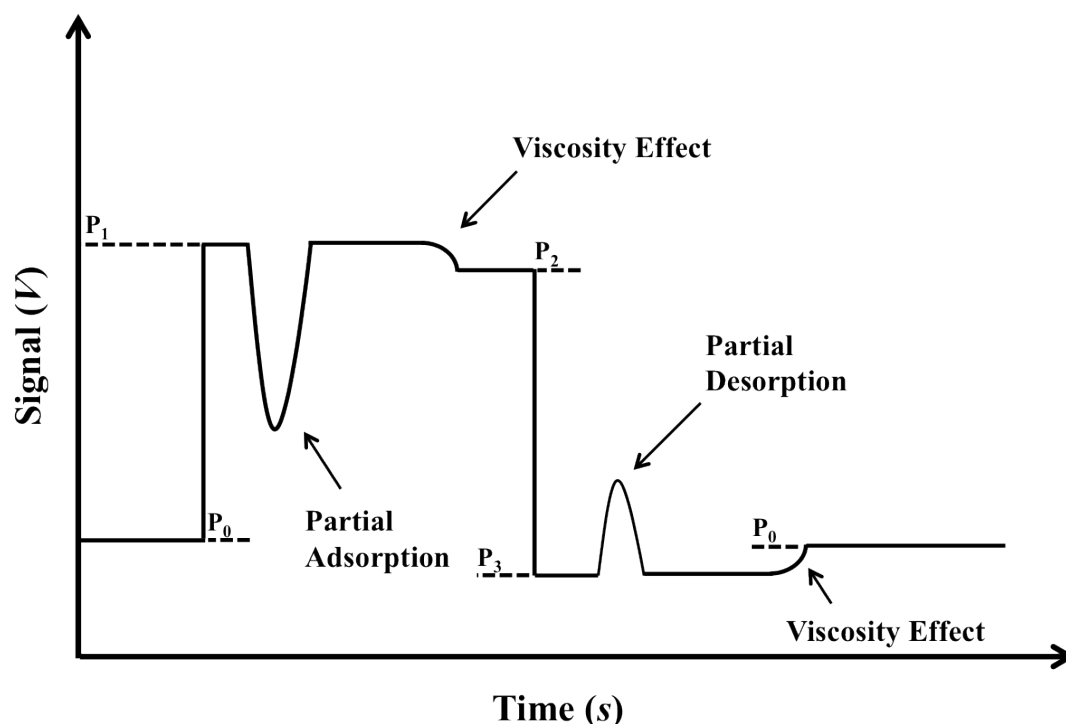


Figure 4.3: Expected flux response profile for NH_3 sorption at constant temperature

4.1.1. Materials

Gases

Interrogations of the zeolite samples were carried out using argon (99.99 %) as the carrier gas and anhydrous ammonia (99.98 %) as the perturbation probe. Both gases were supplied by BOC and transported through the lab manifold system and past $0.5 \mu\text{m}$ in-line filters (Swagelok) before reaching the FRT system. The ammonia stream was also fitted with a moisture trap (Thames Restek) to circumvent erroneous pressure fluctuations from affecting the flux response profiles.

Zeolites

The zeolite test samples required for the NH_3 sorption experiments were obtained from the commercial vendor, Zeolyst International, for each of the required $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Table 3.1 gives the specifications of each of the seven zeolites used during the experimental runs. The zeolite samples under analysis were prepared by crushing and sieving zeolite pellets to a size fraction of $425\text{--}850 \mu\text{m}$ from which point they were activated by heating in a 30 ml/min high purity stream of Ar at 400°C for 12 hours.

Each zeolite sample used in the experimental runs weighed approximately 0.02 g post activation.

Table 4.1: Material properties of zeolite test samples

Zeolite	SiO₂/Al₂O₃ Mole Ratio	Nominal Cation Form	Na₂O Weight %	Surface Area (m²/g)
Ferrierite CP914C (F.CP914C)	20	Ammonium	0.05	400
ZSM-5 CBV 2314 (ZSM 23)	23	Ammonium	0.05	425
ZSM-5 CBV 3024E (ZSM 30)	30	Ammonium	0.05	405
ZSM-5 CBV 5524G (ZSM 55)	50	Ammonium	0.05	425
Ferrierite CP914 (F.CP914)	55	Ammonium	0.05	400
ZSM-5 CBV 8014 (ZSM 80)	80	Ammonium	0.05	425
ZSM-5 CBV 28014 (ZSM 280)	280	Ammonium	0.05	400

4.1.2. Methods

4.1.2.1. Flux response technology

General Operating Procedure

Acid site quantification was carried out using the upstream FRT system described earlier in Chapter 3. Each zeolite sample used in the experimental runs was interrogated with a gas mixture of 30 *mol*-% NH₃ as the probe molecule in an Ar carrier gas stream over a high-temperature range between 100-450 °C. The injection of the NH₃ perturbation was carried out until a quasi-steady state equilibrium existed. At this point, the NH₃ perturbation was switched out until the flux response profile exhibited initial conditions. Three perturbation steps were performed at each test temperature to complete a dynamic cycle set. At the end of each dynamic cycle the test sample of zeolite was regenerated *in situ* by heating to 400 °C for 30 mins, after which it was left to cool down to the next investigation temperature.

Calibration

In order to interpret and quantify the probe molecules adsorbed and desorbed from the flux response profiles, the flowrate change caused by the perturbation of NH_3 probe molecules was calibrated using a soap film meter. The calibration produced an accurate linear correlation between the change in signal, measured in volts, and a change in volumetric flowrate, measured in millilitres per minute. Consequently, the areas of the sharp peaks on the flux response profiles illustrated in Figure 4.3 correspond to the quantities of NH_3 probe molecules adsorbed or desorbed onto the surface of the zeolite. The areas of the sharp peaks can be determined easily from the flux response profile using the curve fitting software, Curve Expert.

4.1.2.2. Material Characterisation

4.1.2.2.1. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed as a quality control measure to validate the calcination temperature used to free the zeolite channels for adsorption and establish the base dry weight of the samples. In the TGA characterisation, the weights of the samples were recorded as a function of temperature. The analysis was carried out on a TGA Q500 from TA Instruments using a flow of nitrogen gas of 60 ml/min . The temperature was increased from 25 to 400°C at 10°C/min .

4.1.2.2.2. Solid-State Nuclear Magnetic Resonance (NMR)

The framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the extent of the dealumination for each of the zeolite samples were determined by means of solid-state NMR spectroscopy (Cryomagnetic, Spectr spin, Bruker). This was carried out to determine whether any extra framework Al existed within the framework of the zeolite samples, as this would severely affect the measured flux response sorption values. Operation of solid-state NMR spectroscopy involves employing an electro-magnetic radio frequency pulse as the perturbing frequency, thereby inducing transitions between the magnetic spin energy levels in an atomic nucleus within a magnetic field. These transitions cause chemical shifts, measured as a transition frequency.

By applying the Magic Angle Spinning (MAS) technique (van Bekkum *et al.*, 2001), high resolution NMR spectra of the zeolite samples were obtained. Sample analysis was performed using 4 mm rotators and Al spinning speeds for ZSM 55, ZSM 280, F.CP914C, and F.CP914 of 10799 Hz, 10494 Hz, 1200 Hz, and 3000 Hz respectively. The Si spinning speeds for ZSM 55, ZSM 280, F.CP914C, and F.CP914 were 5574 Hz, 5343 Hz, 5341 Hz, and 5124 Hz respectively. The Al and Si measurements were undertaken at pulse angles of 15 ° and 90 ° respectively. Spectral analysis was carried out using NMR software (dmfit09) in order to establish the chemical shift values and peak intensities.

4.1.2.2.3. X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) is a routine, non-destructive method of chemical analysis, used to determine the concentration of elements in a broad range of materials. When a high energy incident (primary) X-ray collides with an atom, its stability is disturbed, which results in the ejection of an electron from a low energy level. The space created by the ejected electron allows an electron from a higher energy level to fall in its place. This difference in energy produced as the electrons move between energy levels is released as X-rays (secondary) which are characteristic of the element. Zeolite samples were investigated through XRF analysis (S4 Explorer, Bruker AXS) to quantify the SiO₂/Al₂O₃ ratios.

4.1.2.2.4. X-ray Diffraction (XRD)

X-ray diffraction (XRD) offers the possibility of analysing the arrangement of atoms in the crystal structures of solid materials. It is a non-destructive analytical method that can yield the unique fingerprint of Bragg reflections associated with a crystal structure. In understanding the methodology of XRD, one must consider the crystal structure of a sample material as being built of layers, or planes, which act as a semi-transparent mirror. X-rays with wavelengths of a similar distance between these planes can be reflected such that the angle of reflection is equal to the angle of incidence. The positions of such reflections describe the inter-layer spacing of atoms in the crystal structure.

The XRD analysis was carried out using an X Pert PRO system (PANalytical) with a copper alpha source. The start and end angles were 5 and 50 degrees with incremental step sizes set at 0.004 and time per step limited to 10.160 s.

4.1.2.2.5. Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) of ammonia is a well established method of determining the number and strength of acid sites in zeolites. By following the temperature of the desorption peak, the acid strength was characterised simply. The process of TPD involved loading the calcined zeolite samples with ammonia prior to the desorption experiment. The zeolite samples were encased and supported by quartz wool in 4 mm quartz microreactors, connected to a turbomolecular pump, gas-dosing system, and a mass spectrometer to monitor the desorbing species. After the initial adsorption of flowing 30 % NH₃-He at 100 °C, He was pumped at 30 ml/min through the quartz reactor to purge the zeolite surface of weakly held ammonia for 1 hour at 100 °C – the temperature at which the TPD was subsequently started. The ramp rate for the programmable furnace was set at 20 °C/min to the final temperature of 1000 °C.

4.2. FRT Carbon Dioxide Sorption

Carbon dioxide sorption experiments were carried out using FRT to evaluate the basicity of zeolite samples with different frameworks. Acidity and basicity are regarded as paired concepts and are often invoked to describe catalytic properties of materials. The CO₂ sorption capacities were analysed for each zeolite to complement the FRT ammonia sorption investigations of zeolite acidity, and complete the catalytic studies of these materials. The FRT method was adapted for the *in situ* measurement of CO₂ sorption on zeolite samples with varying SiO₂/Al₂O₃ ratios by integrating a temperature programmable furnace with the Wheatstone bridge assembly. The furnace housed the quartz microreactor containing a fixed bed of the test sample. A schematic of the system configuration along with a photograph of the FRT apparatus is presented in Figure 4.4 and Figure 4.5 respectively.

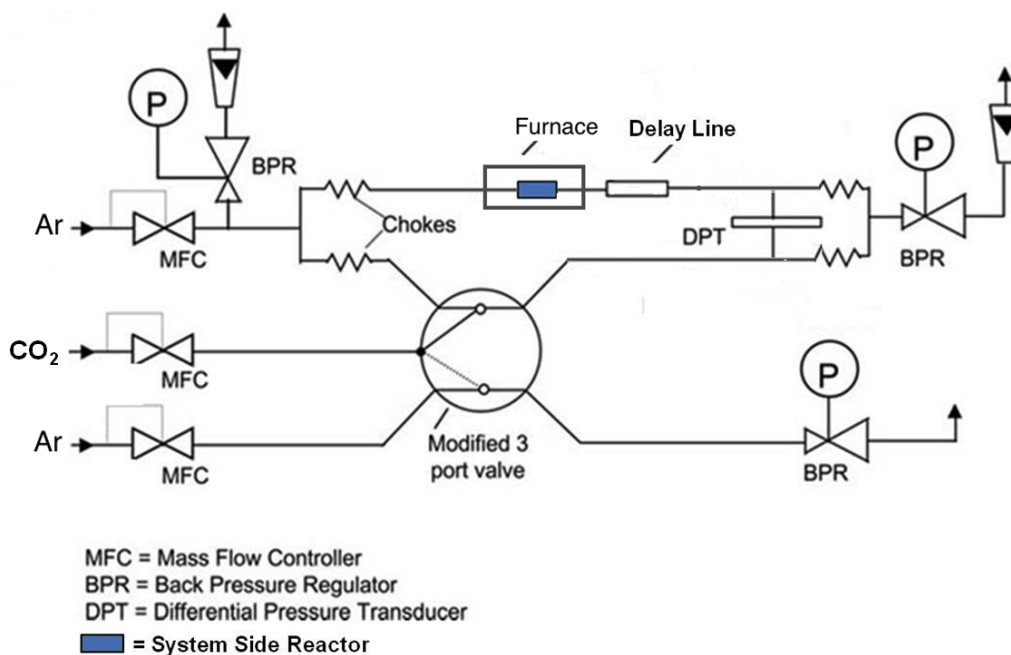


Figure 4.4: Schematic of the upstream stainless steel FRT system

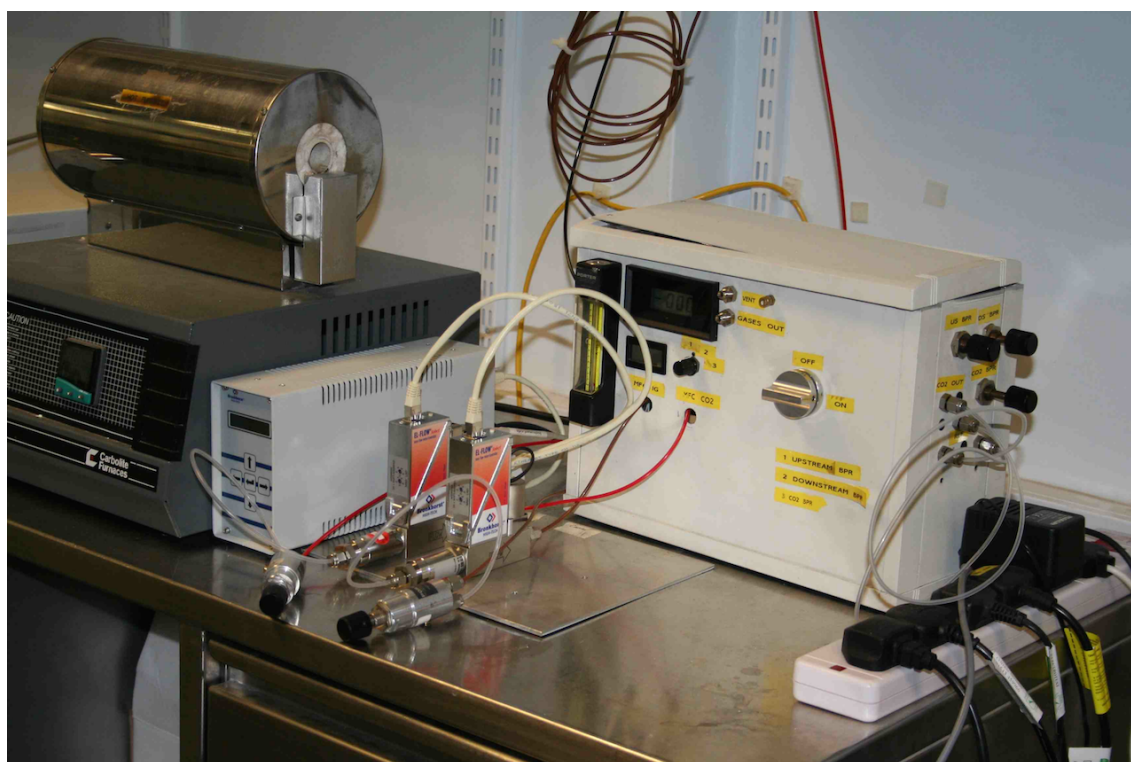


Figure 4.5: FRT apparatus for CO₂ sorption

The expected flux response profile presented in Figure 4.6 is identical to that of the ammonia sorption experiment detailed earlier in Figure 4.3, as the composition effect of

the addition of both of these perturbations causes a decrease in viscosity in their respective combined gas streams.

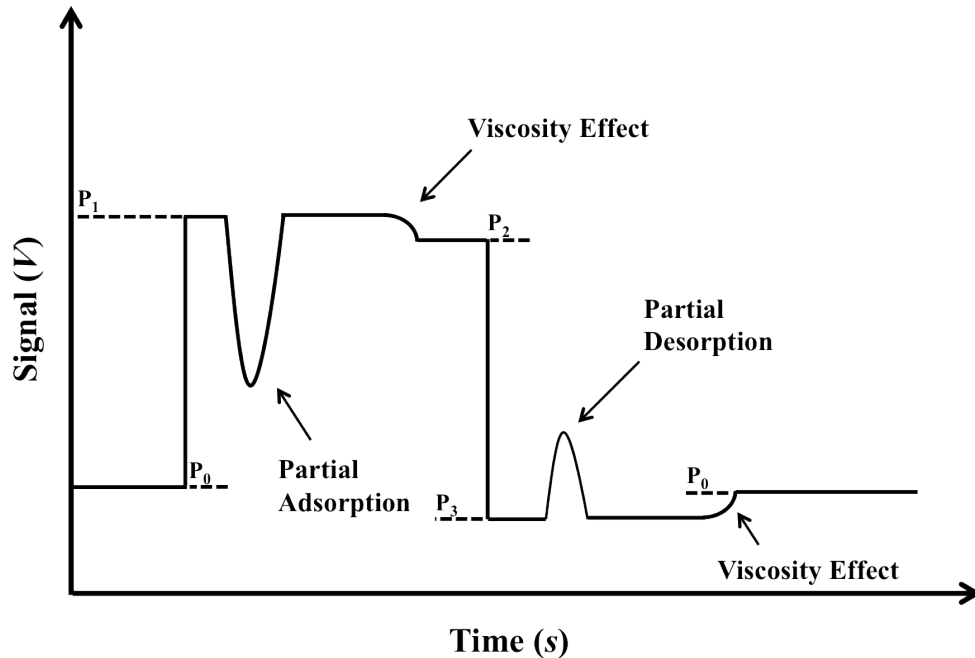


Figure 4.6: Expected flux response profile for CO₂ sorption at constant temperature

It must be noted that the difference in the empirically generated flux response profiles is restricted to the size of the step-change in the measured signal, the subsequent sorption peaks, and the viscosity effect. These differences are the result of two predetermined experimental variables. The size of the step-change is relative to the flowrate of the perturbation stream once it is switched in. Increases in the perturbation flowrate also affect the size of the sorption peaks and is limited by the availability of active sites present on the sorbent sample. The composition of the combined gas stream either increases or decreases the viscosity of the mixture, measured as a rise or loss in viscosity. The second variable relates to the size of the sorbent sample under investigation. The larger the surface area of the active sites, the larger the sorption peaks will be as more perturbation molecules can adsorb and desorb from the surface of the sample. This concept is illustrated in Figure 4.7 for perturbations with varying molar fractions.

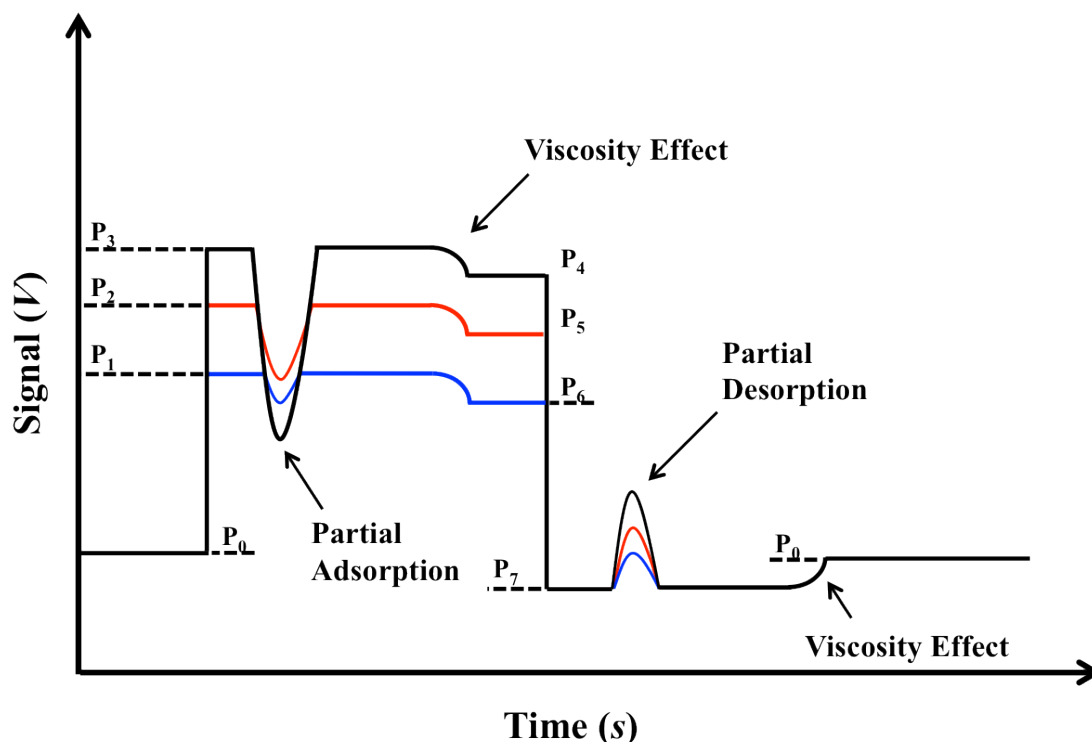


Figure 4.7: Schematic of expected flux response profile for varying molar fractions of perturbation molecules under isothermal conditions

4.2.1. Materials

Gases

Each zeolite sample used in the experimental runs was interrogated with a gas mixture of 30 mol-% CO₂ (99.99 %, BOC) as the probe molecule in an Ar (99.99 %, BOC) carrier gas stream over a temperature range between 25-200 °C. The CO₂ stream was fitted with a moisture trap (Thames Restek) to steady out the measured flux response profiles.

Zeolites

The CO₂ sorption experiments were repeated on the same set of zeolites detailed in 4.1.1 for NH₃ sorption. Table 3.1 gives the specifications of each of the zeolites investigated. The zeolite samples were prepared in the same manner as previously described. Post activation, the zeolite samples weighed approximately 0.018 g.

4.2.2. Methods

4.2.2.1. Flux response technology

Operating Procedure

Quantifying the total number of active basic sites from the zeolite samples was performed using the upstream stainless steel FRT system described. The operating procedure follows the general operating procedure shown for the NH_3 sorption experiment. A set of dynamic cycles was performed at each test temperature between 25-200 °C. The surfaces of the zeolite samples were evacuated *in situ* by heating to 400 °C for 30 min at the end of each dynamic cycle.

4.2.2.2. Material Characterisation

The zeolite samples in question were well characterised making use of solid state NMR, XRF, and XRD to evaluate the existence of extra-framework Al which would compromise the accuracy of the FRT measurements.

4.3. FRT-Zero Length Column (ZLC) Diffusion Studies

Two sets of experiments were performed to extract CO_2 and hydrocarbon diffusion coefficients in zeolite molecular sieves and alumina/CeZrO_x washcoats of cordierite monoliths respectively. The FRT technique was adapted to incorporate the zero length column (ZLC) method of analysing diffusion coefficients. The adsorption and desorption transients from the experimental flux response profiles for both experiments were analysed using the ZLC method to study CO_2 and C_3H_8 diffusivity as a function of temperature. The upstream stainless steel FRT system was fitted with a temperature programmable furnace to facilitate the inclusion of the system reactor used for the test runs. A 4 mm quartz microreactor of length 0.3 m was used to convey a fixed bed of the test samples. This allowed for a well defined reactor geometry. The use of a reference reactor was not required for either experiment as no significant pressure drop across the Wheatstone bridge was experienced during experimentation.

The schematic of the FRT-ZLC CO_2 diffusion study with the accompanying picture of the experimental setup are consistent with Figure 4.4 and Figure 4.5 as the analysis of

the diffusion coefficients was achieved in the same experimental window as the analysis of the effective sorption capacities of CO_2 for the zeolites detailed earlier in the FRT CO_2 sorption experiment. Understandably, the expected flux response profile remains the same as shown in Figure 4.6. The schematic of the FRT-ZLC C_3H_8 diffusion study and the experimental setup are presented in Figure 4.8 and Figure 4.9.

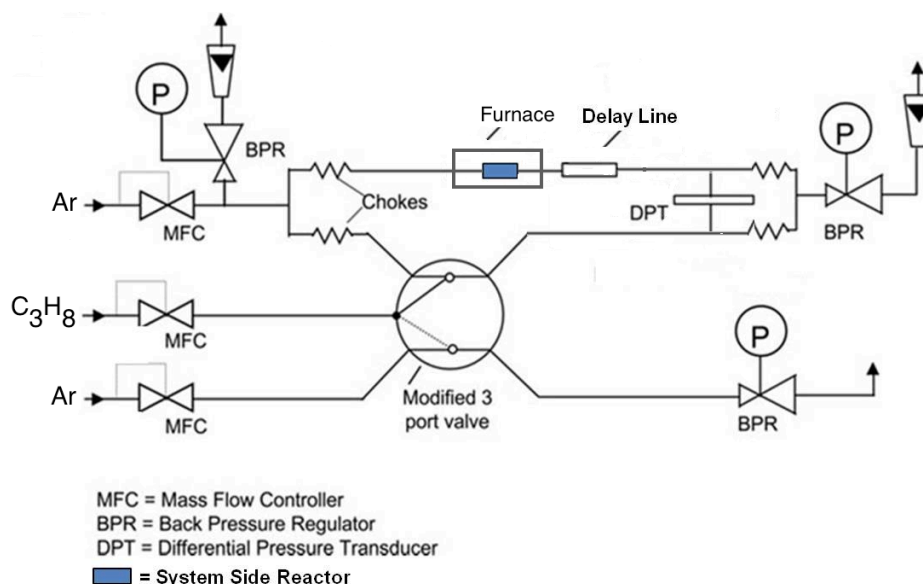


Figure 4.8: Schematic of the upstream stainless steel FRT system used in C_3H_8 diffusivity studies

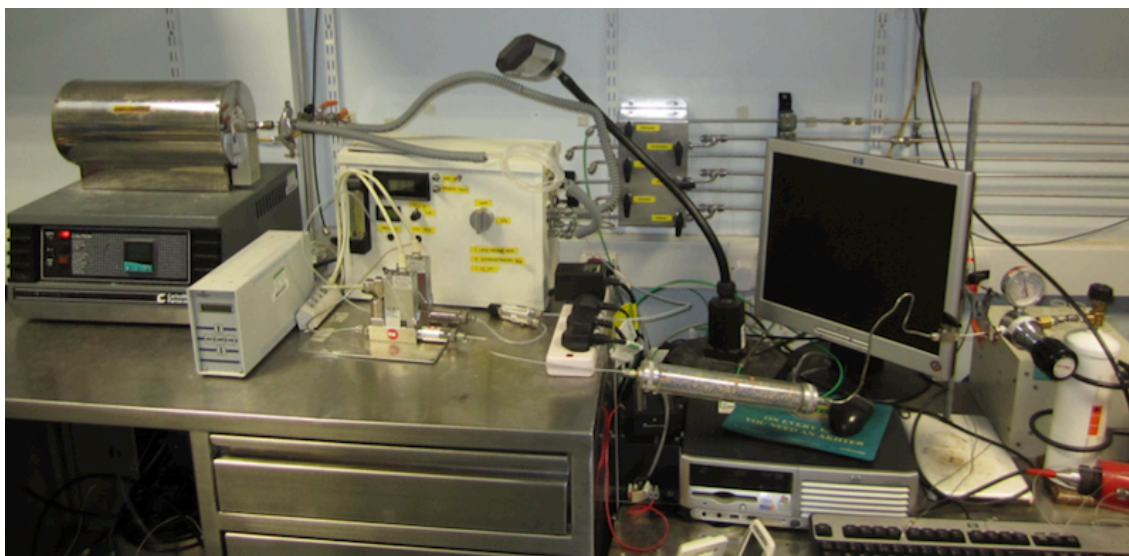


Figure 4.9: FRT-ZLC C_3H_8 diffusivity experimental setup

The expected flux response profile for the C_3H_8 diffusivity experiment is displayed below in Figure 4.10. The adsorption transient required for FRT-ZLC analysis is highlighted through section **a**.

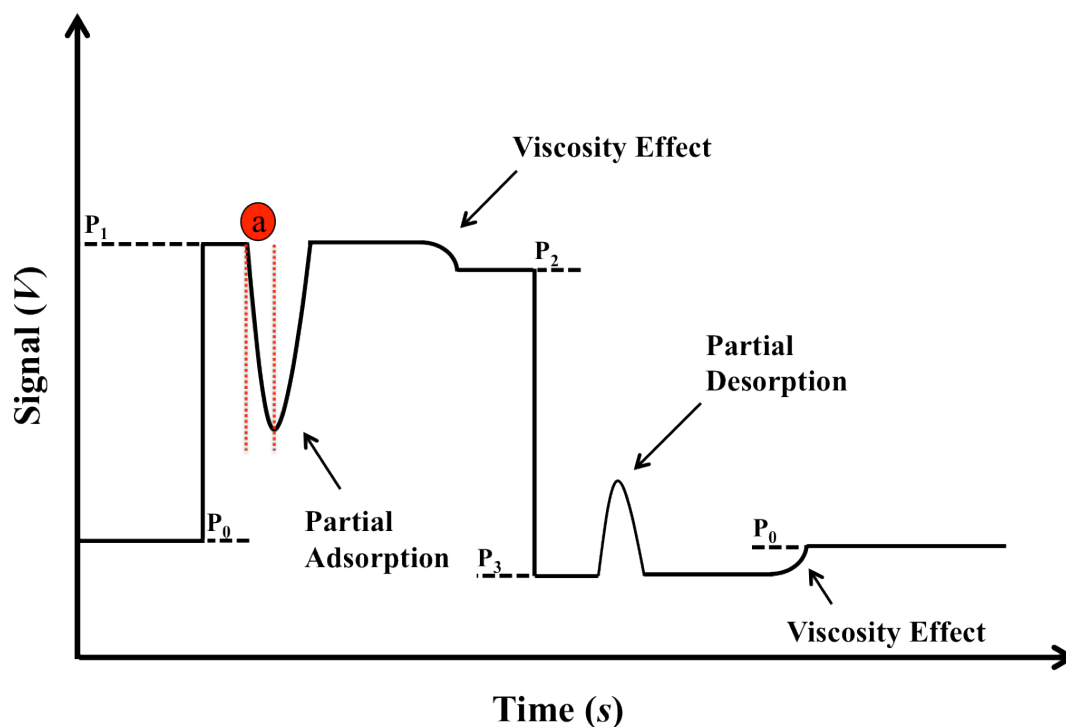


Figure 4.10: Expected flux response profile for the C_3H_8 diffusivity experiment

4.3.1. Materials

Gases

The gases used for the CO_2 diffusion studies of zeolite samples are consistent with the FRT CO_2 sorption experiment specified earlier in 4.2.1.

The sorbate used in the second diffusivity experiment was propane (98 %, Sigma Aldrich) and argon (99.99 %, BOC) was used as the carrier gas. The monolith samples were investigated with 50-mol % C_3H_8 running through the system side of the apparatus during perturbations. A moisture trap (Thames Restek) was fitted to the perturbation stream to circumvent the pressure fluctuations from hampering the accurate measurement of the flux response.

Zeolites

The CO₂ diffusivity experiments were repeated on zeolites F.CP914C, ZSM 55, F.CP914, and ZSM 280 listed in Table 3.1. The zeolite samples were prepared in the exact mould as detailed in 4.2.1 as both of these CO₂ experiments were performed concurrently. The zeolite samples weighed approximately 0.018 g after being heat-treated in a 30 ml/min flowing stream of Ar at 400 °C running for 12 hours.

Cordierite

Four samples of cordierite monoliths with varying alumina/CeZrO_x washcoats were supplied by Johnson Matthey. The cordierite samples were crushed and sieved to size a fraction of 425–850 µm. Preparation of the samples before starting the experiment was achieved by heating in a high purity gas stream of argon (99.99 %, BOC) from room temperature to 400 °C overnight. In order to regenerate the samples after each temperature cycle, they had to be heated at 400 °C for 30 min. Approximately 0.186–0.190 g of each monolith was used in each experiment.

4.3.2. Methods

4.3.2.1. FRT-ZLC

Operating procedure

The operating procedure for the CO₂ and C₃H₈ diffusion follows the general operating procedure outlined in 4.1.2.1 for the respective gas compositions and materials under investigation in both studies.

4.3.2.2. Material Characterisation

4.3.2.2.1. Static Volumetric Method

A Micromeritics Tristar 3000 surface analyser was used to measure nitrogen adsorption isotherms at 77 K and provide an insight into BET derived estimations of the specific surface areas and pore sizes of the zeolite and cordierite samples.

4.3.2.2.2. Temporal Analysis of Products (TAP)

The TAP reactor operates on the premise of injecting a small gas pulse ($\approx 10^{-10}$ mol) over a short duration (250–500 ms) into an evacuated microreactor containing a packed bed of the test samples. TAP pulse experiments were performed as a comparative method of analysing the hydrocarbon diffusion coefficients within the alumina/CeZrO_x washcoats. The intraphase diffusivity within the washcoat of the monolith samples was measured in a TAP-1 reactor (Autoclave Engineers) using a stainless steel microreactor (41 mm long, 5.5 mm i.d.) and the probe gases were recorded at the reactor outlet by a UTI100C quadrupole mass spectrometer.

The monolith samples were prepared by cutting a small square containing 4 channels, 1 mm² per channel, of 2–3 mm in length. The monolith sample was embedded between two layers of inert silicon carbide, particle size 500 mm (VWR). The monoliths were studied over a range of temperatures, 20–100 °C. The gas pulses employed were composed of a 50 mol-% fraction of propane (99 %, BOC) in krypton (99.999 %, BOC) and all masses representative of these molecules were monitored.

4.3.2.3. Models

Diffusion within porous materials

In order to calculate the diffusivity within the washcoats of the zeolites and monolith samples, it was necessary to apply the ZLC mathematical model to analyse the FRT generated sorption curves. The ZLC method of measuring diffusivity depends on following the desorption of sorbate from a previously equilibrated sample of adsorbent into an inert carrier stream. The FRT experimental sorption curves were interpreted according to the original simplified model of Eic and Ruthven where the analysis utilises the long time region of the decay curve (Eic & Ruthven, 1988).

The ZLC method is based on the following assumptions: spherical adsorbent particles, Fickian diffusion, linear sorption isotherm, perfect mixing through the cell, isothermal conditions, high flowrate of the gas stream, and neglect of fluid phase hold-up. From these assumptions, the response curve is given by (Crank, 1979):

$$\frac{c}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{\beta_n^2 Dt}{r^2}\right)}{[\beta_n^2 + L(L-1)]} \quad 4.1$$

where β_n is given by the roots of;

$$\beta_n \cot \beta_n + L - 1 = 0 \quad 4.2$$

and

$$L = \frac{1}{3} \frac{Fr^2}{KV_s D} \quad 4.3$$

In these equations, c represents the concentration at any time t , c_0 is the initial concentration, F signifies the purge flowrate, V_s is the crystal volume in the ZLC cell, K represents the dimensionless Henry law constant, D is the diffusion coefficient, r is the particle radius, while L and β_n are dimensionless parameters. In the long time region (the tail of the respective sorption curves) equation 3.1 reduce to simple exponential decay curves as only the first term of the summation is significant:

$$\frac{c}{c_0} = \frac{2L}{[\beta_n^2 + L(L-1)]} \exp\left(-\frac{\beta_n^2 Dt}{r^2}\right) \quad 4.4$$

A plot of $\ln(c/c_0)$ vs. t should give a linear asymptote in the long time region from which the slope and intercept can be used to calculate parameters D and L .

4.4. FRT Surface Area Characterisation

In the past, FRT has been employed in the *in situ* measurement of nitrogen adsorption isotherms at cryogenic temperatures for the surface area characterisation of fine particles (Palmer *et al.*, 2011). The work carried out for the present study is a continuation of the research and explores the capabilities of FRT as a means of performing ultra-fast measurements of nitrogen adsorption isotherms to significantly reduce the time required to complete the experimental runs. Such a process would significantly improve process times, experimental accuracy and reproducibility of FRT.

Experiments were carried out to improve upon the design and working of the flux response apparatus. One such modification was aimed at eliminating the detection of the viscosity effect in flux response profiles. Eliminating the viscosity effect would enable the investigation of adsorption isotherms across whole composition ranges. Incorporating this modification would significantly reduce the throughput times of experimental runs, thus bringing the system closer to industrial realisation. Test runs were carried out using the downstream FRT system to investigate eliminating the viscosity effect in the sorption of nitrogen on aluminium oxide. The schematic of the experimental setup is showcased in Figure 4.11. Shown in Figure 4.12 and Figure 4.13 are the experimental setups used in previous studies for the measurement of nitrogen isotherms, and, the modified system used in the present study.

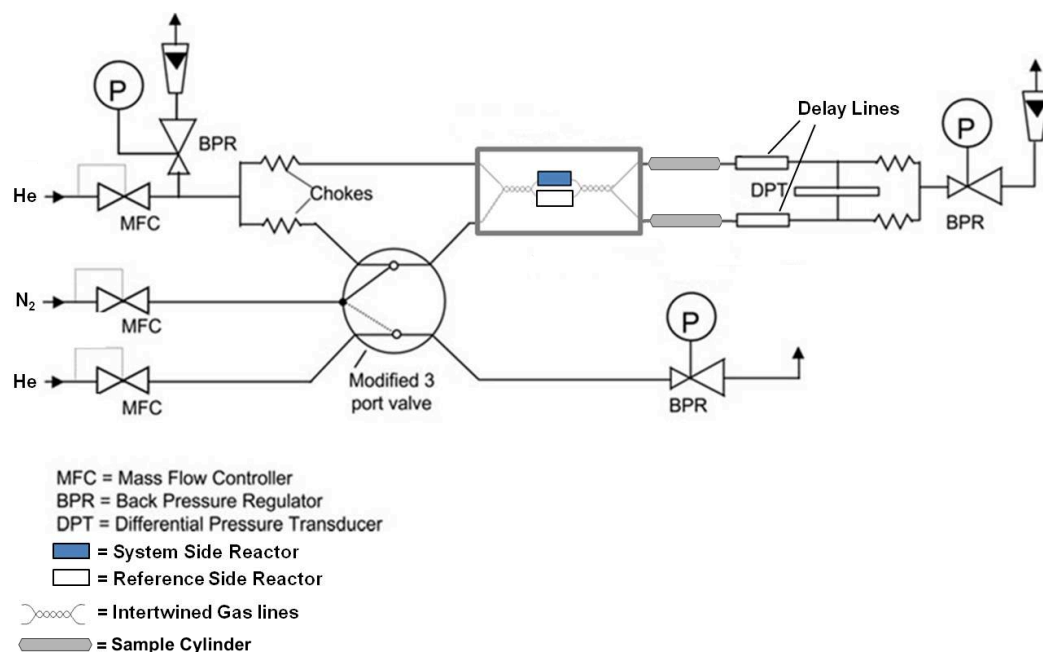


Figure 4.11: Schematic of the modified downstream FRT system

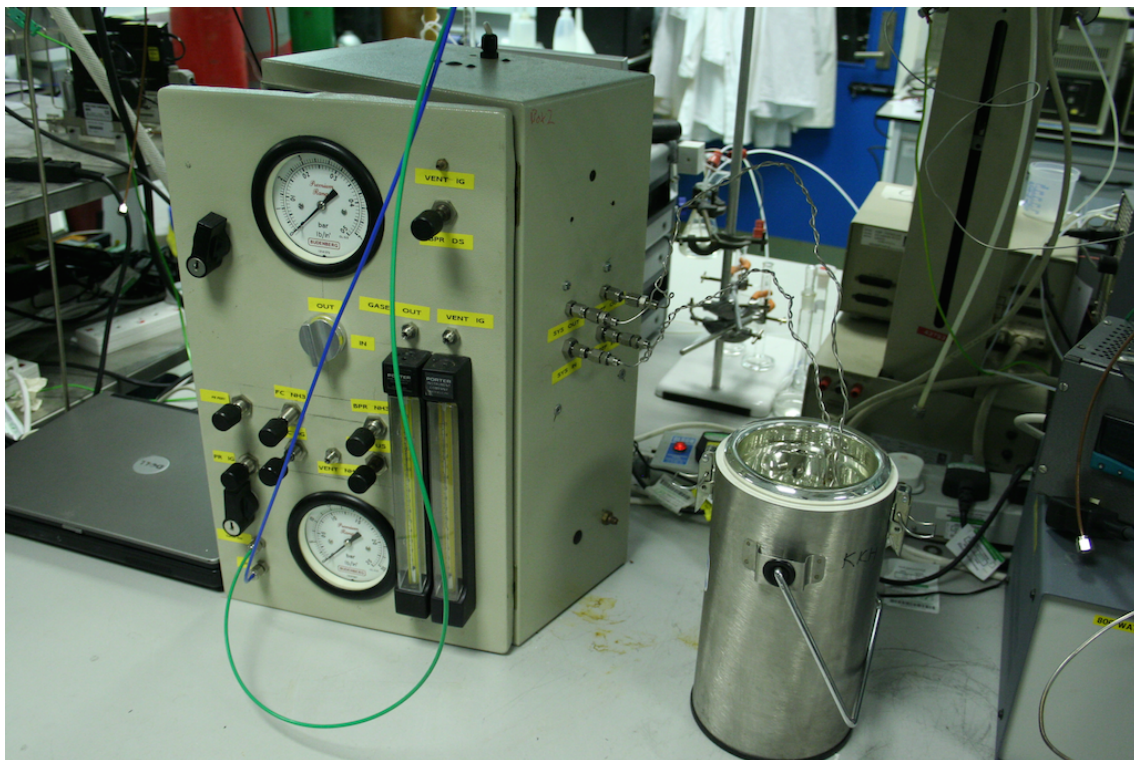


Figure 4.12: Experimental setup of the downstream FRT system used in N_2 isotherm measurements

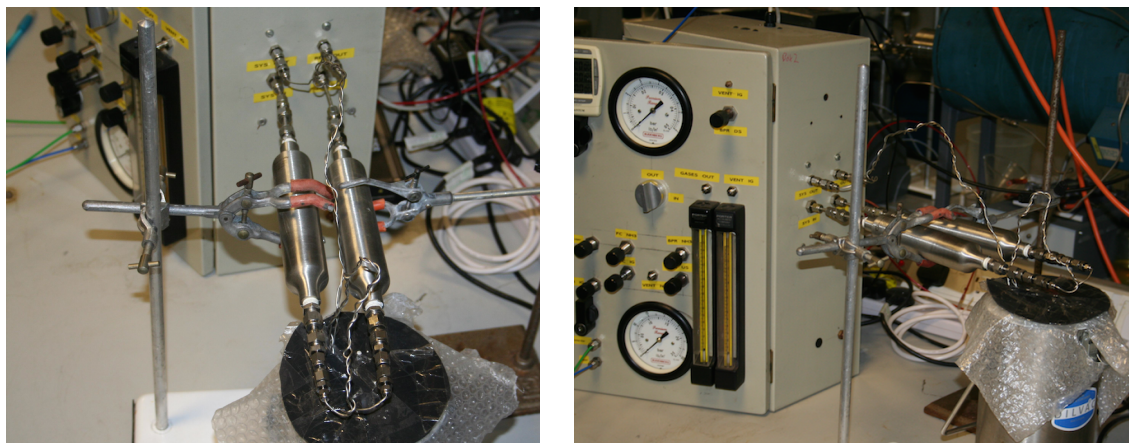


Figure 4.13: Experimental setup of the modified downstream FRT system used in ultra-fast N_2 isotherm measurements showcasing the incorporation of two sample cylinders to the original setup

By comparing Figure 4.12 and Figure 4.13, it is possible to distinguish the retrofitted sample cylinders present on both the system and reference sides of the bridge, downstream of the DPT. The sample cylinders were provided by F.T.I Limited (product code HSSC15-3BH) and used to create a dead volume in the FRT apparatus, rendering the DPT incapable of detecting the sharp viscosity effect upon gas perturbation. Preliminary experiments determined the final size of the cylinders to be 150 cc for both sides of the bridge. Figure 4.14 shows the expected flux response profile upon the minimisation of the viscosity effect. As can be seen in Figure 4.14, a steady drift is

present from the baseline at P_1 to P_2 after the partial adsorption peak and again from P_3 to P_0 after the partial desorption peak. These steady drifts are as a result of the composition changes occurring through the system side reactor – the addition and cessation of the perturbation gas being switched in and out. By eradicating the sharp viscosity effects present within the FRT profiles as a result of the combination of gas streams, the opportunity to showcase FRT as a tool for ultra-fast adsorption isotherm measurements exists. Shown in Figure 4.15 is a schematic of the expected flux response profile for measuring isotherms across a composition range in this manner.

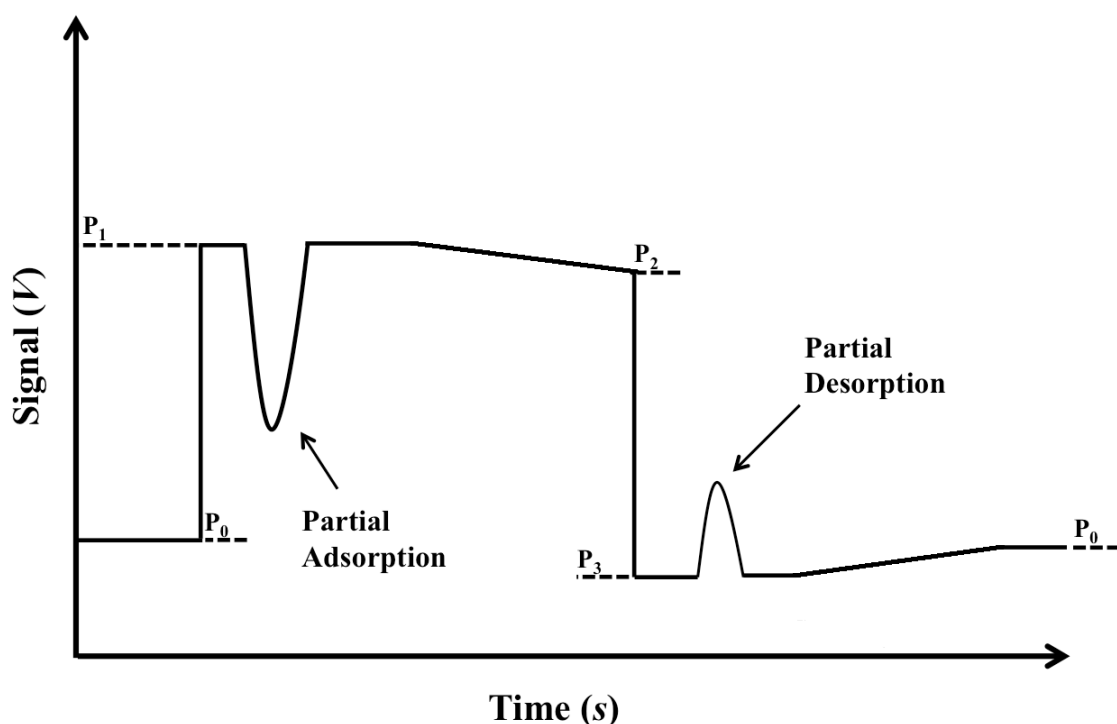


Figure 4.14: Expected flux response profile for the minimisation of the viscosity effect

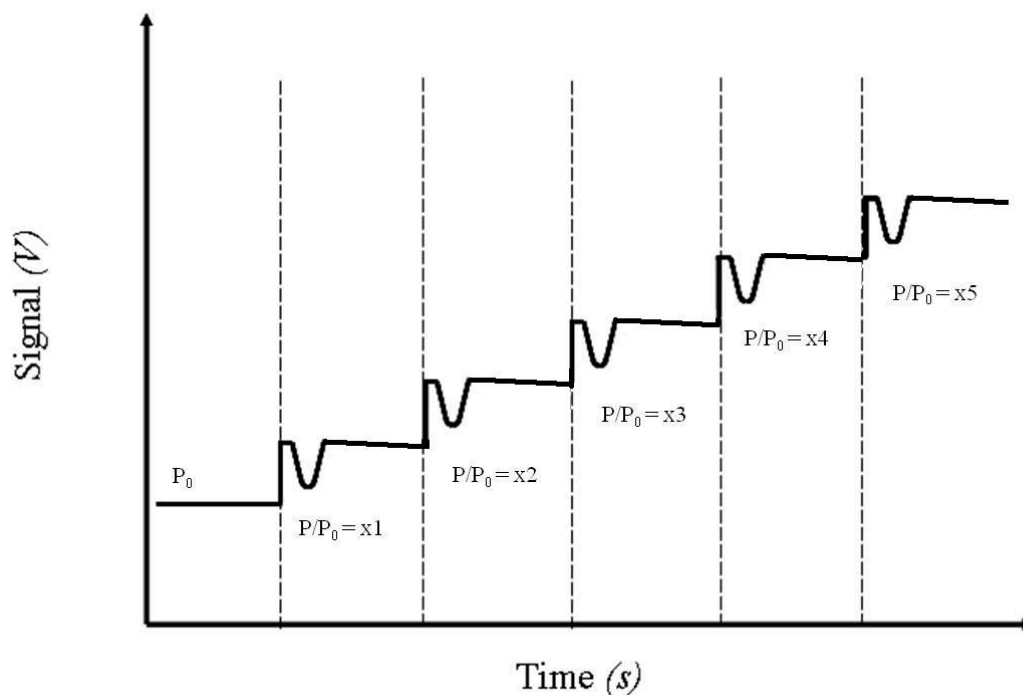


Figure 4.15: Schematic representation of flux response profile for adsorption isotherm over a full composition range

4.4.1. Materials

Gases

Helium (99.997 %, BOC) was used as the carrier gas for the surface area determination experiment. The nitrogen supply was provided by Imperial College's on-site nitrogen generator (99.999 %). The supply line of the nitrogen perturbation was fitted with a moisture trap (Thames Restek).

Aluminium Oxide

Aluminium oxide was used in the investigation of nitrogen adsorption isotherms at 77 K. Samples of intermediate and high surface area 1/8 in pellets of aluminium oxide with product codes 43857 and 43862 were supplied by Alfa Aesar. These pellets were crushed and sieved to a size fraction of 425–850 μm before weighing out samples of 0.017 g for analysis. The test sample was heated at 300 °C for 30 minutes prior to each test run in order to regenerate the surface of the sorbent. Table 4.2 shows the specification of the aluminium oxide samples.

Table 4.2: Material specification of high surface area aluminium oxide

Material	Pore volume (cm^3/g)	Nominal surface area (m^2/g)	Form
Aluminium oxide, catalyst support, intermediate surface area (43857)	0.49	100.00	1/8 inch pellets
Aluminium oxide, gamma phase, catalyst support, high surface area, bimodal (43862)	1.14	255.00	1/8 inch pellets

4.4.2. Methods

4.4.2.1. Flux response technology

Operating procedure

Two separate procedures were performed to compare and contrast any effects that may have been witnessed as a result of using the modified downstream FRT system. The two experiments comprised of testing the aluminium oxide with both the unmodified downstream FRT system as detailed in previous studies (Palmer *et al.*, 2011), and testing with the modified system for a single full composition run. This also allowed for a test of the reproducibility of the obtained results. Before any of the experimental runs were carried out, the FRT system along with the catalysts involved in the experiments were purged with He gas. The catalysts were encapsulated in 4 mm quartz reactors and held in place with the use of quartz wool. The reactors used in the nitrogen sorption measurements were 0.05 m in length. The quartz reactors were placed in a liquid nitrogen dewar supplied by DILVAC®.

Step experiments were undertaken to investigate the dynamic behaviour of nitrogen adsorption isotherms of aluminium oxide. The salient features of the FRT system shown in Figure 4.11 include interlocked gas lines, the use of a dummy reactor on one side of the Wheatstone bridge, the use of a liquid nitrogen dewar, and the inclusion of the two sample cylinders. The two reactors present in the apparatus represent the system and reference reactor respectively. The system reactor contains the test material to be analysed while the reference reactor contains an inert material, explaining its adopted term, ‘dummy’ reactor. The system reactor is connected to the system side of the Wheatstone bridge while the dummy reactor is connected to the reference side.

Setting up the experiment with the masses of test sample and inert material being approximately equal was important in minimising the pressure drop in the Wheatstone bridge assembly. To minimise the local temperature difference between both reactors, the gas lines for both reactors were tightly intertwined. The gas lines are 1/16 in stainless steel tubing of 0.5 m. These gas lines are connected to the reactors using Swagelok fittings. The reactors were submerged in a dewar of height 50 cm and diameter 30 cm. Once the reactors were submerged in the liquid nitrogen, the top of the dewar was sealed with a sheet of Viton® synthetic rubber and bubble wrap to maintain the reactors at cryogenic temperature and minimise the evaporation of liquid nitrogen.

4.4.2.2. Material Characterisation

4.4.2.2.1. Static Volumetric Method

A Micromeritics Tristar 3000 surface analyser was used to evaluate and compare the surface areas measured by the FRT method. The nitrogen adsorption isotherm was analysed for the intermediate and high surface area aluminium oxides with an average mass of 0.1013 g. To ensure the surface sites were free for adsorption of nitrogen molecules, the sample was outgassed overnight at 120 °C prior to the adsorption experiments.

4.5. FRT Dynamic Parallel Performance Testing (DPPT)

Modifications to the design of the upstream FRT rig were undertaken to design a dynamic parallel performance testing (DPPT) FRT rig to be able to directly compare the catalytic activity of catalyst materials simultaneously. Initial experiments were carried out to test the method in view of performing experiments to compare and contrast the reactivities of ammonia decomposition for nickel and platinum catalysts dispersed on identical alumina supports.

The schematic setup and the FRT rig are shown in Figure 4.16 and Figure 4.17. The argon gas carrier stream is split between the two reactors operating on each side of the Wheatstone bridge as is present in all the unmodified FRT systems. The major difference in this setup took place with the additions of another set of capillary chokes

to split the ammonia perturbation stream and the inclusion of a modified 6 port valve to switch the perturbation fluids into both reactor flows.

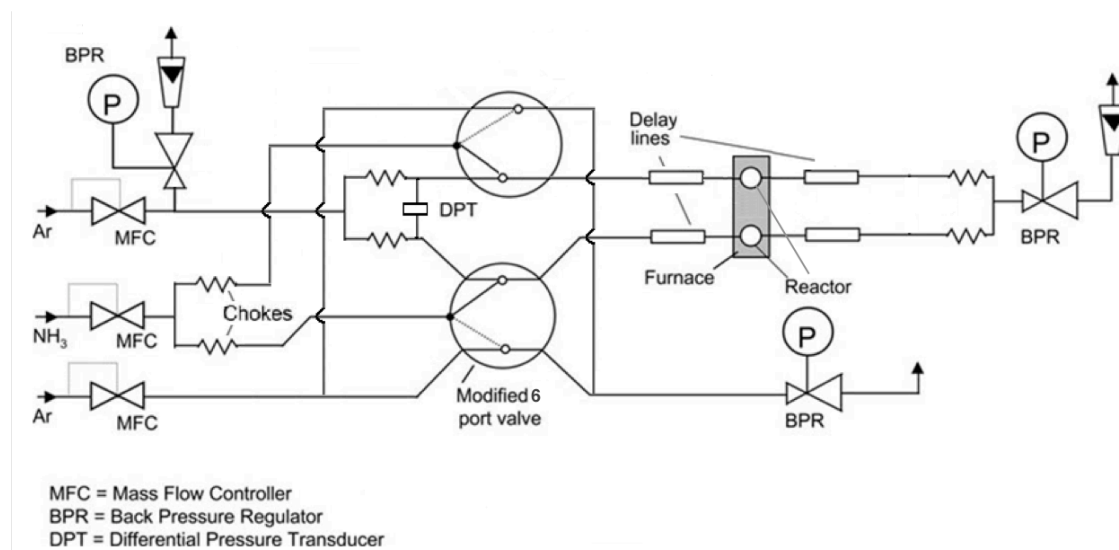


Figure 4.16: Schematic of the modified upstream FRT system for the DPPT experiments

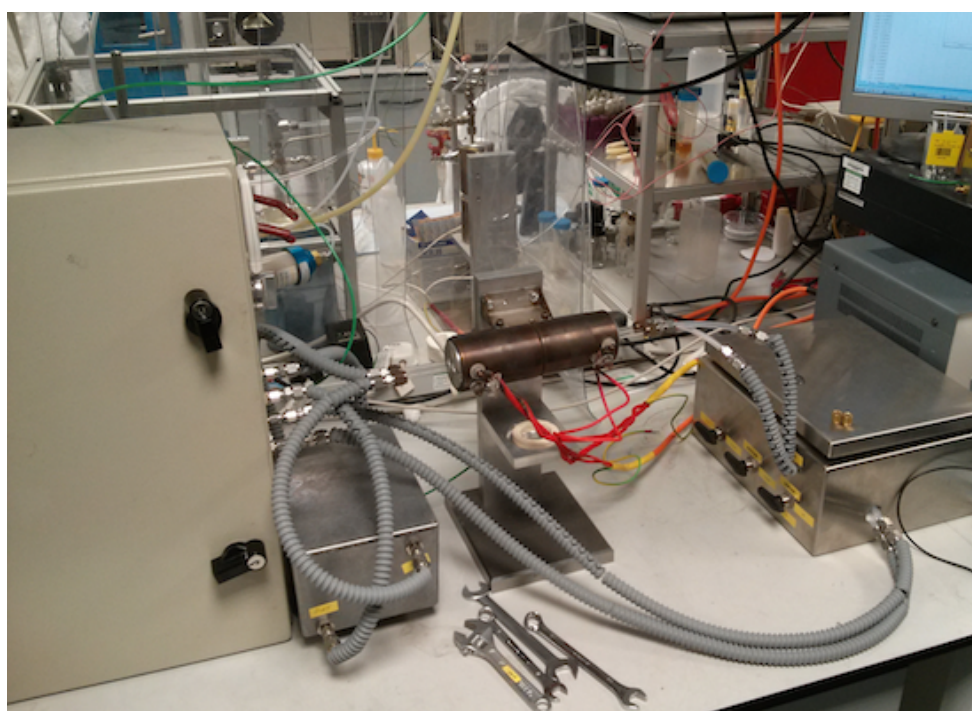


Figure 4.17: Experimental setup of the FRT system for the DPPT experiments

4.5.1. Materials

Gases

Initial interrogations of zeolite samples were carried out using argon (99.99 %) as the carrier gas and anhydrous ammonia (99.98 %) as the perturbation probe to ensure a balanced system existed. The ammonia stream was fitted with a moisture trap (Thames Restek) in accordance with previous operations.

Zeolites

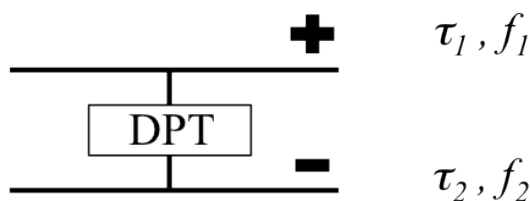
Identical weights of ZSM 55 supplied by Zeolyst International were used in each of the reactors. Table 3.1 gives the specifications of the sample in question. Preparation of the sample involved crushing and sieving the zeolite pellets to a size fraction of 425-850 μm before being activated in a 30 ml/min high purity stream of Ar at 450 $^{\circ}\text{C}$ for 12 hours. Both samples weighed approximately 0.02 g post activation.

4.5.2. Methods

4.5.2.1. Flux response technology

Operating Procedure

In order to achieve interpretable results from the DPPT experiments, it is important that the flow resistances on both sides of the Wheatstone bridge are exactly matched so that a flow change of a given size on either side of the bridge will give the same change in the flux response signal from the DPT. As this was not as important in previous studies where it was only the fluctuations in the flow on one side of the bridge that was of interest, a considerable amount of precision is needed in balancing the fluid flows. To run DPPT experiments, it is necessary to firstly achieve a balanced system using the same gas flowing through both sides of the bridge. It would also be prudent for the initial perturbations to be made with the carrier gas species while balancing the system to reduce the margin for error and complexity with dealing with separate gas species to balance the system. Consider the simplified notational key diagram representing the sides of the Wheatstone bridge in Figure 4.18.



τ = residence time
 f = flowrate

Figure 4.18: Notational key representing the Wheatstone bridge in the DPPT experiment

The residence time, τ , represents the length of tubing through which the fluids make their way around the system. The following checklist is required to achieve a balance in the system:

- Balance flow rates on system I and system II to make sure they are the same – approximately corresponding to 0 V , measured by the data acquisition system.
- Check the perturbation signal.
- If a problem exists with the baseline, possible causes could be related to the carrier gas line (leakages, unbalanced flows across the Wheatstone bridge, pressure drops, or blockages). Whereas, if a problem exists in the baseline after the perturbation, then a host of factors could be prevalent: pressure fluctuations in the perturbation gas line, moisture present in the perturbation gas line, irregularities in the BPR configurations, pressure fluctuations in the mass flow controllers, as well as a variety of other system errors.

As stated earlier, the balance between both sides of the bridge must be equal. As a result, the residence times must be of the same value across the bridge shown in Figure 4.18. Figure 4.19 details possible sets of flux response profiles to be encountered post perturbation in trying to achieve a balanced system setup for a case of identical catalysts present in both reactors.

Part (a) of Figure 4.19 shows the scenario where an imbalance in the residence times exists ($\tau_1 < \tau_2$ or *vice versa*) and the flowrates passing through each side of the bridge are equal ($f_1 = f_2$). Here, the difference in the tubing lengths causes a steep rise and

decay back to the original perturbation baseline. Such settings render the bridge imbalanced and incapable of performing the DPPT experiment. Part (b) shows a similarly imbalanced system, where $\tau_1 < \tau_2$, and an additional offset created by different flows transported through the sides of the bridge, i.e. $f_1 > f_2$. When the residence times are balanced across the bridge but different flowrates exist through each reactor, the DPT measures a signal similar to that of part (c), where the perturbation baseline decays and steadies out at a lower baseline. Finally, part (d) shows a well balanced system where $\tau_1 = \tau_2$ and $f_1 = f_2$. Upon realisation of the balanced system, it is now possible to perform tests on different catalysts to measure the responses to the addition and cessation of perturbation flows.

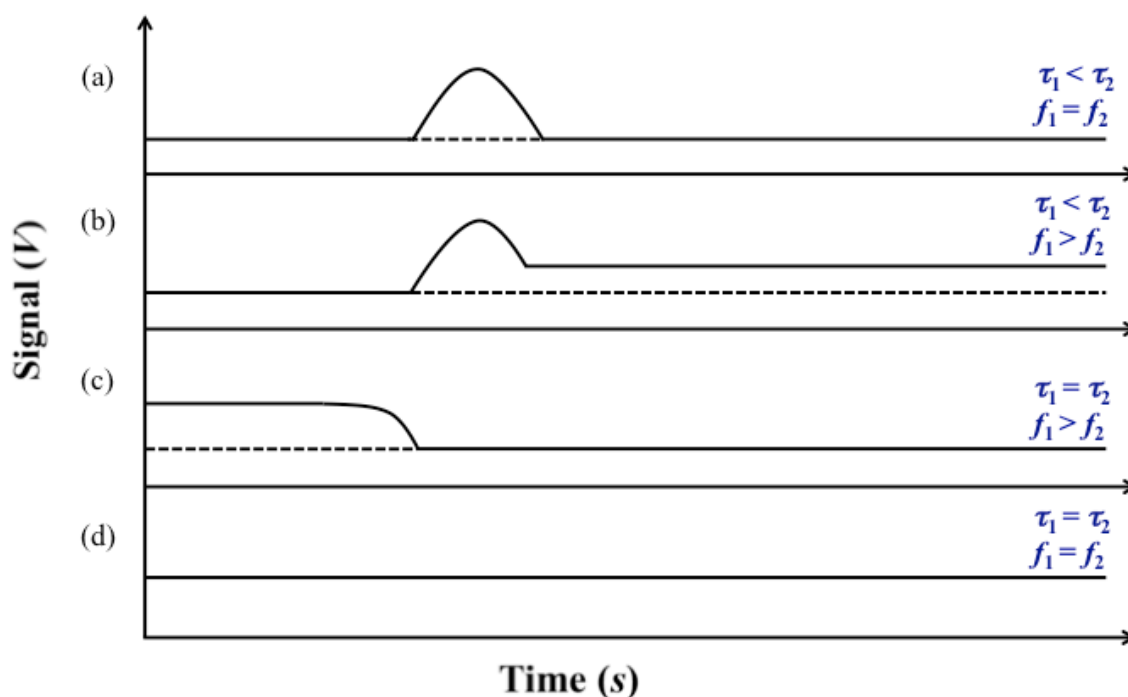


Figure 4.19: Expected DPPT flux response profiles

Referring back to the schematic setup in Figure 4.16, the carrier gas is split into two streams and flows through each reactor on both sides of the Wheatstone bridge. The reactors used were 4 mm ID quartz tubes of length 0.3 m each. In order to carry out temperature programmable experiments, a temperature programmable furnace is used. Once steady state is reached, it is possible to investigate the test materials by ramping the temperature.

Figure 4.20 illustrates the expected DPPT flux response profiles when comparing both reactors with identical quantities of catalyst material and when comparing with one reactor possessing a significantly higher quantity than the other. For the experiments here, ammonia would be added to both sides of the system at the same flowrate. Once steady state has been achieved, the temperature would be ramped and the flux response recorded. It is expected that the flux response profile showing the experiment with a single 1/8 *in* zeolite pellet in each reactor would generate the red line shown in Figure 4.20, similar to part (d) of Figure 4.19. The blue line in Figure 4.20 shows that, by contrast, doubling the amount of catalyst in one reactor results in a significant improvement in the performance of that reactor relative to the other.

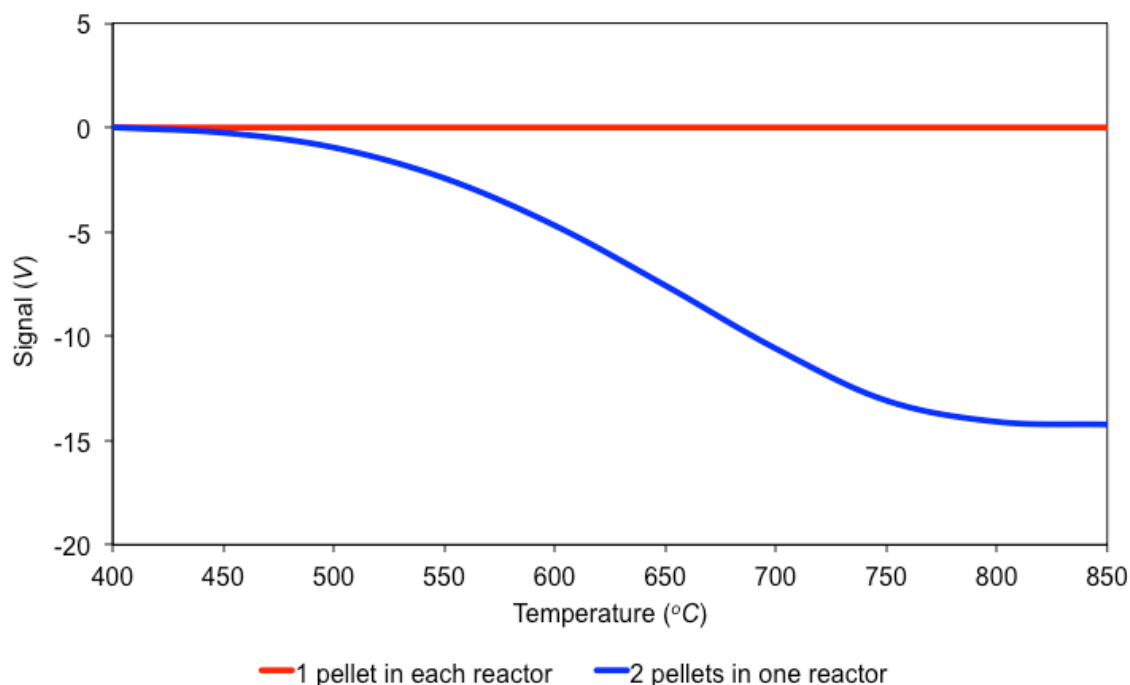


Figure 4.20: Expected DPPT flux response profiles showing the difference between reactors with the same quantities and reactors with differing quantities of catalyst material.

Previous FRT experiments studying ammonia decomposition over Pt/Alumina were successful at measuring conversions and demonstrated that the conversions obtained were in excellent agreement with those measured by mass spectrometry (Richardson *et al.*, 2004). A marked advancement in the method requires the investigation and comparison between samples of differing catalytic material. A suitable option would be the comparison between nickel and platinum catalysts supported on the same batch of porous alumina. The theoretical flux response profiles presented in Figure 4.21 are

demonstrative of such an experiment with the 3 flux response profiles shown comparing ammonia decomposition between both sets of catalysts.

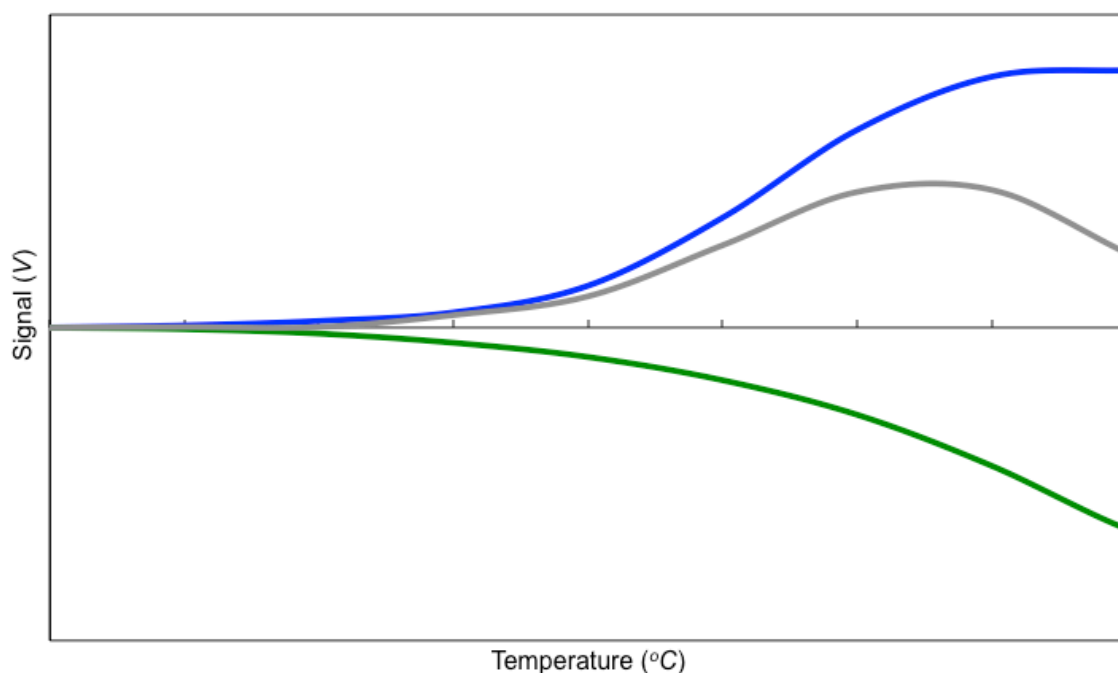


Figure 4.21: Expected DPPT flux response profiles comparing Ni/Al (—) and Pt/Al (—) catalysts with their parallel performance (—)

In this scenario, steady state is achieved using the carrier gas then a small concentration of ammonia is continuously added to one side of the bridge. The temperature is then ramped and the flux response recorded. The process is replicated for the other side of the system containing the other catalyst material before the third experiment where the ammonia perturbation stream is switched into both sides of the system concurrently. It is expected that upon the ammonia perturbation delivery, one side of the system would depict a positive flux response with the increase in effluent flow while the other side would exhibit a negative flux response with an increase in effluent flow. It is also expected that the nickel catalyst would perform better than the platinum at lower temperatures but would converge to become similar at higher temperatures. A line showing the sum of both individual flux responses for the first two experiments would also be expected to closely follow the results of the parallel performance, presented as the grey line in Figure 4.21.

The preliminary experiments into balancing the system setup carried out using the modified upstream FRT system involved investigating the flux response profiles generated when 30 *mol*-% NH₃ was switched in to interrogate the ZSM 55 samples present in both reactors.

4.5.2.2. Material Characterisation

A plethora of techniques have been used to characterise the zeolite sample in question, including solid-state NMR, XRF, and XRD analysis to evaluate the possible existence of extra-framework Al.

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Chapter 5

FRT-Zero Length Column Diffusion Studies

Diffusion within porous materials has been widely studied by scientists and industry for its useful and important applications in molecular separation, heterogeneous catalysis, membrane technology, fuel cells, soil mechanics and petroleum engineering. The importance of accurately being able to model diffusivity is highlighted extensively in many catalytic combustion applications associated with power generation and pollution control (Boger *et al.*, 2004; Chen *et al.*, 2004; Gonzo & Gottifredi, 2010; Heck *et al.*, 2010; James *et al.*, 2003; Tomašić, 2007).

The well-known automotive catalytic converter makes use of a catalytic monolith reactor in a ‘honeycomb’ configuration to oxidise carbon monoxide and unburned hydrocarbons while reducing oxides of nitrogen. These reactors possess several obvious advantages over traditional reactors packed with catalyst particles – lower pressure drop, uniform flow distributions, uniform residence times and less hot-spot formation (Armenise *et al.*, 2010; Heck *et al.*, 2001). Metals and ceramic materials such as cordierite are commonly used as monolith materials. Cordierite is a material chosen due to its high melting point of over 1000 °C, resistance to oxidation and resistance to thermal shock, which is required to meet the severe operating conditions in automotive exhausts (Brito *et al.*, 2005; Ciambelli *et al.*, 2010). Metallic monoliths have been used since the early 1990s and offer advantages when compared to cordierite such as higher frontal areas approaching 90 %, which provide higher geometric surface areas while offering low resistance to flow. However, due to their metallic nature, the expansion coefficient is much greater than ceramics, thereby requiring special bonding techniques to produce an adherent washcoat (Heck *et al.*, 2001). The washcoat found typically on monolithic ceramic substrates contain the active catalyst layer of fine precious metal particles for example, platinum and rhodium in the case of the automotive industry (Plummer *et al.*, 2003).

The ability to model the performance of monolith supported catalysts is a crucial tool required by manufacturers in order to rapidly explore alternative system designs, lower development costs and increase speed of production. To this effect, understanding the diffusion that occurs within the washcoat and substrate material which strongly affects reactor performance is essential in the design of monolith supported catalysts (Koci *et al.*, 2007; More *et al.*, 2006; Zhang *et al.*, 2004).

With these factors in mind, it must be acknowledged that the diffusion coefficients reported in literature for microporous materials often vary with differences as large as five orders of magnitude being reported for different techniques (Kärger, 2012). The discrepancies between different techniques have since been resolved and can be traced to the different length scales over which diffusion is measured (Chmelik *et al.*, 2011). Measured diffusivities were found to be smaller when the path length covered in the measurement is large (macro-measurements) suggesting the intrusion of extra-crystalline transport resistances in addition to the diffusional resistance of the pore system (Chmelik *et al.*, 2011; García-Sánchez *et al.*, 2012; Ruthven, 2001). Flux Response Technology was used to measure propane diffusivity in the washcoat of monolith samples and CO₂ diffusion in commercial zeolites by analysing the adsorption and desorption transients in the FRT dynamic cycle profiles. By applying the Zero Length Column (ZLC) method to analyse the sorption curves generated by the FRT system, the diffusion coefficients were extracted.

5.1. Results and Discussion

5.1.1. Material Characterisation

5.1.1.1. Textural Characteristics

Four cordierite monoliths with varying alumina/CeZrO_x washcoats and four zeolite samples were supplied by Johnson Matthey and Zeolyst respectively. These samples were analysed to characterise the structural properties of the materials using a Micromeritics Tristar 3000 surface analyser and SEM with the resultant data compiled in Table 5.1 and Table 5.2.

Table 5.1: Physical characterisation of cordierite monolith with alumina/CeZrO_x washcoat

Material	S _{BET} (m ² /g)	Pore length (μm)	Macropore (μm)
Sample 1	23.79	21	-
Sample 2	21.63	52	3
Sample 3	26.79	47	5
Sample 4	25.60	46	10

Table 5.2: Physical characterisation of zeolite test samples

Zeolite	SiO ₂ /Al ₂ O ₃ Ratio	S _{BET} (m ² /g)	Pore size (×10 ⁻⁹ m)	Pore volume (cm ³ /g)
F.CP914C	20	296	2.87	0.21
ZSM 55	50	282	2.97	0.21
F.CP914	55	396	2.51	0.25
ZSM 280	280	386	2.20	0.21

5.1.1.2. Propane Diffusion in alumina/CeZrO_x Washcoats

5.1.1.2.1. Temporal Analysis of Products (TAP)

The analysis of hydrocarbon diffusivities within the cordierite washcoats was undertaken utilising TAP reactor measurements as a useful comparison to the FRT measurements discussed further on in Chapter 5.1.1.2.3. To analyse the samples, the thin zone TAP reactor (TZTR) method developed by Shekhtman *et al.* was used (Maguire *et al.*, 2013). Figure 5.1 shows the pulse response observed for Sample 1 at 60 °C. By applying moment-based analysis of the response curves, it was possible to determine adsorption information directly related to the effective diffusivity of propane within the washcoat materials. Both the intensity and the shape of the curve were analysed by taking integrals of the observed TAP responses weighted with different powers of time, illustrated in equation 5.1.

$$M_n = \int_0^{+\infty} t^n F(t) dt \quad \frac{M_1}{M_0} = \tau_{res} \quad 5.1$$

where, M_n is the moment of n^{th} order ($\text{mole} \cdot \text{s}^n$), F_{exit} is the area-normalised exit flow ($1/\text{s}$), M_0 is the zeroth moment (mole), M_1 is the first moment ($\text{mole} \cdot \text{s}$), M_2 is the

second moment ($\text{mole} \cdot \text{s}^2$), and τ_{res} is the residence time of the molecules (Shekhtman *et al.*, 1999).

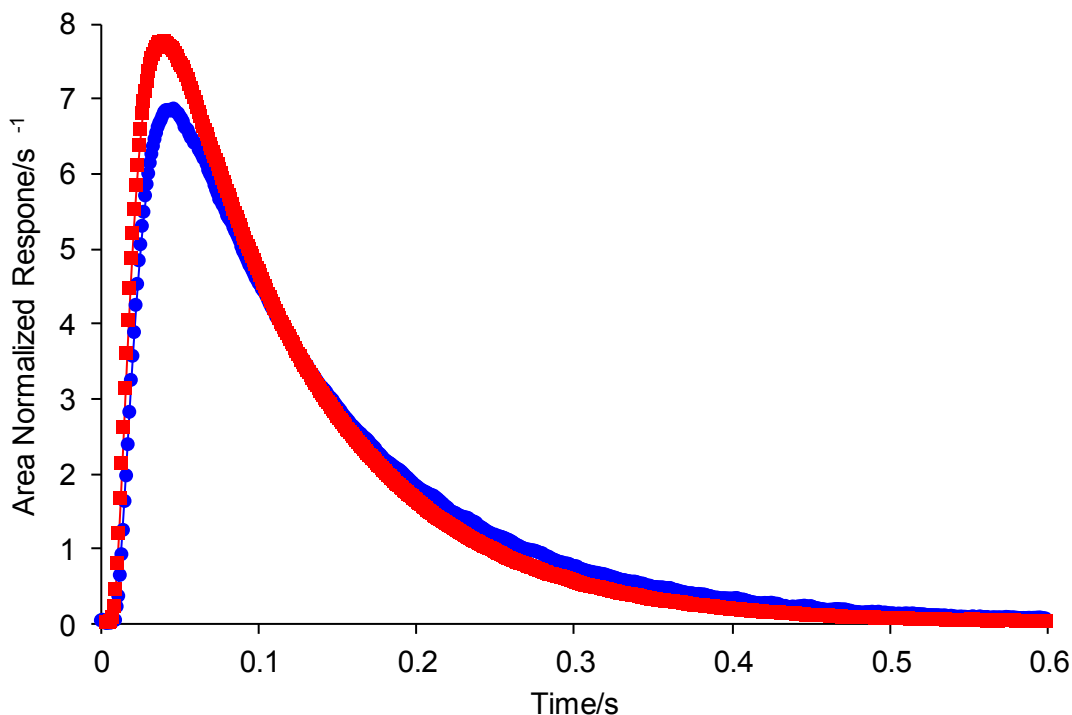


Figure 5.1: TAP response curves at 60 °C for propane (■) and krypton (●) with theoretical fits (solid lines) (Maguire *et al.*, 2013)

For this analysis, evaluating the first moment, M_1 , gave a measure of the apparent intermediate gas constant, K_p , which can be viewed as the equilibrium adsorption constant. The evaluation of the second moment, M_2 , gave access to the apparent time delay, τ_{app} , corresponding to the residence time of the molecule inside the porous network. Figure 5.2 shows the calculated TAP parameters, K_p , obtained for the four monolith samples across 20 – 100 °C. When viewing Figure 5.2, a clear trend can be seen when comparing Samples 2 – 4, indicative of similar adsorption properties existing for the three samples. Sample 1 showed lower values in comparison to the other samples, reflective of its lack of macroporosity (shown in Table 5.1). Another possibility for the difference can be attributed to the structural variance of the porous networks and the preparation methods used could affect the type of adsorption sites present in each sample. However, the slopes of all the sample curves are comparable, irrespective of preparation method, indicating the presence of similar adsorption sites for each material.

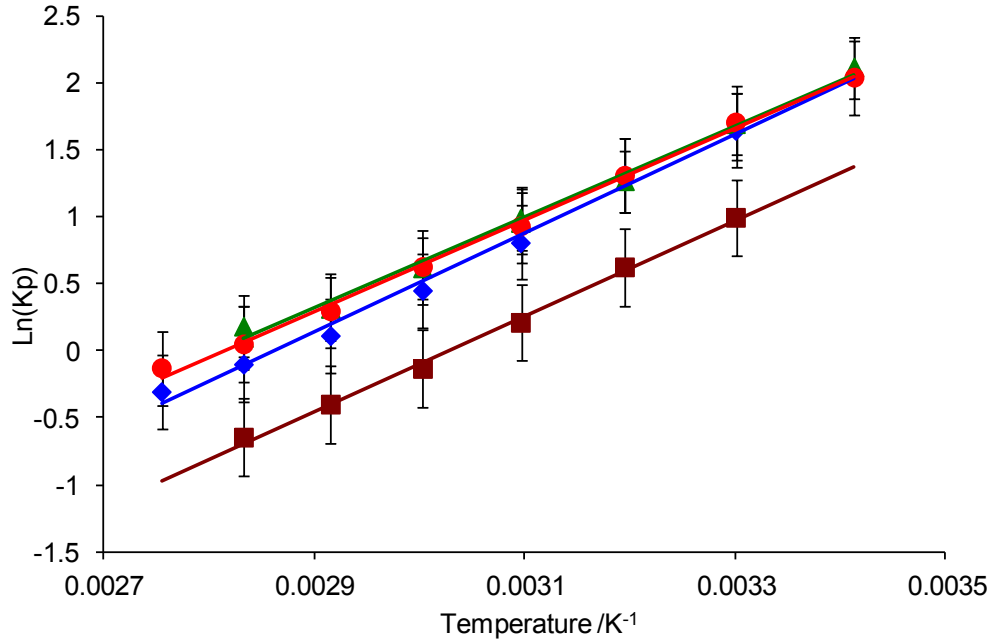


Figure 5.2: TAP derived $\text{Ln}(K_p)$ as a function of temperature for Sample 1 (■), Sample 2 (◆), Sample 3 (▲) and Sample 4 (●) (Maguire *et al.*, 2013)

The calculated activation energy of desorption for all four monolith samples was estimated as 30 kJ mol^{-1} . Figure 5.3 shows the parameter τ_{app} , as a function against temperature. The temperature dependence of the residence times show a wide range of values due to the differences in the mesoporous and macroporous structures within the alumina/CeZrO_x washcoats. It is possible to interpret the overall diffusion resistance of the material to be a characteristic of the residence time dependence, as this factor is relative to the time period for molecules being transported into and out of the porous network. Equation 5.2 gives the formula used to calculate the effective diffusivity within the washcoat,

$$\tau_{app} \approx \frac{L_{ave}^2}{D_{eff}} \quad 5.2$$

where L_{ave} is the average pore length and D_{eff} is the effective diffusivity.

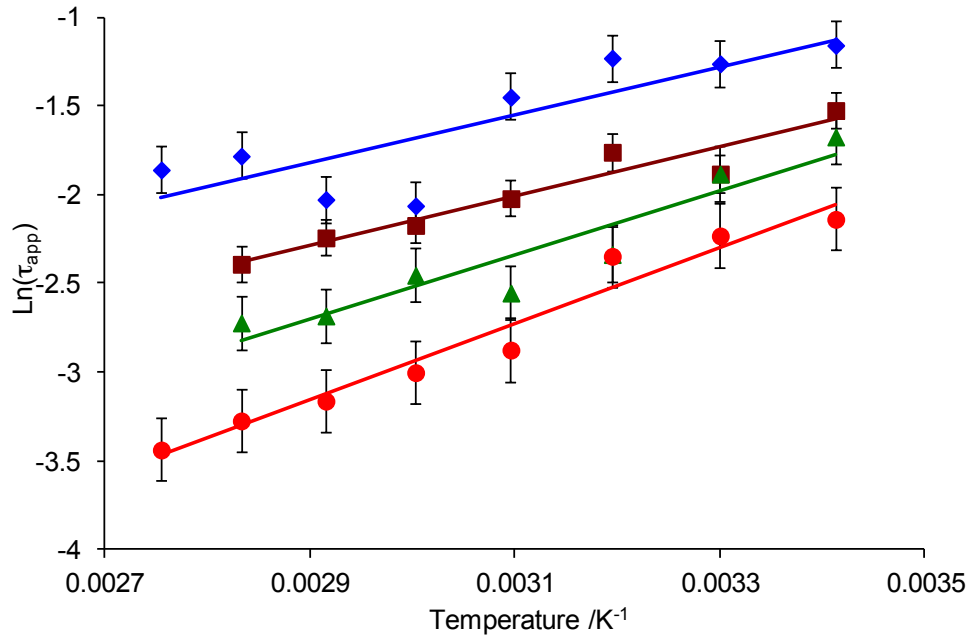


Figure 5.3: TAP derived $\text{Ln}(\tau_{app})$ as a function of temperature for Sample 1 (■), Sample 2 (◆), Sample 3 (▲) and Sample 4 (●) (Maguire *et al.*, 2013)

Figure 5.4 displays D_{eff} as a function of temperature. As expected, an increase in diffusivity with temperature and macropore diameter is exhibited.

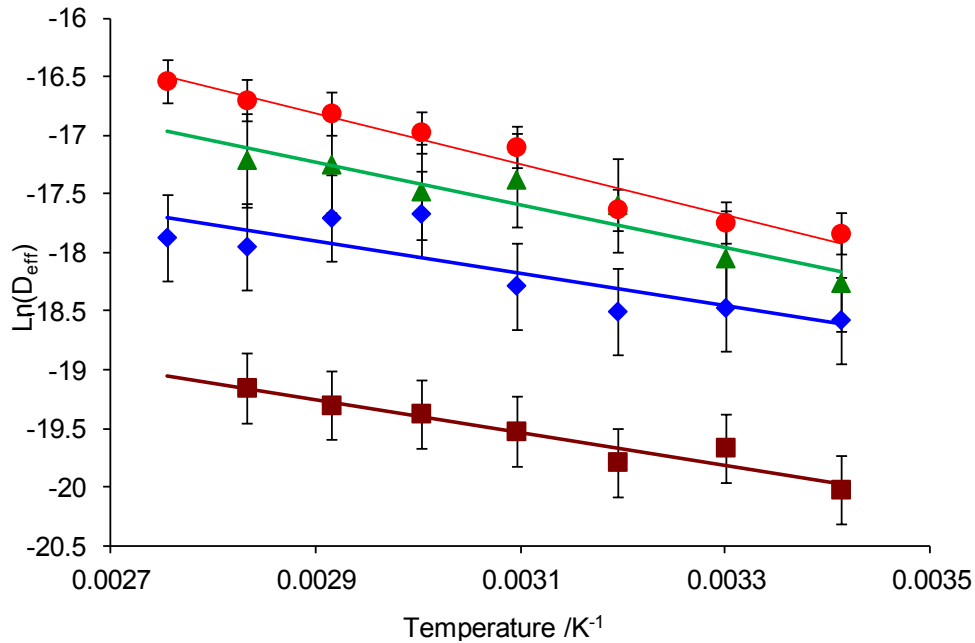


Figure 5.4: TAP derived $\text{Ln}(D_{eff})$ as a function of temperature for Sample 1 (■), Sample 2 (◆), Sample 3 (▲) and Sample 4 (●) (Maguire *et al.*, 2013)

5.1.1.2.2. FRT-ZLC

Shown in Figure 5.5 is an example of the flux response profile for Sample 3. Part (a) shows an expanded view of the first dynamic cycle and highlights the partial desorption effect. Part (b) presents the entire FRT experiment by showing the three dynamic cycles. As expected, a strong correlation between the expected flux response profile detailed earlier and the experimental flux response profile shown is apparent. The key effects are the propane partial adsorption peak; the viscosity effect caused by the propane perturbation into argon carrier gas; propane partial desorption peak; and the viscosity effect caused by the composition of the gas changing from a propane/argon mixture to purely argon carrier gas.

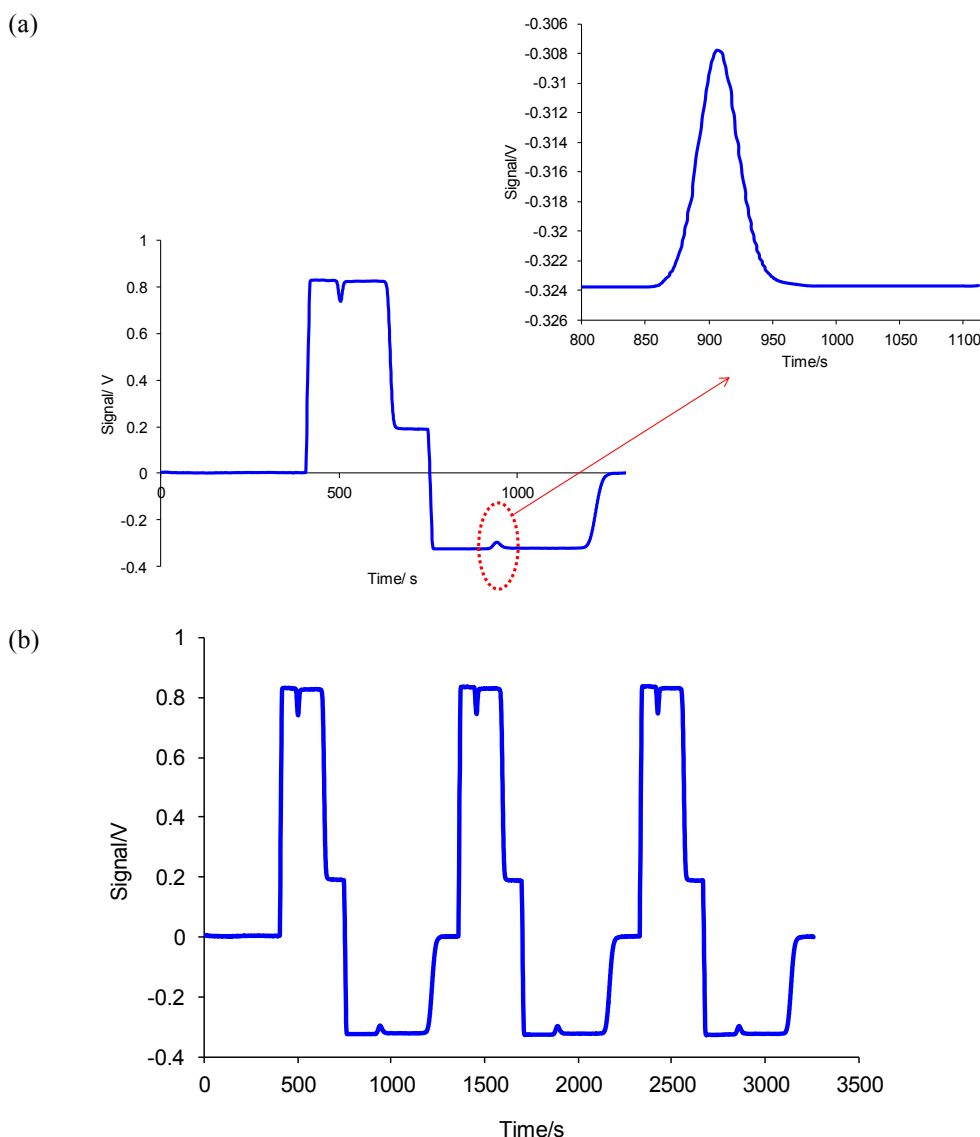


Figure 5.5: Flux response profile for Sample 3 at C_3H_8 mole fraction of 0.5 (a) first sorption cycle (b) complete experiment showing three sorption cycles

For the investigation of diffusivities within the washcoats of the cordierite samples, it was necessary to analyse the concentration of the adsorbable species (C_3H_8 in this instance) in the effluent stream in order to apply the ZLC analysis. As stated earlier, the measuring element within the FRT apparatus is an extremely sensitive DPT capable of measuring flowrate changes of the order of $10^{-2} \mu l/min$. The differential pressures measured by the DPT are directly proportional to the amount of probe molecules ad/desorbed onto or from the surface of the adsorbent (Richardson *et al.*, 2008). As such, with reasonable accuracy, the responses by the DPT in the flux response profiles can be considered linear and directly proportional to the quantity of C_3H_8 released into the effluent stream.

Figure 5.5 (a) presents the partial adsorption and desorption curves that are required for the analysis of propane diffusivity. The analysis of the FRT partial sorption curve required the response curves to be normalized to the initial concentration by using the following equation (Brandani 2002):

$$\frac{c(t)}{c_0} = \frac{\sigma(t) - \sigma_{inf}}{\sigma_0 - \sigma_{inf}} \quad 5.3$$

where, σ_0 is the value of the FRT signal at time zero and σ_{inf} is the value of the FRT signal at the respective sorption completion times. The data acquisition from the DataShuttle/USB 54 system (Adept scientific) linked to a desktop computer was started at the beginning of the experiment, recording all the FRT responses to the C_3H_8 perturbation. Consequently, in order to clearly evaluate σ_0 , the time scale from the data acquisition had to be shifted back by t_0 seconds for each sorption curve. It was also necessary to invert the FRT profile along the x –axis at the region correspondent to the partial adsorption effect to be able to analyse its decay.

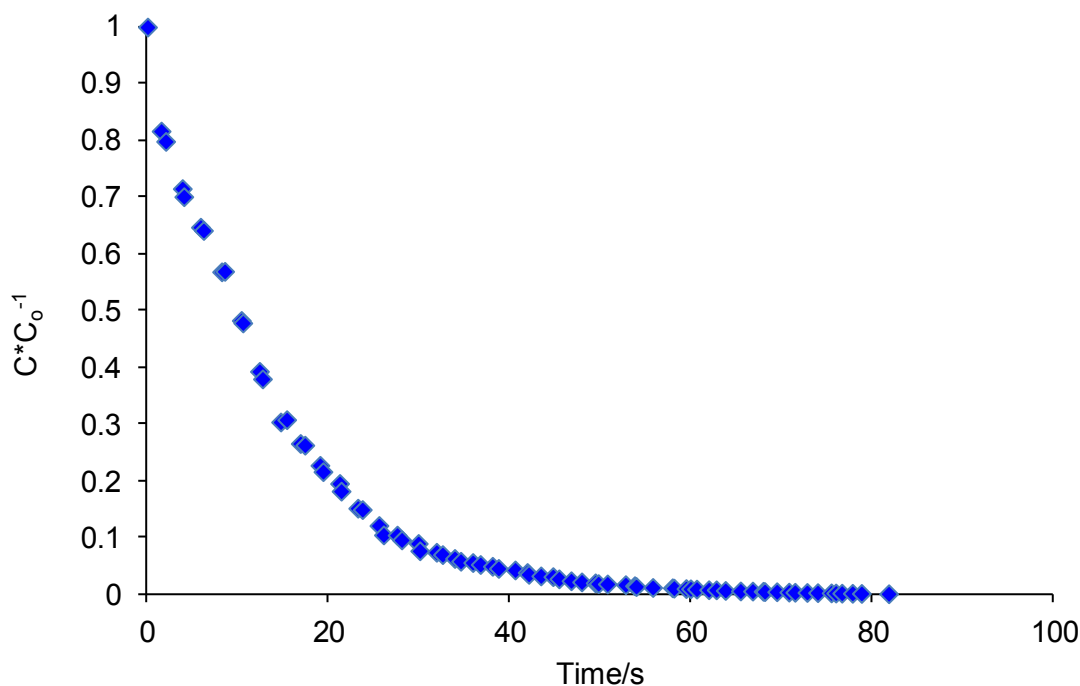


Figure 5.6: Experimental FRT-ZLC desorption curve of Sample 3 at 25 °C ($X_{C_3H_8} = 0.5$)

Figure 5.6 represents the normalised decay curve from the FRT generated desorption curve for ZLC analysis. It is worth noting the form of the FRT profile displayed above. Ruthven *et al.* have shown the concentration profile for a sample which is subjected to a step change in surface concentration where the slope is curved, increasing from high to low concentration, much akin to that shown in Figure 5.6 is characteristic of a system where surface resistance controls the diffusivity within the sample (Ruthven *et al.*, 2010). The initial step drop in concentration is signature in samples where diffusivity within the sample is dominated by surface barrier control. Independent tests are required in line with measuring the FRT-ZLC response at very low flow rates under conditions of equilibrium control and crosschecking with the current responses (kinetic control) for consistency. This would enable tests for a clear distinction between intracrystalline diffusion and surface barrier controlled resistance to be carried out (Ruthven & Brandani, 2005).

Once this curve was generated, it was necessary to account for apparatus effects influencing the measured signal response such as dispersion, dead volume and adsorption on tube walls. When the perturbation gas is switched in during the experiment, the dispersion of the probe molecules through the tubes connected to the switch-in valve can have a significant role on data analysis. Such an effect can dominate

the signal response as is shown in Figure 5.7 and needs to be corrected for using a blank run. The trade-off between systematic errors brought about through pressure drops within the FRT apparatus and dispersion effects through the tubes of the apparatus had to be limited during the building of the FRT system and as such, such apparatus effects would have to be accounted for during data analysis. By comparing the curves of the FRT setup in the presence and absence of the test sample, it was possible to evaluate the full extent of the dispersion effect for identical system conditions. Figure 5.7 shows the comparison of response with the test sample and the corresponding blank.

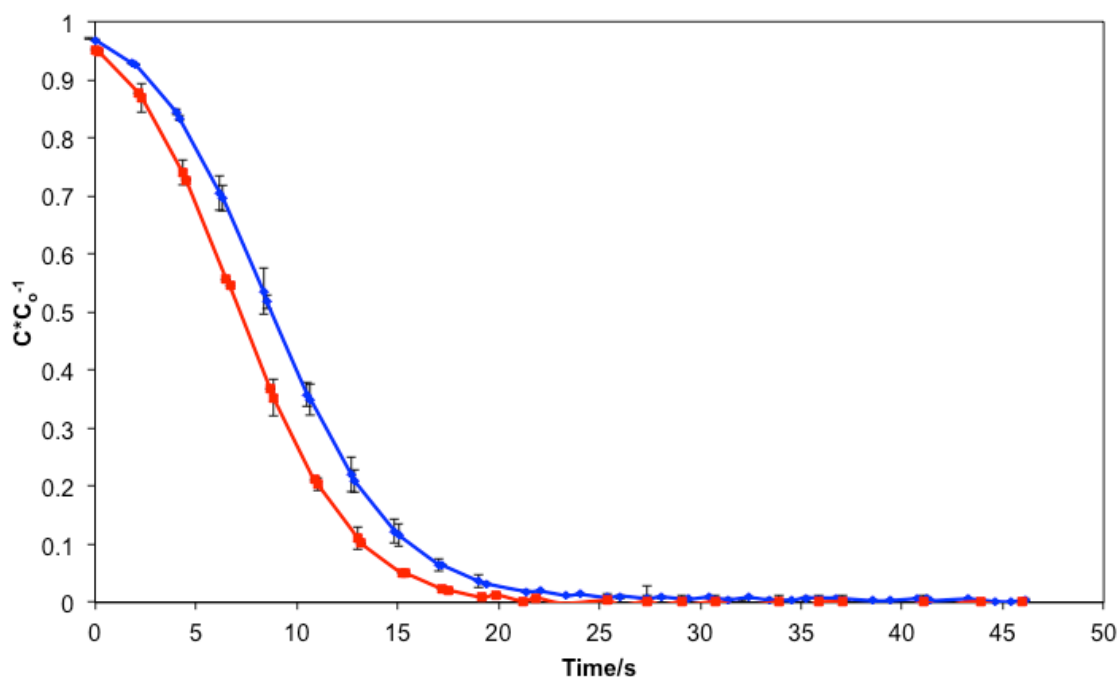


Figure 5.7: Comparison of the FRT-ZLC curves measured for FRT system in the presence (♦), and absence (■) of Sample 3 at 25 °C (C_3H_8 mole fraction, 0.5)

The reason for performing the blank experiments as a comparative tool stemmed from preliminary experiments where the generated ZLC models for the FRT desorption curves fitted the long time region of the curves accurately but seriously underpredicted the initial concentrations. As is shown in Figure 5.7 the concentration ratio falls to approximately zero in roughly 17 s when no sample is present while it takes approximately 21 s when a sample is present. This result negates the possibility of the underprediction being due simply to a slow system response time. Both experiments show a pronounced tail from 21 s, which indicates the likely cause is due to an apparatus effect associated with dispersion through the system as stated earlier. From the developed double exponential (Loos, 2000), it was possible to limit the influence of

this dispersion by simply subtracting the difference between the models generated for the blank experiment from those with the sample present to allow the accurate application of the ZLC equations. The exponential function in equation 5.4 was used to model the dispersion effect where the characteristic times, τ_1 and τ_2 are the characteristic times for the dispersion effect, I and I_0 are the intensity at any time t and the maximum intensity at the start of the decay, respectively, and t_0 is an offset depending on whether the curve starts at time = 0.

$$I = I_0 e^{\left(\frac{t_0-t}{\tau_1}\right)} + (1 - I_0) e^{\left(\frac{t_0-t}{\tau_2}\right)} \quad 5.4$$

The results of the blank experiments were also able to yield valuable information relative to the working of the FRT system. Adapting the ZLC technique in FRT system provided the additional capability of measuring fast diffusion processes by taking advantage of the very sensitive DPT. The FRT system responds to any substance whose extent of sorption differs from that of the carrier, thereby making it possible to measure flow rate changes instantaneously as the capillary detection system behaves as though it has no volume (Buffham *et al.*, 1993). The arrangement of the DPT and matched capillaries provide the system with a resolution of one part in ten thousand, however, the response time of the system can be reduced further still at the expense of the sensitivity and vice-versa (Buffham *et al.*, 1986). The internal diameter of the capillaries which control the pneumatic resistances are a compromise between these conflicting system requirements whereby the gas species are conveyed as quickly as possible to the packed bed, minimizing dispersion within the system without restricting the sensitivity of the DPT to perform differential measurements. The system runs with and without an adsorbent present are showcased in Figure 5.7 and are normalised relative to their initial concentrations. Each run was performed to indicate the level of dispersion within the system, which was subsequently subtracted from the generated sorption curves to account for this dispersion. The slow response time can be explained by considering the size of the perturbation stream, which was set at 0.5 *mole* fraction.

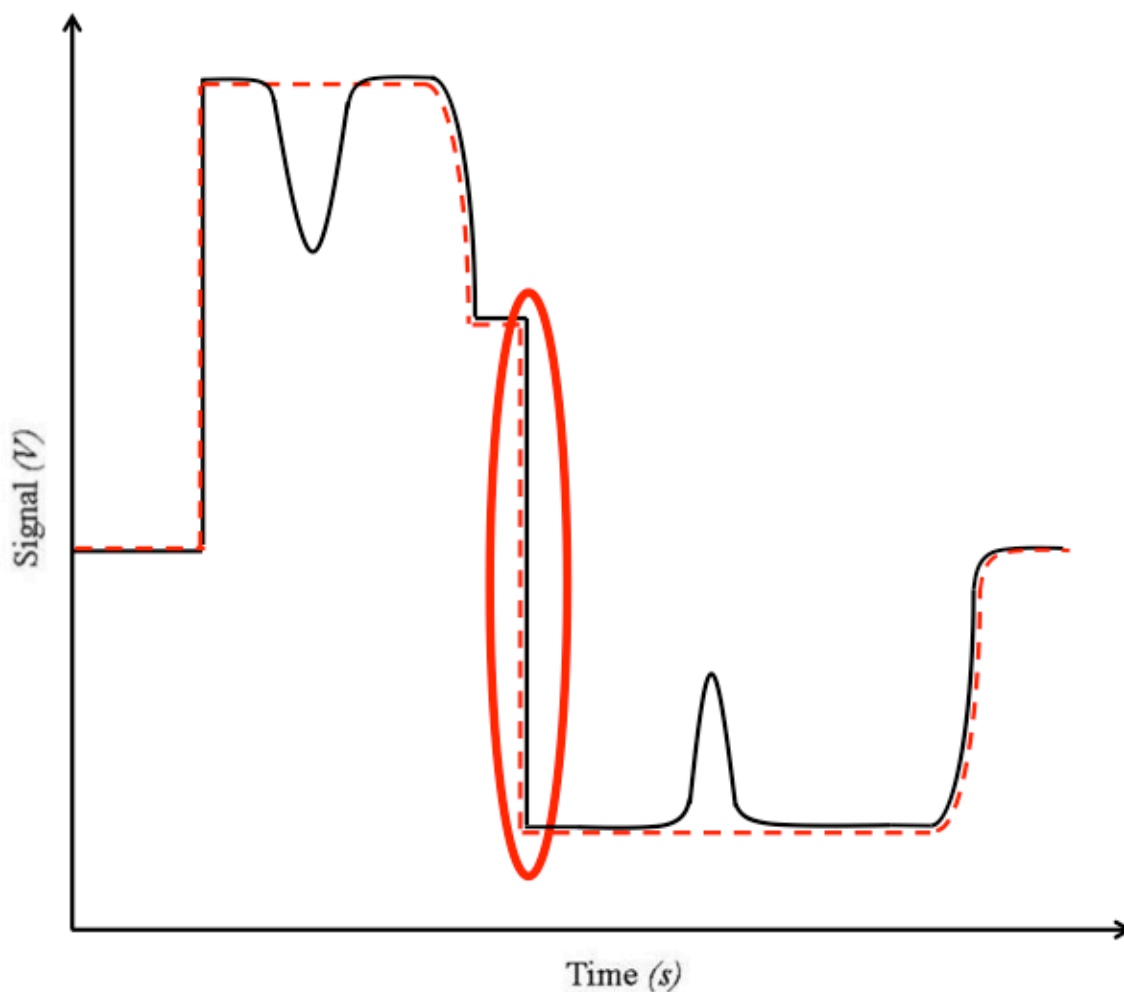


Figure 5.8: Schematic flux response profile for case with and without adsorbent present

Shown in Figure 5.8 above is a schematic flux response profile for the present study. The black line represents the expected flux response profile with an adsorbent present while the dashed red line represents the blank system. Evaluating the dispersion in the system was carried out by comparing the profiles at the circled region – the point at which the perturbation stream is switched out leaving the carrier gas to flow on its own through the reactor. As can be noticed from the graph, a large step change is exhibited and attributed to the perturbation stream. Measurements acquired by the data acquisition software across this region where the blank response was evaluated do show a prolonged signal response due to the large pressure change but this is expected as the signal simply follows the path length through the system of the loss in pressure from the perturbation stream being switched out. The effective time constant of this system can therefore be evaluated by considering the blank response time of the propane probe. From Figure 5.7, it is clear that equilibrium is achieved after approximately 17 s, but already between 0 – 5 s, the average of the data collected is equal to 72 % of the

equilibrium value. By programming the data logger to record acquisitions at shorter time intervals, the transient responses would be recorded much more accurately. Analysing the decay of the response with the effects of thermal noise and dispersion that are specific to the FRT system, it was possible to estimate the maximum measurable value of the effective time constant by fitting an exponential curve to the response. This yielded a value of 0.6 s^{-1} .

Having taken the dispersion effect into account, it was then possible to evaluate the ZLC parameters, D and L from equation 3.1 below. By generating a plot of $\ln(c/c_0)$ against t , it was possible to calculate these parameters by using the slope and intercept of the linear asymptote in the long time region. This is known as the long time (LT) analysis in ZLC studies (F. Brandani, 2002):

$$\frac{c}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{\beta_n^2 D t}{r^2}\right)}{[\beta_n^2 + L(L-1)]} \quad 5.5$$

$$\beta_n \cot \beta_n + L - 1 = 0 \quad 5.6$$

$$L = \frac{1}{3} \frac{Fr^2}{KV_s D} \quad 5.7$$

where only the first term of the summation in equation 3.1 is significant:

$$\frac{c}{c_0} = \frac{2L}{[\beta_1^2 + L(L-1)]} \exp\left(-\frac{\beta_1^2 D t}{r^2}\right) \quad 5.8$$

The slope and intercept of the semilogarithmic plot of c/c_0 vs. t are given, according to equation 5.8 by:

$$S = \frac{\beta_1^2 D}{r^2}; \quad I = \frac{2L}{[\beta_1^2 + L(L-1)]} \quad 5.9$$

By combining the intercept with the transcendental equation shown in equation 5.6, the root β_1 was found using equation 5.10.

$$\beta_1 - \cot\beta_1 + \beta_1 \cot^2\beta_1 + \frac{2\beta_1 \cot\beta_1 - 2}{\beta_1 \text{Intercept}} = 0; \quad 5.10$$

$$\beta_1 \in (0, \pi)$$

Equation 5.9 was solved analytically using Maple software, from which the value of the time constant, D/r^2 and hence the diffusion coefficient could be solved. The source code and sample calculation file can be found in Appendix A.

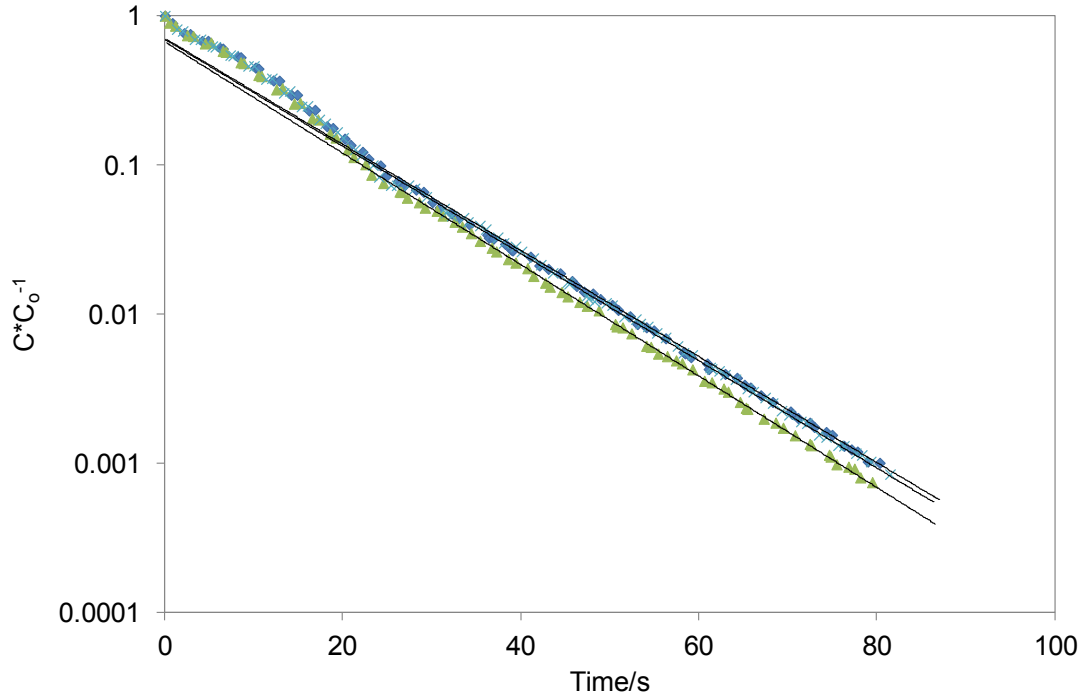


Figure 5.9: Experimental FRT-ZLC desorption curve for Sample 3 at 40 °C (C_3H_8 mole fraction, 0.5) for all three cycles (1st cycle - ◆, 2nd cycle - ▲, 3rd cycle - ×) showing the long time asymptote approach

Presented in Figure 5.9 is the log-scale approach of the long time asymptote for all 3 cycles of Sample 3 at 40 °C. It is clear that the asymptotes of these response curves are similar. This is in accordance with equation 5.7, where for a given temperature, L should be proportional to the purge flowrate. As the purge flowrate at each cycle was the same, it was expected that the generated asymptotes would be similar. One of the advantages of the ZLC experimental method is that for any particular system, the validity of the basic assumptions under the experimental conditions can be verified directly by a series of simple experiments. In performing the three cycles required for the complete FRT-ZLC experiment and comparing their asymptotes, a test for the validity of the ZLC assumptions was inadvertently carried out. Other researchers have performed similar tests by varying the flowrate of the purge gas and comparing the long

time asymptotes. In such cases, the generated asymptotes would be expected to be parallel from one another (Gobin, 2006; Guimarães *et al.*, 2010; Karge *et al.*, 2008).

From the evaluated ZLC parameters, it was possible to construct the FRT-ZLC plots with the experimental sorption curves fitted with the ZLC model. Figure 5.10 is an example of the experimental curves with their appropriate models.

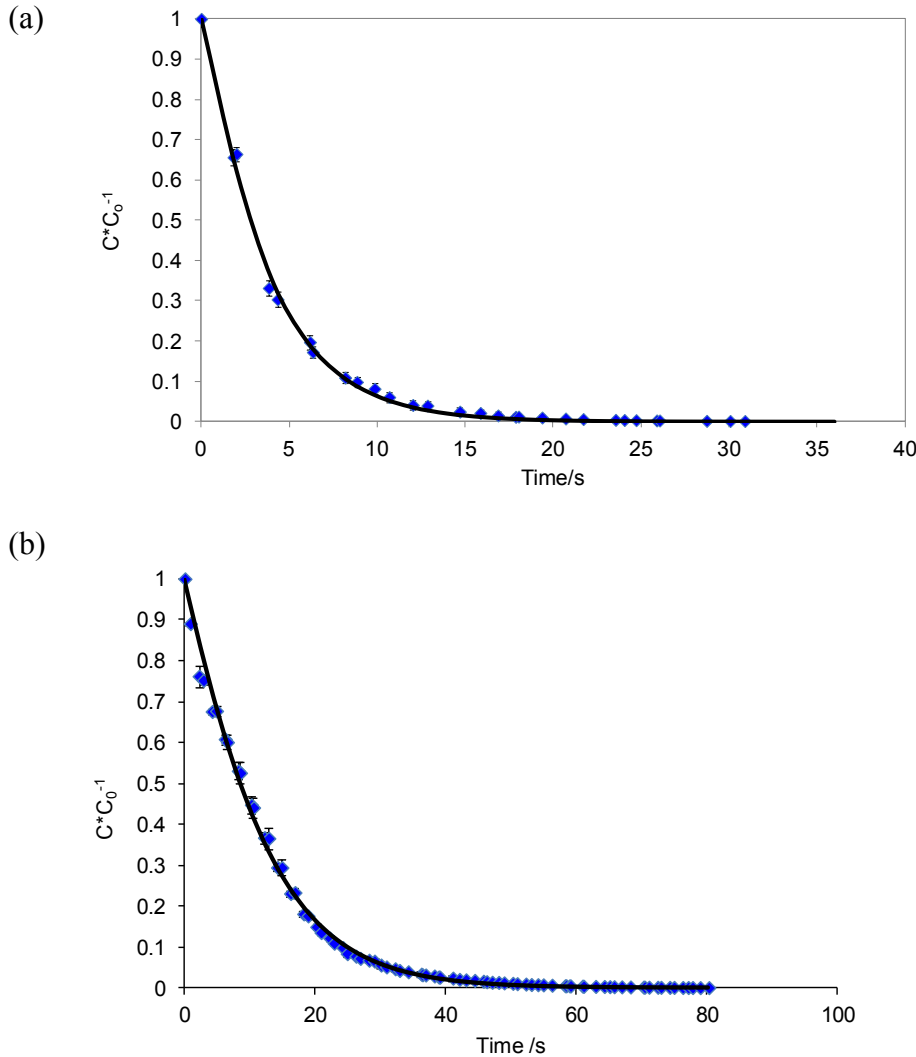


Figure 5.10: FRT Experimental (points) and fitted (solid line) curves for Sample 3 (a) adsorption transient (b) desorption transient, using propane (mole fraction, 0.5) at 40 °C

It is clear from Figure 5.10 that a good agreement exists between both experimental adsorption and desorption curves and the LT model for ZLC diffusion, thereby confirming the validity of the experimental method and analysis. Graphs of the diffusion coefficients for each of the monolith samples were plotted against temperature

to compare both ad and desorption transients and to analyse the respective activation energies of diffusion.

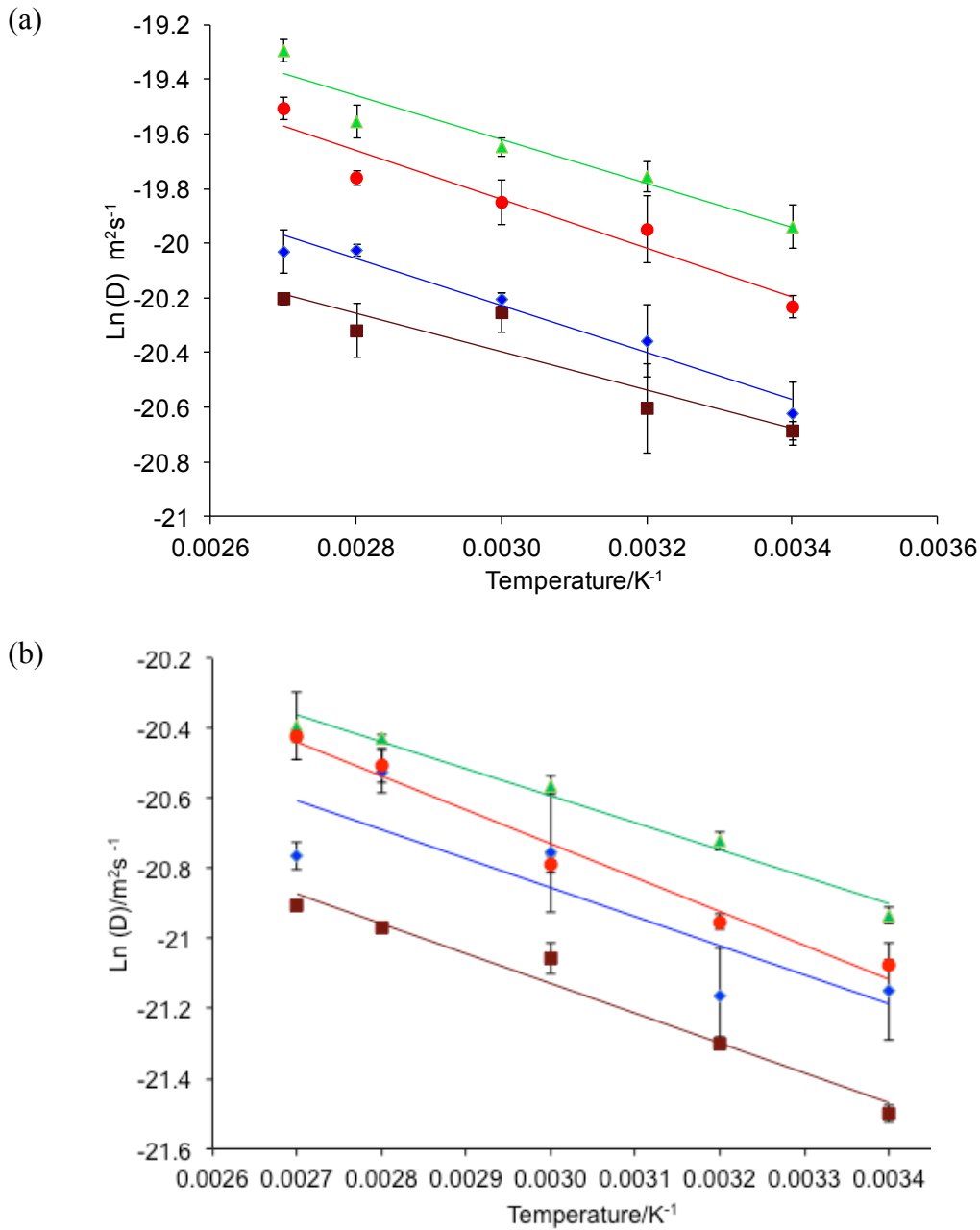


Figure 5.11: FRT Diffusion coefficients at temperatures between 25 – 100 °C for (a) averaged adsorption cycles (b) averaged desorption cycles, showing Sample 1 (■), Sample 2 (◆), Sample 3 (▲), and Sample 4 (●)

Figure 5.11 summarises the variation of the diffusion coefficients of the samples with respect to temperature. The first observation that can be deduced from the graphs show that the diffusion coefficients from the adsorption transient in part (a) are larger than those from the desorption transient in part (b). However, both show a similar linear

trend for the variation of the diffusivity coefficients with respect to increasing temperature, as expected. By taking the average of the adsorption and desorption values, a good estimate of the diffusivity coefficients of the samples can be evaluated and is shown in Table 5.3.

Table 5.3: Diffusivity coefficients of averaged FRT response transients.

Sample	Temperature/ <i>K</i>	$D/ m^2 s^{-1}$
Sample 1	298	7.5×10^{-10}
	313	8.5×10^{-10}
	333	1.2×10^{-9}
	353	1.1×10^{-9}
	373	1.3×10^{-9}
Sample 2	298	8.8×10^{-10}
	313	1.0×10^{-9}
	333	1.3×10^{-9}
	353	1.6×10^{-9}
	373	1.5×10^{-9}
Sample 3	298	1.5×10^{-9}
	313	1.8×10^{-9}
	333	2.1×10^{-9}
	353	2.3×10^{-9}
	373	2.8×10^{-9}
Sample 4	298	1.2×10^{-9}
	313	1.5×10^{-9}
	333	1.7×10^{-9}
	353	1.9×10^{-9}
	373	2.4×10^{-9}

The activation energies and pre-exponential factors for diffusion were determined from the Arrhenius-plots given in Figure 5.11, in accordance with equation 5.11.

$$D_{eff} = D^0 e^{-\frac{E_A}{RT}} \quad 5.11$$

The reported values in Table 5.4 show that the activation energies of diffusion for the adsorption transient were lower than those of the desorption transient. This is an expected result as the activation energies of the adsorption process are nearly always smaller than those of desorption (Ranke & Joseph, 2002).

Table 5.4: Comparison of activation energy (E_A) parameters of FRT transients

Material	Pre-exponential factor/ $m^2 s^{-1}$		Activation Energy/ $kJ mol^{-1}$	
	FRT - adsorption	FRT - desorption	FRT - adsorption	FRT - desorption
Sample 1	1.1×10^{-8}	8.3×10^{-9}	6 ± 0.6	7 ± 0.4
Sample 2	1.4×10^{-8}	9.5×10^{-9}	6 ± 2.2	7 ± 1.6
Sample 3	2.6×10^{-8}	1.0×10^{-8}	6 ± 1.0	6 ± 0.8
Sample 4	3.2×10^{-8}	1.7×10^{-8}	7 ± 1.1	8 ± 0.1

Table 5.5 shows the derived diffusivity values with the evaluated ZLC model parameter L as well as the temperature dependence of the evaluated Henry constants for each sample.

Table 5.5: Diffusivity and model parameters for FRT-ZLC experiments.

Sample	Temperature/ K	$D/ m^2 s^{-1}$ (ads)	L / dimensionless	K / dimensionless
Sample 1	298	1.0×10^{-9}	4.78	23 355.38
	313	1.1×10^{-9}	4.68	21 958.50
	333	1.6×10^{-9}	4.42	16 374.04
	353	1.5×10^{-9}	4.83	16 024.85
	373	1.7×10^{-9}	4.88	14 096.21
Sample 2	298	1.1×10^{-9}	4.46	23 498.55
	313	1.4×10^{-9}	4.08	19 711.73
	333	1.7×10^{-9}	4.12	16 739.19
	353	2.0×10^{-9}	3.99	14 442.57
	373	2.0×10^{-9}	4.70	12 333.27
Sample 3	298	2.2×10^{-9}	1.97	26 862.74
	313	2.6×10^{-9}	2.00	22 297.33
	333	2.9×10^{-9}	2.01	19 623.74
	353	3.2×10^{-9}	2.00	18 647.26
	373	4.2×10^{-9}	2.29	12 121.30
Sample 4	298	1.7×10^{-9}	2.70	26 266.28
	313	2.2×10^{-9}	2.66	20 120.96
	333	2.4×10^{-9}	2.59	18 670.92
	353	2.6×10^{-9}	2.73	18 158.81
	373	3.4×10^{-9}	2.74	12 521.28

It can be observed that the Henry's constants are inversely proportional to temperature as is expected. The Henry's constants show that the affinity of propane to the cordierite samples is as follows: Sample 3 > Sample 4 > Sample 1 > Sample 2. Table 5.6 compares evaluated Henry's constants for Sample 3 with literature values.

Table 5.6: Comparison of Henry's constants (dimensionless).

Sample	Sorbate	Temperature / K	Technique	K / -	Reference
Sample 3	Propane	313	FRT-ZLC	22 297.33	This work
Sample 3	Propane	333	FRT-ZLC	19 623.74	This work
Sample 3	Propane	353	FRT-ZLC	18 647.26	This work
Sample 3	Propane	373	FRT-ZLC	12 121.30	This work
Zeolite Beta	n-Hexane	473	ZLC	7 909.00	(Bárcia <i>et al.</i> , 2005)
amino- MIL-53 (Al) (MOF)	n-Heptane	453	Pulse Chromatography	1087.00	(Couck <i>et al.</i> , 2010)
Cerium oxide	n-Hexane	523	IG Chromatography	17.00	(Díaz <i>et al.</i> , 2006)

The evaluated Henry's constants in Table 5.6 once again show the dependence on temperature for similar adsorbates. The values of the Henry's constants also show a marked decrease with increasing adsorbate chain length.

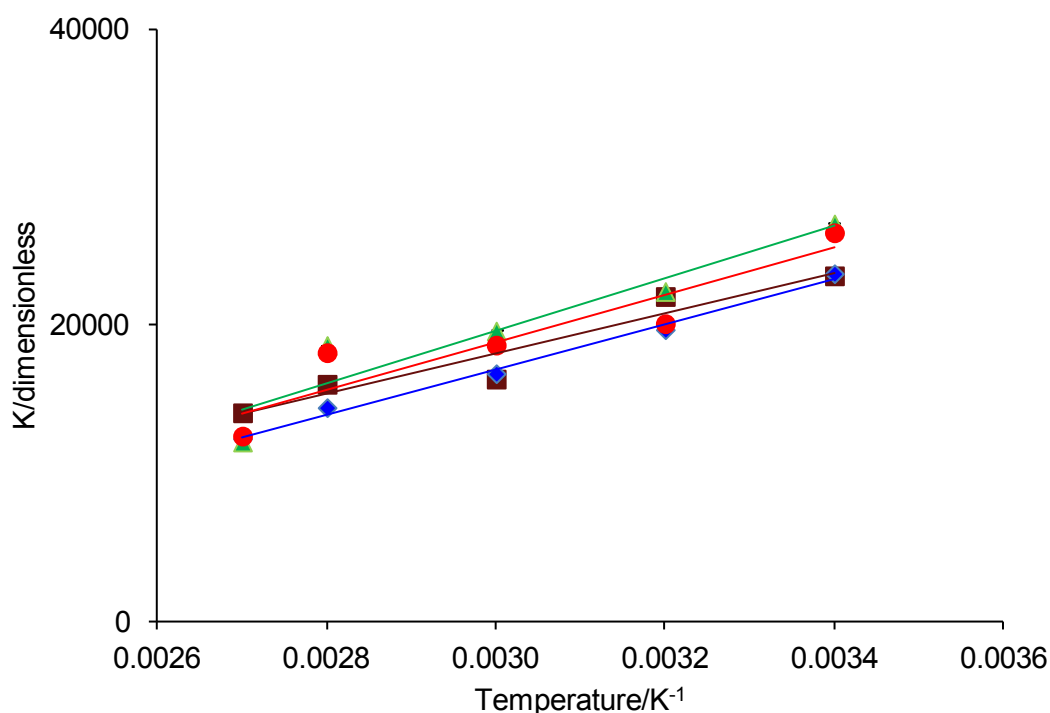


Figure 5.12: Henry's constants at temperatures between 25 – 100 °C showing temperature dependence of Sample 1 (■), Sample 2 (◆), Sample 3 (▲), and Sample 4 (●)

Table 5.7 gives the activation energies for diffusion determined by other techniques to compare with this study. Large variations between the measured values are observed dependant on whether the technique is microscopic or macroscopic in nature (Eic &

Ruthven, 1989; Granato *et al.*, 2010; Sun *et al.*, 1996). The microscopic techniques generally result in high diffusivities and low activation energies for diffusion. Conversely, the macroscopic techniques generally have high activation energies for diffusion and diffusivity values as much as five orders of magnitude lower when compared with the microscopic techniques.

Table 5.7: Overview of diffusivity parameters calculated for different techniques

Gas	Sorbent	$E_A /$ kJ mol^{-1}	Technique	Temp/ K	$D / \text{m}^2 \text{s}^{-1}$ (ads)	Reference
Propane	Cordierite monolith	6.0 ± 2.2	FRT-ZLC	373	2.0×10^{-9}	this study
Propane	Zeolite NaCa-LTA-2	-	PFG-NMR	353	1.5×10^{-11}	(Mehlhorn <i>et al.</i> , 2012)
Propane	Silica Mesopore	-	MD Simulations	300	2.0×10^{-8}	(Krishna & van Baten, 2011)
isobutane	Mesoporous glass	-	MD Simulations	300	1.0×10^{-10}	(Fernandes & Gavalas, 1999)
Propane	Silicalite-1	6.7	FR	333	5.0×10^{-9}	(Van-Den-Begin <i>et al.</i> , 1989)
Propane	Silicalite-1	13.0	ZLC	300	3.5×10^{-11}	(Eic & Ruthven, 1989)
Propane	Silicalite-1	25.6	CPC	500	3.0×10^{-9}	(Hufton & Ruthven, 1993)
Propane	Silicalite-1	8.0	Wicke-Kallenbach	298-334	5.0×10^{-10}	(Sun <i>et al.</i> , 1996)
Propane	ZSM-5	5.0	QENS	300	2.0×10^{-11}	(Jobic <i>et al.</i> , 1992)
Propane	NaX zeolite	7.9	PFG-NMR	307	7.0×10^{-10}	(Schwarz <i>et al.</i> , 1995)
Propane	13X zeolite	7.9	MD simulations	373	2.9×10^{-9}	(Granato <i>et al.</i> , 2010)

It is reassuring to observe that the calculated activation energy for propane diffusion in alumina/CeZrOx (extracted from the Arrhenius plot of diffusivities measured at different temperatures, Figure 5.11) compares well to that predicted by Granato *et al.*, based on theoretical molecular dynamics simulations of propane diffusion in 13X, and pulse field gradient nuclear magnetic resonance (PFG-NMR) data by Schwarz *et al.*, (Granato *et al.*, 2010; Schwarz *et al.*, 1995). The results also compare well to the values

of Sun *et al.*, who employed a Wicke-Kallenbach type method using a zeolite membrane and report diffusivities of propane in silicalite in the temperature range between 30 to 70 °C as $4 - 6 \times 10^{-10} \text{ m}^2/\text{s}$ (Sun *et al.*, 1996).

Brandani *et al.*, observed that propane diffusivity in 13X is much smaller when measured with the ZLC approach as compared to PFG-NMR (Brandani *et al.*, 1995). Banas *et al.*, suggest that this may be due to the PFG-NMR technique returning intra-crystalline diffusivities whereas ZLC experiments result in the observation of combined diffusion and desorption processes (Banas *et al.*, 2005). By observing the dispersion corrected decay curves of the adsorption transient, FRT was able to measure the transport kinetics of the washcoat material without interfering concurrent desorption. This appears to yield satisfactory results as the dispersion corrected adsorption parameters of diffusivity compare particularly well with other macroscopic techniques (Karger & Ruthven, 1992). Another advantage of the technique is that FRT measures the diffusivity into the washcoats of the monoliths at the instance of propane reaching the bed of the material thereby reducing the error margins suffered by other chromatographic techniques in which dispersion through the column affects the accuracy of such results.

5.1.1.2.3. Comparing TAP & FRT Results

Figure 5.13 summarises the variation of the FRT diffusion coefficients with respect to temperature using the first desorption as well as the average value over three desorption cycles for each sample. Slight variations are found when comparing the diffusion coefficients using the desorption data from the 1st desorption and the average of 3 complete cycles. However, all the plots show a similar increasing linear trend for the variation of the diffusivity coefficients with respect to increasing temperature, as expected.

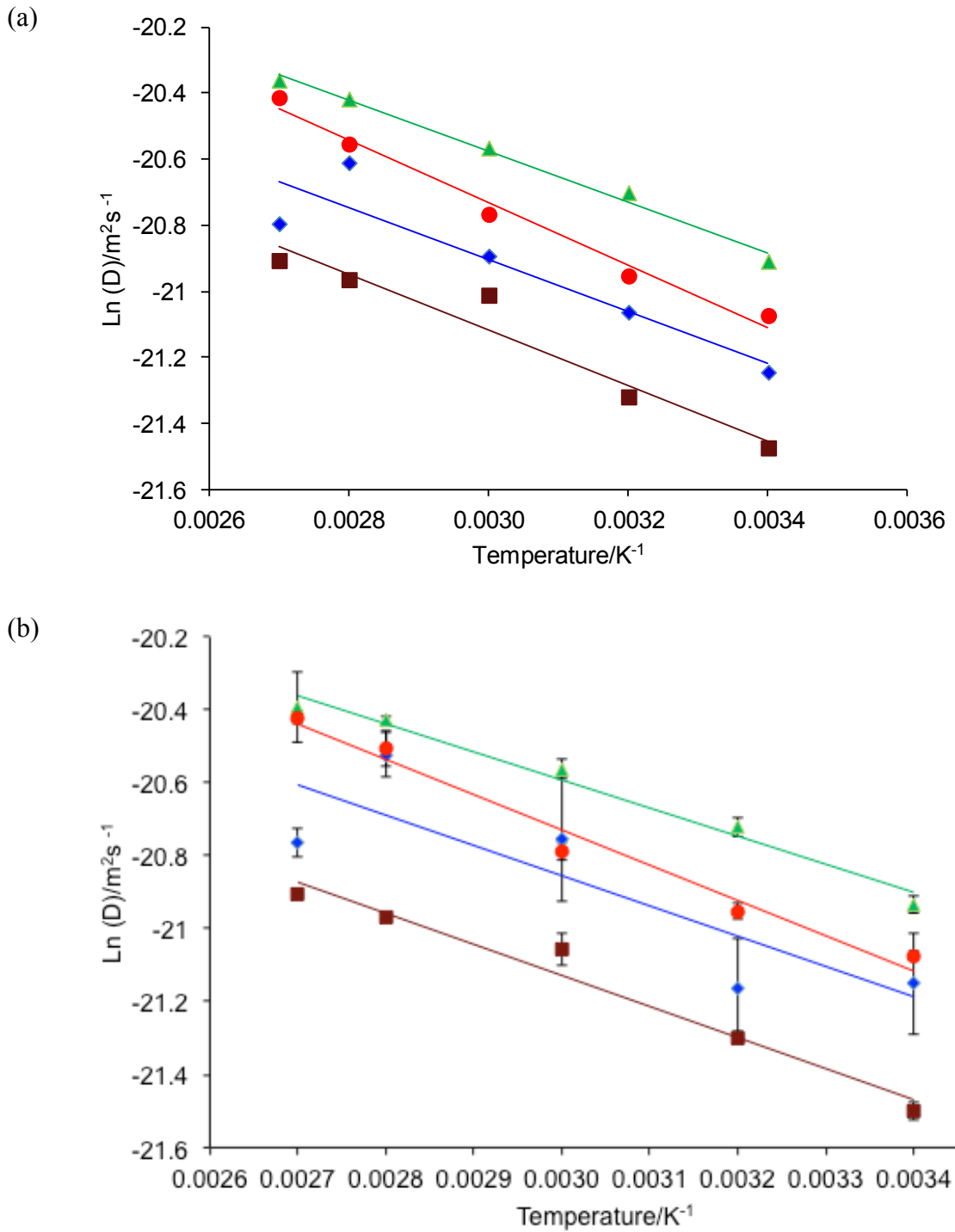


Figure 5.13: FRT Diffusion coefficients at temperatures between 25 – 100 °C for (a) 1st desorption cycle and (b) averaged desorption cycles, showing Sample 1 (■), Sample 2 (◆), Sample 3 (▲), and Sample 4 (●)

The FRT data has been shown to compare well with other reported values for the diffusivity of propane in silicalite (Sun *et al.*, 1996). Therein, a diffusion coefficient between $4 - 6 \times 10^{-10} m^2 s^{-1}$ was determined over the temperature range of 30 – 70 °C which may be compared with values of $4 - 10 \times 10^{-10} m^2 s^{-1}$ between 25 – 80 °C from

the present study. The range of values reported in Figure 5.13 can be attributed to the structural difference within the washcoats of the samples.

A comparison of the diffusion coefficients for all the samples as determined by FRT Figure 5.13 shows a similar trend to that found using the TAP methodology Figure 5.4. However, it is evident that the values differ by approximately an order of magnitude. Table 5.8 compares the diffusion coefficients between both techniques. To evaluate the limits of effective diffusivity in the cordierite samples shown by both techniques, one should consider the sensitivities of the two methodologies. TAP measurements are sensitive to the slowest diffusing species, operating within the Knudsen regime where the translational mobility of individual species is dominant. However, in the FRT-ZLC measurement of diffusivity, Fickian diffusion dominates and the transport diffusion coefficient accounts for the motion of species under the influence of a concentration gradient.

Table 5.8: Diffusivity parameters calculated for TAP and FRT techniques

Sample	Temp/ K	Diffusivity (m^2/s)	
		TAP	FRT
Sample 1	313	2.55×10^{-9}	5.60×10^{-10}
	333	3.86×10^{-9}	7.21×10^{-10}
	353	4.80×10^{-9}	7.82×10^{-10}
Sample 2	313	9.20×10^{-9}	6.40×10^{-10}
	333	2.12×10^{-8}	9.70×10^{-10}
	353	1.60×10^{-8}	1.20×10^{-9}
Sample 3	313	2.28×10^{-8}	1.01×10^{-9}
	333	2.56×10^{-8}	1.22×10^{-9}
	353	3.22×10^{-8}	1.30×10^{-9}
Sample 4	313	2.20×10^{-8}	7.90×10^{-10}
	333	4.25×10^{-8}	9.43×10^{-10}
	353	5.58×10^{-8}	1.20×10^{-9}

The reported activation energies and pre-exponential factors for diffusion were determined from the Arrhenius-plots given in Figure 5.4 and Figure 5.13, in accordance with equation 5.11. In Table 5.9, the activation energies for diffusion and pre-exponential factors determined by both methods are given for all four samples. Table

5.10 gives the activation energies for diffusion determined by other techniques to compare with this study.

Table 5.9: Pre-exponential factors and activation energies of diffusion in Samples 1-4 determined using the TAP and FRT methodologies

Sample	Pre-exponential factor/ m^2s^{-1}		Activation Energy/ $kJ mol^{-1}$	
	TAP	FRT	TAP	FRT
Sample 1	1.7×10^{-7}	8.3×10^{-9}	12.0 ± 0.3	7.0 ± 0.4
Sample 2	6.5×10^{-7}	9.5×10^{-9}	11.0 ± 0.4	7.0 ± 1.6
Sample 3	6.6×10^{-6}	1.0×10^{-8}	14.0 ± 0.4	6.0 ± 0.8
Sample 4	2.5×10^{-5}	1.7×10^{-8}	16.0 ± 0.5	8.0 ± 0.1

Table 5.10: Overview of activation energies for diffusion calculated using different techniques

Gas	Sorbent	$E_A / kJ mol^{-1}$	Technique	Reference
Propane	Cordierite monolith	12–16	TAP	this study
		6–8	FRT-ZLC	this study
	Silicalite-1	7.2	Multitrack	(Nijhuis, van den Broeke, Linders, Makkee, <i>et al.</i> , 1999)
		6.7	FR	(Van-Den-Begin <i>et al.</i> , 1989)
		13.0	ZLC	(Eic & Ruthven, 1989)
		25.6	CPC	(Hufton & Ruthven, 1993)
		8.0	Wicke-Kallenbach	(Sun <i>et al.</i> , 1996)
		5.0	QENS ^a	(Jobic <i>et al.</i> , 1992)
		6.0	PFG-NMR ^a	(Heink <i>et al.</i> , 1992)
		7.9	MD simulations	(Granato <i>et al.</i> , 2010)

^aMicroscopic methods

The variation between the methods is observed and has been highlighted previously to be dependent on whether the technique interrogates the sample on a microscopic or macroscopic level. These changes may be associated with the macroscopic techniques observing other effects such as desorption during measurements as well as the actual diffusion of the molecules in the micropores. These additional effects have been shown to strongly influence the diffusivities observed (Cavalcante *et al.*, 1997; Crank, 1979; Eic & Ruthven, 1988, 1989; Gobin, 2006; Guimarães *et al.*, 2010; Gunadi & Brandani, 2006; Heink *et al.*, 1992; Hufton & Ruthven, 1993; Jobic *et al.*, 1992; Karge *et al.*, 2008; Loos, 2000; Nijhuis *et al.*, 1999; Richardson *et al.*, 2008; Ruthven & Brandani, 2000; Silva, 1996; Sun *et al.*, 1996; Van-Den-Begin *et al.*, 1989).

The TAP reactor successfully determined the effective porous diffusivities by utilising residence times in the pores for transport calculations, using approximate values of pore lengths for the four samples, while the FRT technique was successfully adapted for the *in situ* measurement of zero length column diffusion within the cordierite washcoats. As such, the lower and upper limit of effective diffusivity for the samples was calculated by way of the TAP and FRT methodologies respectively.

5.2. Summary

The modification of the FRT apparatus to measure the diffusivity parameters of propane in the washcoats of cordierite monoliths has been accomplished (Sasegbon & Hellgardt, 2012). A novel approach of analysing the flux response profiles and making use of the Long Time Zero Length Column analytical approach yielded reliable results when compared with the literature. The FRT system was shown to enable rapid and accurate measurements of the key parameters present in the diffusion of propane in alumina/CeZrO_x washcoats under carefully controlled conditions. A collaborative project between the department of Chemical Engineering and Chemical Technology, Imperial College London and the School of Chemistry and Chemical Engineering, Queen's University Belfast was carried out to compare and contrast the diffusivity coefficients of the cordierite wash coats using FRT and TAP respectively (Maguire *et al.*, 2013). Both techniques were successful at determining the effects of the different wash coats on the diffusion coefficients as well as being able to establish the upper and lower limits of effective diffusion based on the modes of operation of each technique.

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Chapter 6

FRT

Ammonia Sorption

One of the main properties that characterise the catalytic activity of zeolites is their variable acidity. The total acidity of a zeolite depends on the amount, strength, nature, and accessibility of the acid sites. The zeolite surface may exhibit protonic (Brønsted) and aprotic (Lewis) acid sites.

Brønsted-acid sites develop as a result of the isomorphous substitution of Si^{4+} by a metal trivalent cation, such as Al^{3+} , whereby the negative charge created in the lattice is compensated for by a proton. The proton attaches to the oxygen atom connected to the neighbouring silicon and aluminium atoms, resulting in a bridged hydroxyl group that is responsible for the Brønsted acidity. Brønsted-acid sites can be generated through the process of ion-exchanging the zeolite with an acid solution or via thermal decomposition of nominal ammonium ions as is the case for the zeolites investigated in this study. Lewis-acid sites display the ability of accepting electron pairs, thus can be surface cations or charge-compensating cations. Lewis-acid sites are normally formed as a result of the dehydroxylation of Brønsted-acid sites by thermal treatment or the dealumination of the zeolite framework during chemical or thermal treatments (Brodu *et al.*, 2013; Chen *et al.*, 1996; Gounder *et al.*, 2012; Kim *et al.*, 2012).

The schematic shown in Figure 6.1 depicts the Brønsted-acid hydroxyl and the subsequent Lewis-acid site formed through Brønsted-acid dehydroxylation.

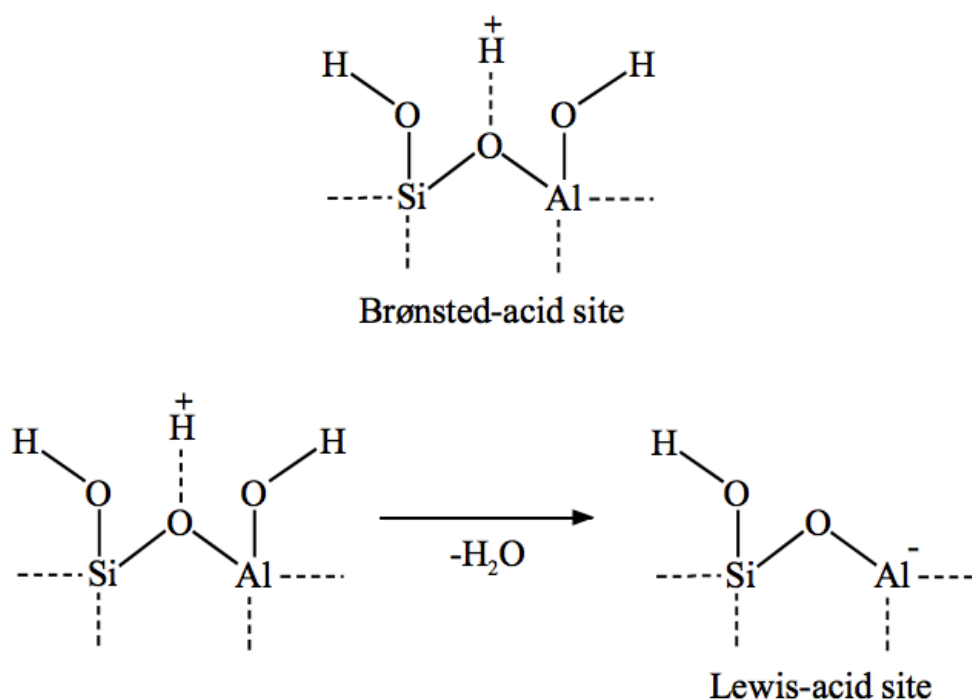


Figure 6.1: Schematic of zeolitic Brønsted-acid and Lewis-acid sites formed through dehydroxylation (Barzetti *et al.*, 1996)

The characterisation of these acid sites with basic molecular probes has been well documented and can be found extensively in the literature. Of all the bases analysed, the two most commonly preferred probes at a molecular level are ammonia and pyridine (Damjanović & Auroux, 2010; Derouane *et al.*, 2013; Fierro, 2005). Both bases form a chemical bond with the protons of the hydroxyl groups, thus supplying useful information on the concentration of acid sites of zeolites. Ammonia was selected as the basic probe molecule for FRT experiments due to the practical advantages it possesses over pyridine, namely; possessing a smaller kinetic diameter allowing it to easily reach acid sites situated in smaller pores, and being less toxic and easier to use (Barzetti *et al.*, 1996; Bradley *et al.*, 2010; Li & Wu, 2003).

6.1. Results and Discussion

6.1.1. Material Characterisation

6.1.1.1. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the calcined zeolite samples was carried out to determine the desorption amount and removal rate of water and to confirm that the tetrapropylammonium structure-directing agent (template) had been removed, leaving the zeolite channels free for adsorption. The experiments were carried out in an inert carrier flow of nitrogen gas at 60 *ml/min* in the temperature range of 25 – 400 °C, with the heating rate set at 10 °C/*min*.

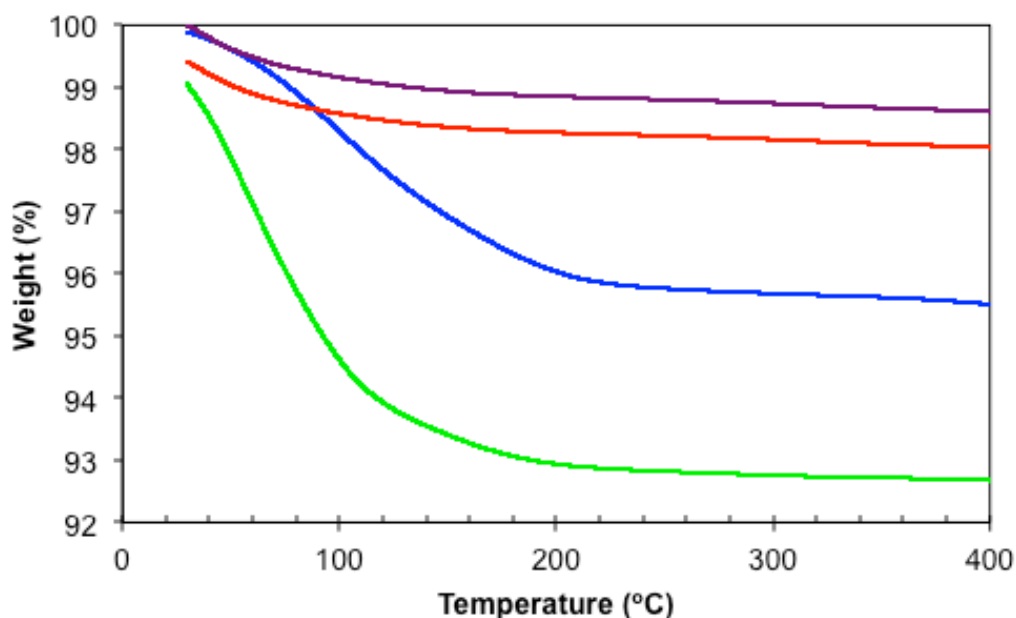


Figure 6.2: TGA curve of zeolites F.CP914C (green), ZSM 55 (blue), F.CP914 (red), and ZSM 280 (purple)

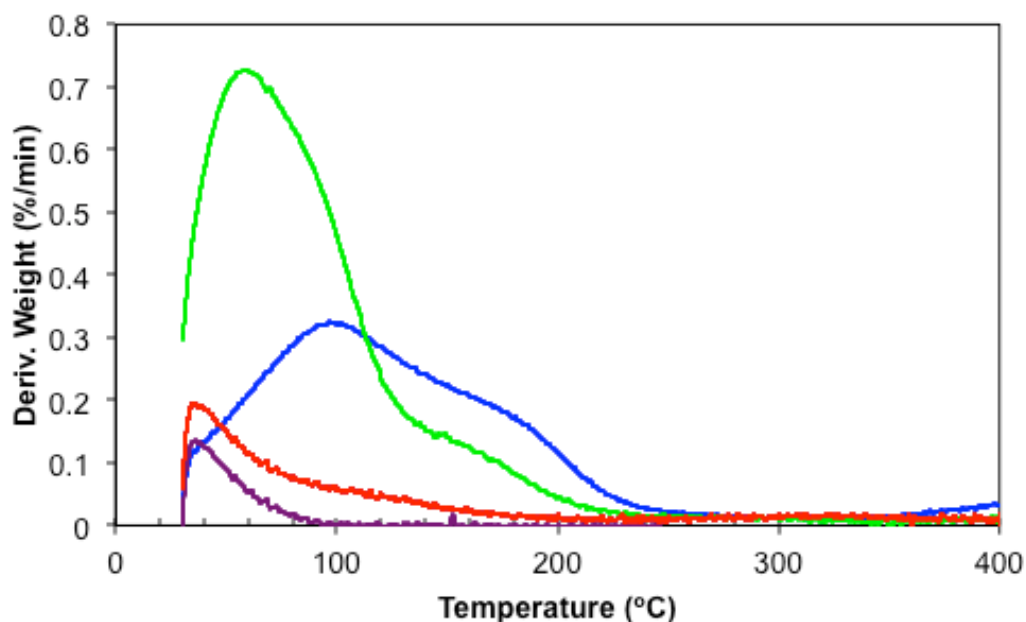


Figure 6.3: DTA curve of zeolites F.CP914C (green), ZSM 55 (blue), F.CP914 (red), and ZSM 280 (purple)

The TGA and DTA curves of the calcined zeolite samples are shown in Figure 6.2 and Figure 6.3. The broad region in the thermogram up to $\sim 200^{\circ}\text{C}$ represents the weight loss through the desorption of water. This correlates well with the temperature value found in the literature for TGA experiments of preheated zeolite samples where TGA experiments coupled with an MS clearly showed the evaporation peak with its minimum at 200°C being associated with water desorption (Cheng *et al.*, 2005; Hemalatha *et al.*, 2013; Humplik, 2010). The water loss is shown to be inversely proportional with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, decreasing as the ratio increases. This is an expected result as the acidity of the zeolite samples decrease with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, thereby increasing their hydrophobicity as the acid sites decrease in number. All of the zeolite samples shown in Figure 6.2 and Figure 6.3 reach their dry weight value at $\sim 200^{\circ}\text{C}$, indicating that the calcination procedure used in preparing the zeolites for FRT experiments was sufficient.

6.1.1.2. Solid-State Nuclear Magnetic Resonance (NMR)

The framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the extent of the dealumination for each of the zeolite samples were determined by means of solid-state NMR spectroscopy (Cryomagnetic, Spectr spin, Bruker). By applying the Magic Angle Spinning (MAS) technique, high resolution NMR spectra of the zeolite samples were obtained (van

Bekkum *et al.*, 2001). The ^{29}Si MAS NMR spectra for the zeolite samples are shown in Figure 6.4 – Figure 6.7. Spectral analysis was carried out using the NMR program software, dmfit09, in order to establish the chemical shift values and peak intensities.

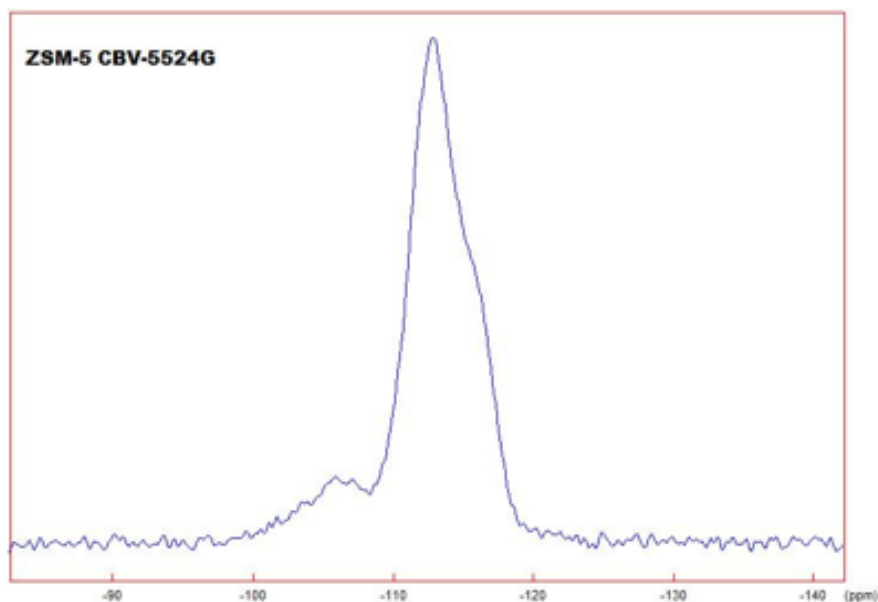


Figure 6.4: ^{29}Si MAS NMR Spectra profiling zeolite sample ZSM 55

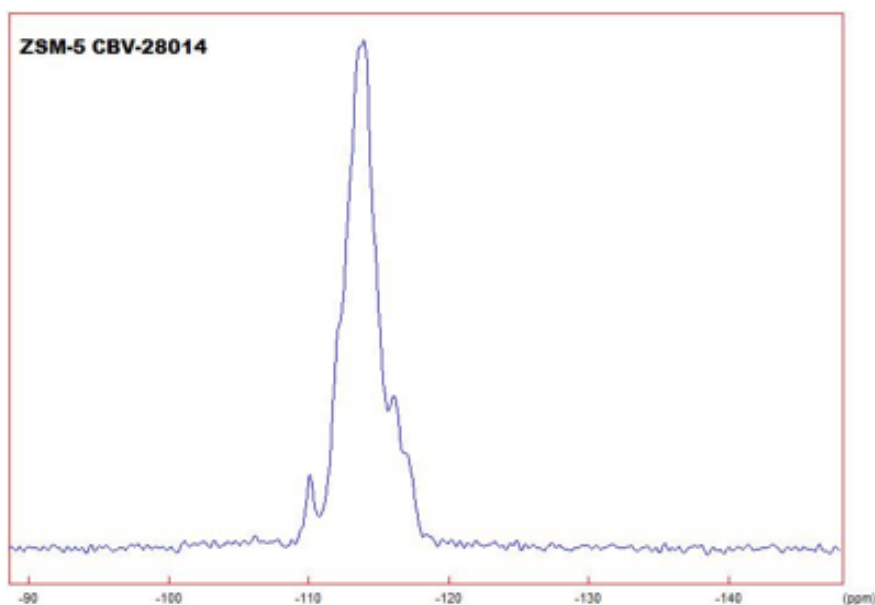


Figure 6.5: ^{29}Si MAS NMR Spectra profiling zeolite sample ZSM 280

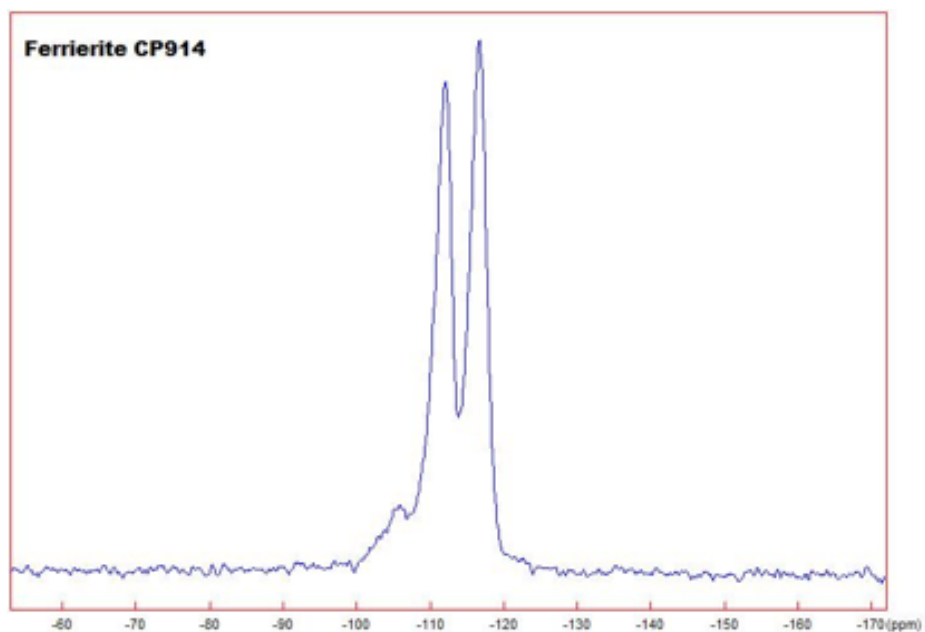


Figure 6.6: ^{29}Si MAS NMR Spectra profiling zeolite sample F.CP914

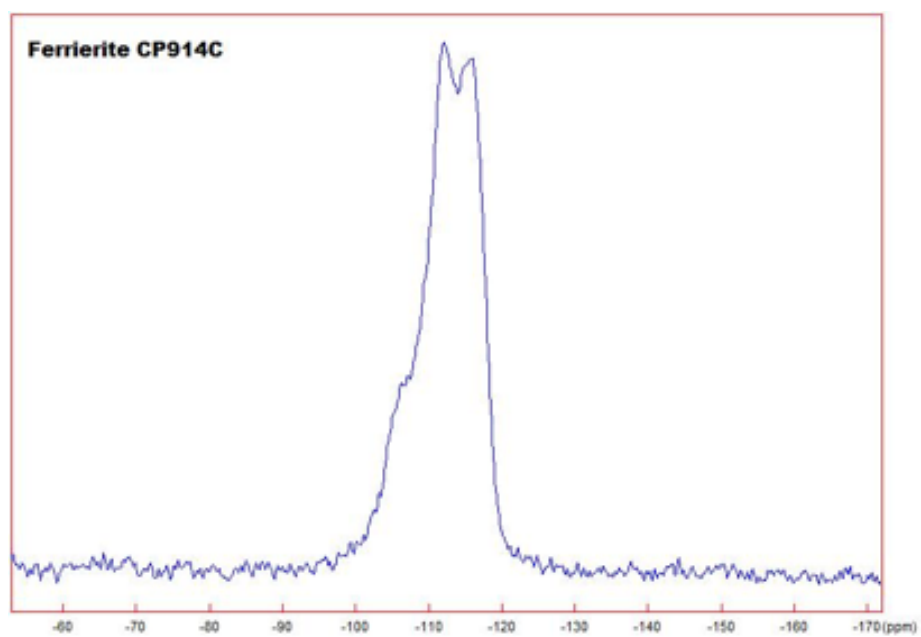


Figure 6.7: ^{29}Si MAS NMR Spectra profiling zeolite sample F.CP914C

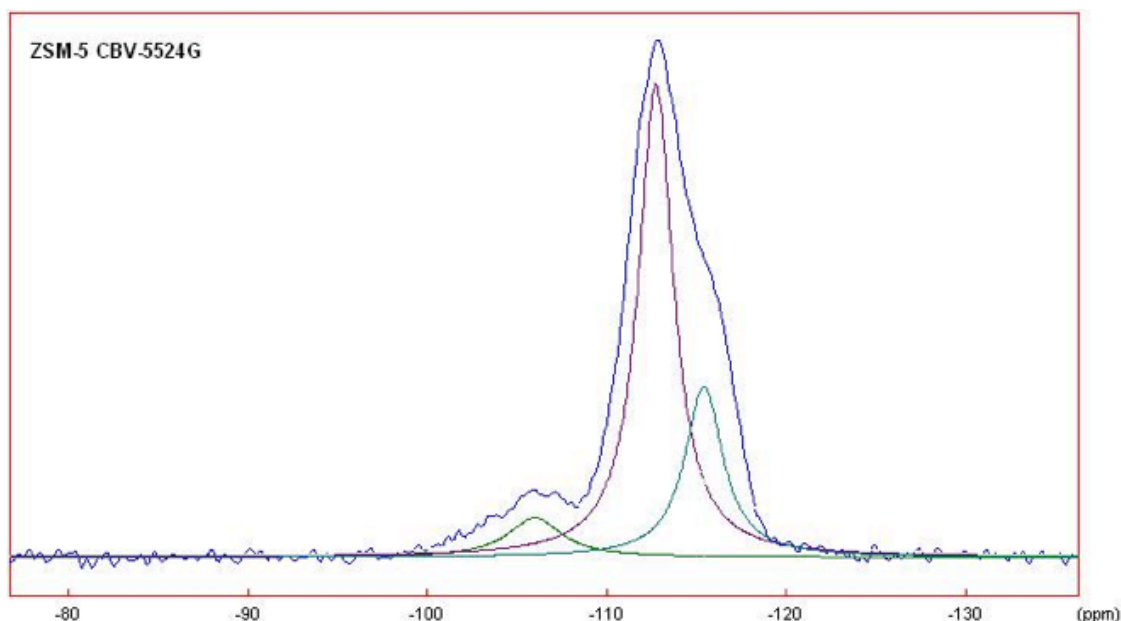


Figure 6.8: ^{29}Si MAS NMR spectra of the ZSM 55 sample with (lower) deconvolution

Table 6.1: Chemical shift positions for ZSM 55 with corresponding peak intensities

Line	Chemical shift (ppm)	% integral (I)
0 -	-105.97	8.45
1 -	-112.72	65.69
2 -	-115.40	25.85

Figure 6.8 shows an example of the deconvolution of the MAS ^{29}Si NMR of ZSM 55. Table 6.1 shows the relative chemical shift values and intensities of the analysed peaks. In this analysis, the MAS ^{29}Si spectrum provided three key pieces of information used in determining the framework of the zeolite samples. Whereas most silicates contain four-fold coordinated silicon, i.e. SiO_4 tetrahedra as their basic unit, a few silicate structures may contain six-fold coordination silicon, i.e. SiO_6 octahedra (Engelhardt & Michel, 1987; Engelhardt, 2007). Using ^{29}Si NMR, SiO_4 and SiO_6 units are unambiguously distinguished by means of their large chemical shift difference: SiO_4 units range between chemical shift values of -60 to -120 ppm while SiO_6 units lie between -179.9 and -191.3 ppm. By observing Figure 6.4 – Figure 6.7, it is possible to distinguish the zeolite samples used in this analysis as containing SiO_4 tetrahedra.

Secondly, the framework of the zeolites were further determined by analysing their individual chemical shifts. Figure 6.9 and Figure 6.10 show the ranges of ^{29}Si chemical

shifts for $Q_4(\text{mAl})$ units and a ^{29}Si NMR spectrum of a microcrystalline zeolite showing the whole set of $Q_4(\text{mAl})$ peaks respectively.

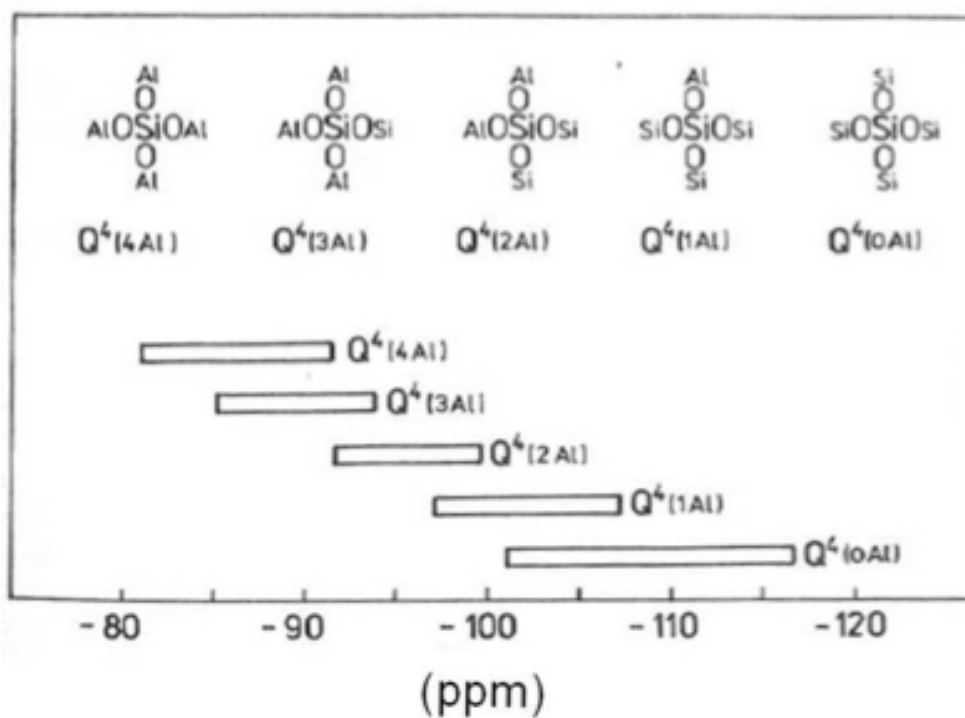


Figure 6.9: ^{29}Si chemical shift range of $Q_4(\text{mAl})$ units present in aluminosilicates (Engelhardt & Michel, 1987)

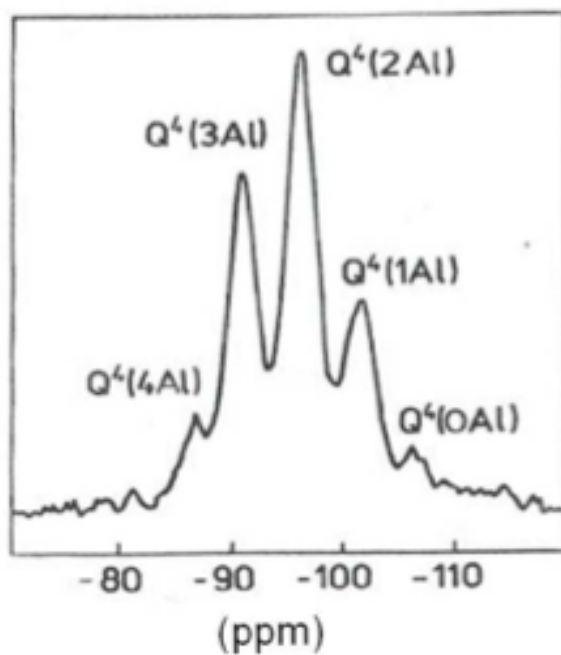


Figure 6.10: ^{29}Si NMR spectrum of microcrystalline zeolite with the whole set of $Q_4(\text{mAl})$ peaks present (Engelhardt & Michel, 1987)

The two features used in determining the shift of a SiO_4 group are the degree of SiO_4 polymerization, that is, the number of SiO- bridges formed by the given tetrahedron, and the degree of tetrahedral Al substitution i.e. the number of Si or Al atoms in the second coordination sphere of the central silicon atom. By referring to the literature and comparing the chemical shift values of the zeolite samples, it was obvious that present within the zeolites were the distinctive $\text{Q}^4(0\text{Al})$ and $\text{Q}^4(1\text{Al})$, present between -100 to -116 ppm.

The final piece of information obtainable from the analysis of the MAS ^{29}Si NMR spectra is able to quantify the distribution of the aluminosilicates framework within the zeolites. According to Löwenstein's rule, the Si atoms can be surrounded by up to four Al atoms. From this, it is possible to calculate the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the framework directly from the MAS ^{29}Si NMR spectra using the relative intensities of the $\text{Q}^4(\text{mAl})$ peaks (van Bekkum *et al.*, 2001).

$$\text{Si}/\text{Al} = \frac{\sum_{m=0}^n I_{n,m}}{\sum_{m=0}^n (m/n) I_{n,m}} \quad 6.1$$

Equation 6.1 is used to work out the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, where, n is the Q unit, m is the number of attached Al atoms and I is the relative peak shift intensity (Engelhardt & Michel, 1987). This simplifies out to become,

$$\text{Si}/\text{Al} = \frac{\sum_{m=0}^4 I_{4,m}}{\sum_{m=0}^4 0.25 I_{4,m}} \quad 6.2$$

Table 6.2 shows the nominal $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the sample zeolites compared to the ratios obtained through solid-NMR analysis.

Table 6.2: Comparison of the MAS ^{29}Si NMR evaluated $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios with nominal values

Zeolite Material	Nominal $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	Experimental $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio
F.CP914C	20	21
ZSM 55	50	47
F.CP914	55	53
ZSM 280	280	NA

As can be seen in Table 6.2, the evaluated $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are highly correlated with the nominal values of the zeolite samples. Difficulties arose in determining the framework of zeolite sample ZSM 280. Reports in the literature have shown that the framework of zeolite samples with very low Al content ($\text{Si}/\text{Al} > 50$) are in many circumstances impossible to determine using MAS ^{29}Si NMR alone (Engelhardt & Michel, 1987). This is because the intensities of the $\text{Q}^n(\text{mAl})$ peaks with $m \neq 0$ would be too small or not measurable at all. Such was the case for the zeolite sample ZSM 280 as can be seen in Figure 6.5. By referring to Figure 6.9, it can be observed that the chemical shift range of the $\text{Q}^4(1\text{Al})$ unit ends at approximately -107 ppm . The ^{29}Si spectrum for ZSM 280 shows peak intensities ranging from -110 to -117 ppm , well outside the range of the $\text{Q}^4(1\text{Al})$ unit. Thus, the theory postulated by Engelhardt is proved to be correct. Although the ^{29}Si NMR spectrum is unable in this case to provide the details required to calculate the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, it is safe to assume that the spectrum shows no extra framework aluminium (EFAL) present in the sample.

6.1.1.3. X-ray Fluorescence (XRF) & X-ray Diffraction (XRD)

XRF and XRD analysis were used to determine the element concentration and the atom arrangement of the zeolite samples respectively. Application of these techniques provided another measure of screening the zeolites for EFAL. Shown in Table 6.3 are the constituent XRF concentrations expressed in weight %. It is reassuring to observe negligible concentrations of the impurities Na_2O and K_2O .

Table 6.3: XRF element analysis

Zeolite Material	SiO_2	Al_2O_3	Na_2O	K_2O
F.CP914C	56.831	1.664	0.040	0.012
ZSM 55	56.514	0.352	0.042	0.012
F.CP914	52.558	4.298	0.061	0.014
ZSM 280	63.183	1.983	0.058	0.013

Verification of the zeolite structures shown in Figure 6.11 – Figure 6.14 was completed by comparing the XRD results to reference diffraction patterns found in the literature (Treacy & Higgins, 2007). The zeolite samples analysed exhibited the characteristic diffraction patterns of ferrierite for Figure 6.11 and Figure 6.12, and ZSM-5 for Figure 6.13 and Figure 6.14 (Hemalatha *et al.*, 2012).

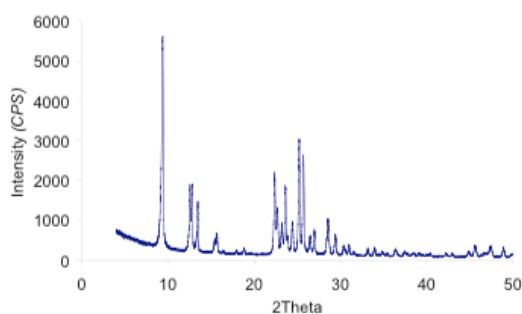


Figure 6.11: XRD pattern for F.CP914C

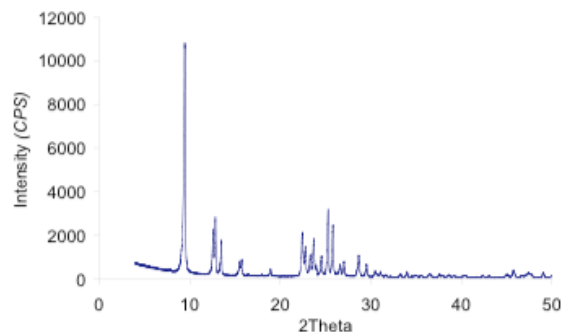


Figure 6.12: XRD pattern for F.CP914

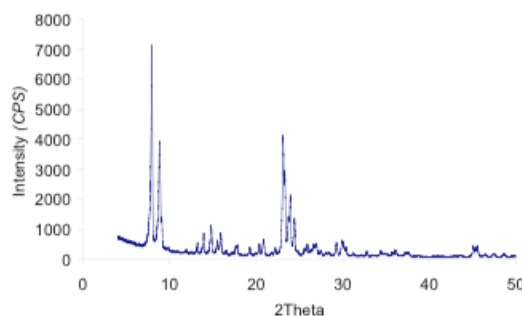


Figure 6.13: XRD pattern for ZSM 55

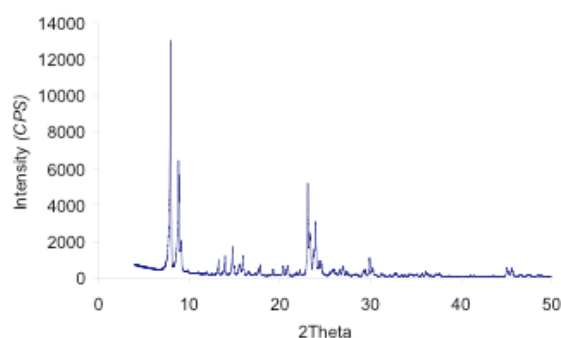


Figure 6.14: XRD pattern for ZSM 280

6.1.1.4. Temperature Programmed Desorption (TPD)

Figure 6.16 shows the NH_3 -TPD profiles of the zeolite samples. All of the samples exhibit two well resolved desorption peaks centred at $\sim 200^\circ\text{C}$ and at $\sim 460^\circ\text{C}$. The low temperature peaks appearing at about 200°C correspond to acid sites of low strength, while the high temperature peaks at 460°C are attributed to strong acid sites. This is in good agreement with published literature data (Dondur *et al.*, 2005; Rodríguez-González *et al.*, 2007, 2008). The *l*-peak is characteristic of evolution from the weaker sorption sites but remains ambiguous in the nature of the acid site in question. Several accounts in the literature have postulated the presence of Lewis acid sites in which Al–O bonds have been transformed due to hydrolysis from sample calcination or from EFAL (Auroux, 1997; Niwa & Katada, 2013; Wei *et al.*, 2013; Woolery & Kuehl, 1997). Another proposed option is attributed to weakly bound NH_3 by hydrogen bonding to NH_4^+ cations on a given strong acid site. This is another association that has been inferred progressively in the literature (Bonelli *et al.*, 2010; Kouva *et al.*, 2013; Lónyi & Valyon, 2001; Martins *et al.*, 2008; Rodríguez-González *et al.*, 2007, 2008; Zecchina *et al.*, 1997). The *h*-peak is relative to strong Brønsted-acid sites and is

correlated to the density of aluminium ions in the zeolite framework. The NH_3 -TPD desorption process is schematically illustrated in Figure 6.15

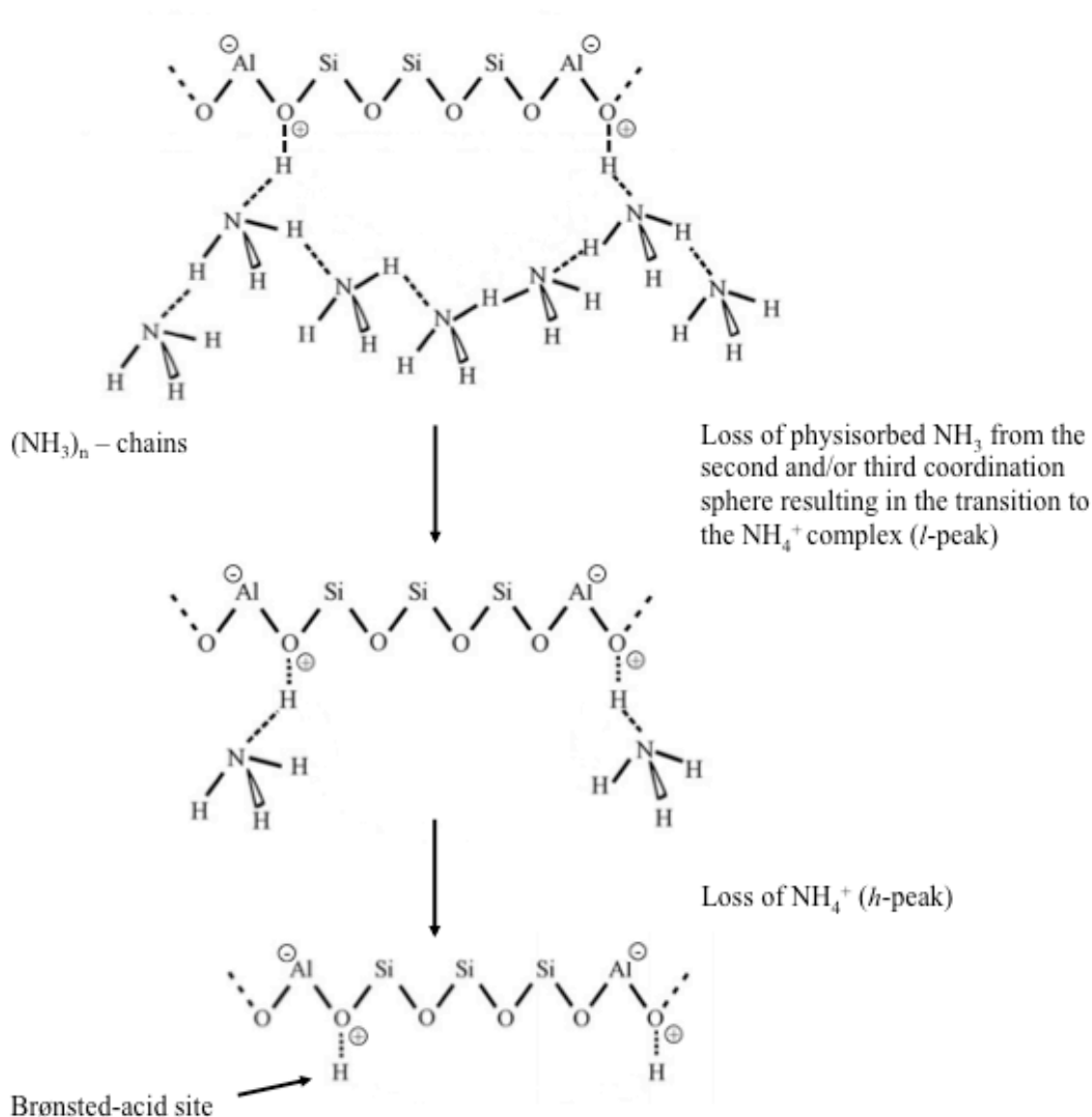


Figure 6.15: Schematic illustration of the characteristic features of NH_3 -TPD measurements

As ammonia is a very basic molecule capable of titrating weak acid sites that may not contribute to the activity of the zeolites, it is useful to be able to distinguish between these weak acid sites, the weakly bound ammonia to the strongly polar adsorbed ammonia, and the strongly adsorbed acid sites.

As shown in Figure 6.16, the peak intensity of the *h*-peak increased as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolites decreased. This is attributed to the increase in the aluminium content present within the framework. Table 6.4 summarises the quantitative data

obtained by ammonia desorption. It was possible to calculate these quantities by decoupling the peaks and integrating the areas underneath the desorption curves. By determining the amount of NH_3 strongly interacting with the Brønsted-acid sites as determined by the h -peak measurements, it was possible to distinguish the nature of the sites in a broad sense. These results are presented further on in Chapter 6.1.2.2.

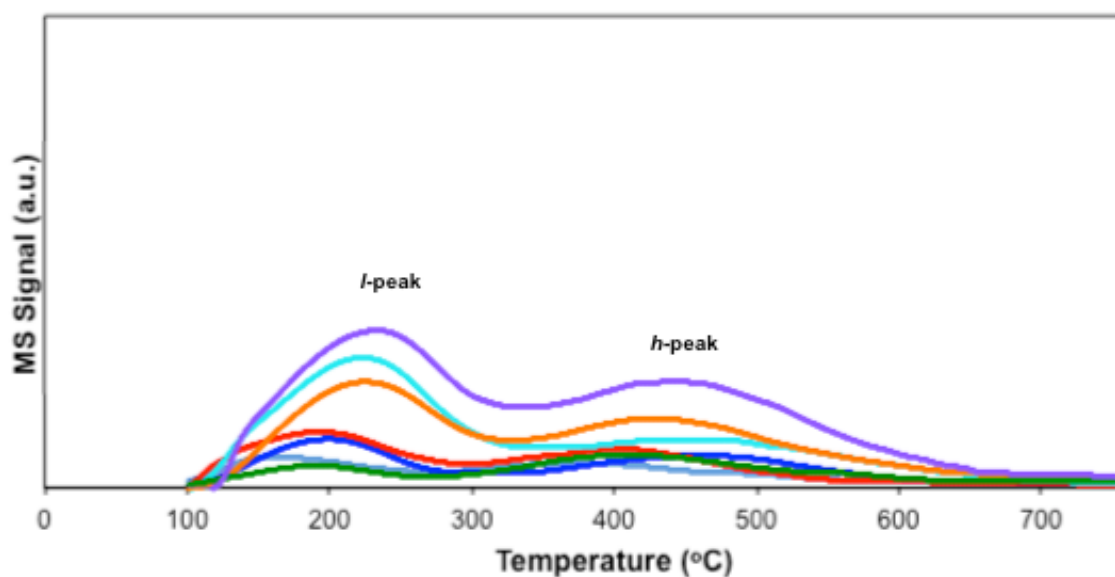


Figure 6.16: NH_3 -TPD profiles observed for zeolite samples F.CP914C (✦), ZBV 23 (●), ZBV 30 (✕), ZSM 55 (■), F.CP914 (◆), ZBV 80 (▲), ZSM 280 (◇)

Table 6.4: Quantitative results from NH₃-TPD analysis

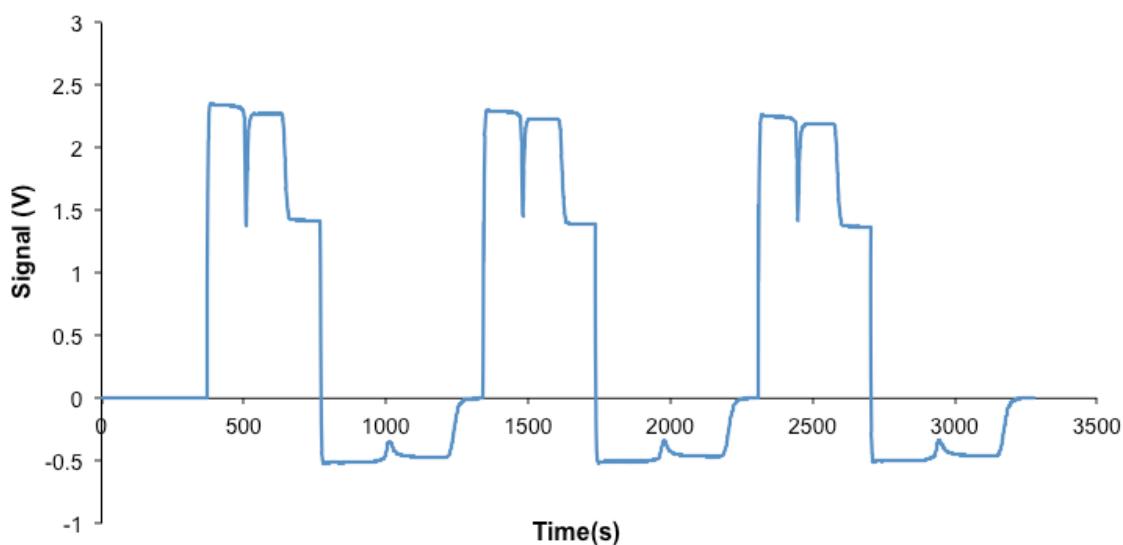
Zeolite Material	<i>l</i> -peak (mol/kg)	<i>h</i> -peak (mol/kg)	Total (mol/kg)
F.CP914C	0.886	1.407	2.293
ZBV 23	0.610	1.110	1.720
ZBV 30	0.638	0.785	1.423
ZSM 55	0.349	0.569	0.918
F.CP914	0.311	0.508	0.819
ZBV 80	0.134	0.213	0.347
ZSM 280	0.148	0.166	0.314

6.1.2. FRT Ammonia Sorption Results

Flux Response Technology has been used to analyse the sorption behaviour of ammonia on zeolites and also as a method of investigating and deriving the total acidity of zeolites when operated in conjunction with TPD. This way, the density of active acid sites (amount of sites per gram of zeolite per unit surface area) and their distribution (density of sites on specific site families) could be characterised.

6.1.2.1. FRT Profiles

Shown in Figure 6.17 is a successful FRT profile generated for F.CP914C for the first experiment carried out at 100 °C. The separation between the sorption and viscosity peaks affirms that the experimental conditions are adequate for the present analysis.

**Figure 6.17: Dynamic cycle set for F.CP914C at 100 °C**

Integrating the areas underneath the sorption peaks provided a measure of the acid site densities. As a consequence of this, it was important to attain a steady baseline prior to and after the sorption peaks had been established. Preliminary experimentation had highlighted several causes of unsteady baselines, namely; improper zeolite packing, loosely tightened and over tightened fittings, over saturation of the moisture trap for the probe gas, and temperature effects brought about by improper insulation. Modifications to the FRT system were carried out to account for these instabilities and minimise the instances where small imbalances were recorded. All FRT cycles for the zeolites examined can be found in Appendix C.

When measuring the acid site density, it was decided to make use of the adsorption peak from the FRT profiles. This was due to there being a lower *uncertainty* when extrapolating the data from this peak. Both the adsorption and desorption peak can be used to quantify the acid site density but it must be noted that the term *uncertainty* pertains to the time limit used to determine the area underneath the respective peaks. A high degree of uncertainty exists when the integration time limit cuts short the baseline of the peak, thereby affecting the measurement of the area under the peak and *vice versa*. Because the desorption peaks exhibit a prolonged approach to the baseline, it was decided to make use of the adsorption peaks to measure the acid site density.

6.1.2.2. Total Acidity

Both the adsorption and desorption peaks were used to quantify the acid site densities. However, it must be noted that a degree of *uncertainty* exists when analysing the desorption peaks. This *uncertainty* pertains to the time limit used to determine the area underneath the respective peaks. A higher degree of uncertainty exists when the integration time limit cuts short the baseline of the peak, thereby affecting the measurement of the area under the peak and *vice versa*. Because the desorption peaks exhibited a prolonged approach to the baseline when compared to their adsorption counterparts, a higher degree of uncertainty existed when analysing these peaks.

Figure 6.18 and Figure 6.19 illustrate the results obtained from single cycle analysis where the sorption from the first dynamic cycle is considered, and average cycle analysis, which considers the sorption values for subsequent cycles. The plots show an

inverse relationship between the number of acid sites and temperature, an expected result when considering the Langmuir isotherm. By observing the general expressions for the rate of adsorption and desorption, the reasoning becomes much clearer.

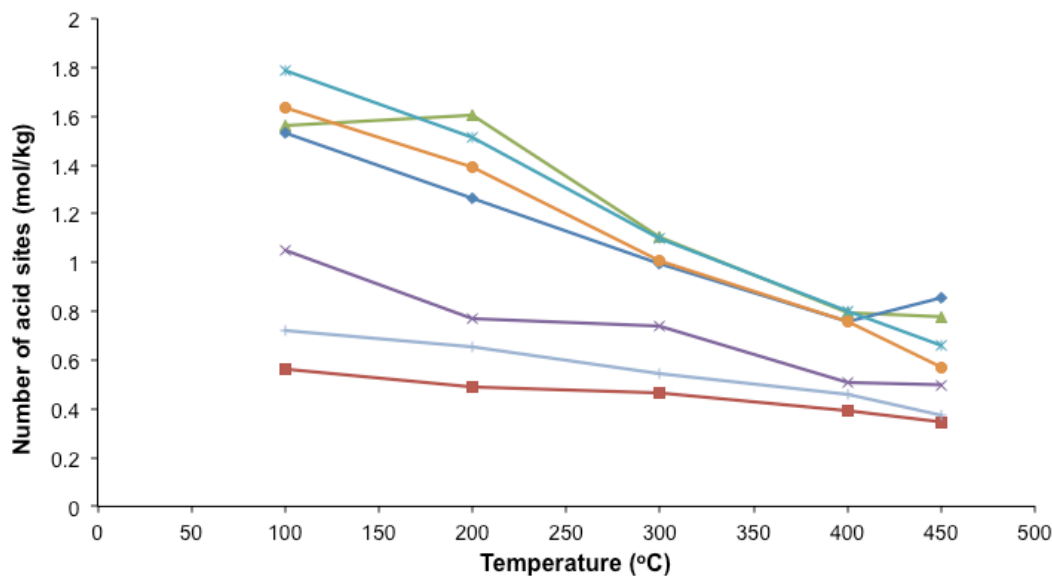


Figure 6.18: FRT results for single cycle analysis between 100 – 450 °C for F.CP914C ($\blacktriangle$), ZBV 23 ($\ast$), ZBV 30 ($\circ$), ZSM 55 ($\diamond$), F.CP914 ($\times$), ZBV 80 ($+$), and ZSM 280 ($\blacksquare$) using adsorption data

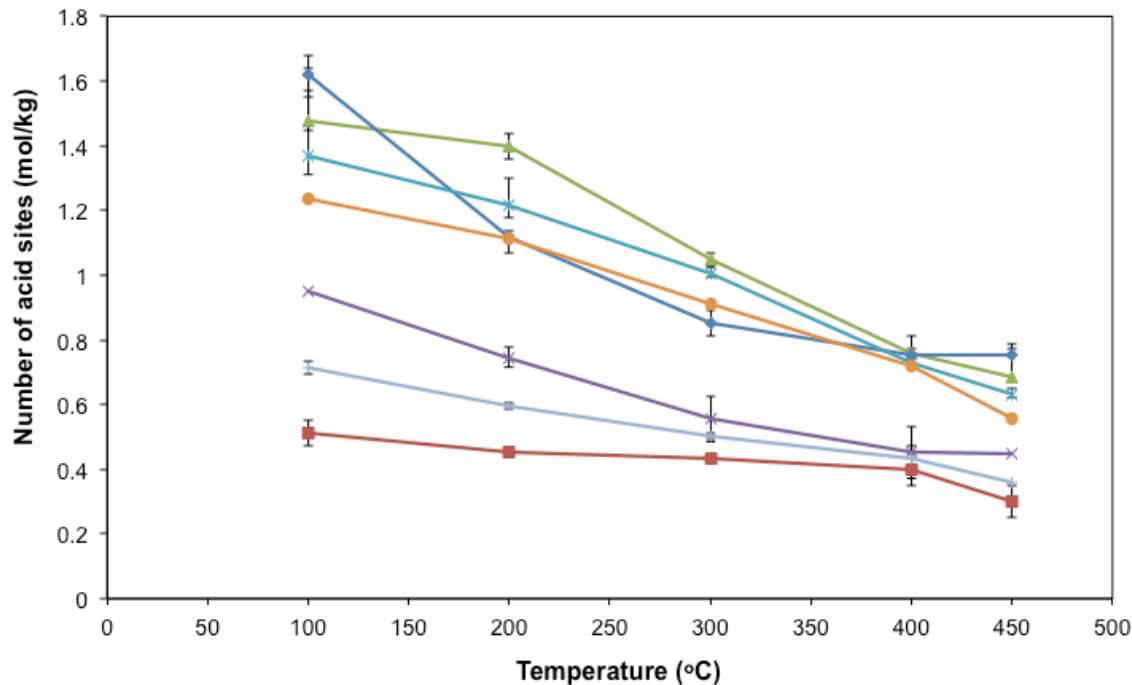


Figure 6.19: FRT results for average cycle analysis between 100 – 450 °C for F.CP914C ($\blacktriangle$), ZBV 23 ($\ast$), ZBV 30 ($\circ$), ZSM 55 ($\diamond$), F.CP914 ($\times$), ZBV 80 ($+$), and ZSM 280 ($\blacksquare$) using adsorption data

$$r_A = \alpha \frac{P}{(2\pi mkT)^{1/2}} (1 - \theta) \quad 6.3$$

The rate of adsorption per unit surface area is displayed in equation 6.3 where α is the sticking coefficient, P is the gas pressure, m is the molecular mass, k is the Boltzmann constant, T is the temperature, and θ is the fractional coverage. Similarly, equation 6.4 describes the rate of desorption per unit surface area where β is the adsorption rate constant, E_d is the activation energy for desorption that equals Q , the heat of adsorption for physically adsorbed species, and R , the molar gas constant.

$$r_D = \beta \theta e^{-E_d/RT} = \beta \theta e^{-Q/RT} \quad 6.4$$

Equation 6.3 describes how the rate of adsorption decreases with a rise in temperature while the converse is true for the rate of desorption as shown in equation 6.4. This trend is well documented in the literature and the results shown in Figure 6.18 and Figure 6.19 go on further to characterise and explain the relationship between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the acid site densities. The total number of acid sites is shown to decrease with an increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio where,

$$\text{F.CP914C} > \text{ZBV 23} > \text{ZBV 30} > \text{ZSM 55} > \text{F.CP914} > \text{ZBV 80} > \text{ZSM 280}$$

This observation is another that is expected as the acid site density of the zeolite samples depend on the availability of unoccupied sites, sites that become more prevalent as the aluminium content within the zeolite framework increases (Contescu & Schwarz, 1999).

Another key observation from Figure 6.18 and Figure 6.19 is the levelling off of the acid site curves over 300 °C. These phenomena may be attributed to the dehydroxylation of the hydroxyl groups within the zeolite to form extra framework species in the form of Lewis acid sites. Thus, the emergence of the trend towards steady state values as shown from 300 °C and above could be argued as being the total number of Lewis acid sites present in the zeolite samples. Research studies found in the literature arrived at this conclusion by comparing the non-framework aluminium within a zeolite sample before and after calcinations at elevated temperatures (Chen, 1996;

Chen *et al.*, 1996). Results here were conclusive in showing that there was an increase in the non-framework aluminium due to dehydroxylation during calcination. Such effects would change the distribution of framework aluminium atoms within the zeolite, thereby affecting the acid strength of the hydroxyl groups. Further studies complemented this theory by reporting on the formation of Lewis acid sites in zeolites caused by steaming, which created lattice defects and extra framework aluminium clusters (Huang *et al.*, 2008). The next step in investigating the total acid sites was done by comparing the FRT results with the TPD results discussed previously.

Table 6.5: Total acid site densities measured by FRT and NH₃-TPD

Zeolite Material	FRT single cycle (mol/kg)	FRT average cycle (mol/kg)	TPD (mol/kg)
F.CP914C	1.564	1.477	2.293
ZBV 23	1.788	1.371	1.720
ZBV 30	1.637	1.238	1.423
ZSM 55	1.530	1.619	0.918
F.CP914	1.050	0.951	0.819
ZBV 80	0.724	0.713	0.347
ZSM 280	0.561	0.511	0.314

The results shown in Table 6.5 relate to the FRT experiment performed at 100 °C and the TPD experiment. Loading of the zeolite samples prior to NH₃-TPD was carried out at 100 °C and was soaked at this temperature for the exact time period as the FRT adsorption step. This provided an adequate basis for both techniques to be compared. Both techniques compare satisfactorily with one another for all seven zeolites analysed. On average, the slight difference in measurements between both techniques yielded a standard deviation of 0.24 mol/kg. In order to explain these differences, it is worth noting the sensitivity of FRT as an *in situ* technique in comparison to TPD as highlighted earlier. It must also be stated that the FRT single cycle results presented in Figure 6.18 show a marked anomaly in the measured acid site density for F.CP914C at 100 °C. Comparing the sample with ZBV 23, which had a similar SiO₂/Al₂O₃ ratio, it was expected that the quantity adsorbed would be greater than 1.788 mol/kg. Such a value compares more favourable with the TPD value for F.CP914C, measured at 2.293 mol/kg. This anomaly could have been caused by an error in the FRT system attributed to the wrongful packing of the sample within the reactor, thereby restricting the surface of the zeolite from being fully exposed to the ammonia probe molecules. Having

determined the correlation between both sets of experimental techniques, it was possible to analyse the nature of the acid sites by comparing the TPD results with literature values.

Referring back to Table 6.4 it was possible to classify both the weak and the strong acid sites using TPD, which by nature are said to relate to either weakly bound NH_3 to the strongly bonded Brønsted-acid sites and the Brønsted-acid sites, or Lewis and Brønsted-acid sites respectively. The results are listed in Table 6.6 and compared with literature values of similar zeolitic materials.

Table 6.6: Comparison of strong acid sites with FRT and NH_3 -TPD results

Zeolite Material	$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	Technique	<i>h</i>-peak (mol/kg)	Reference
Cu-ZnO- Al_2O_3 -Zr- FER	25	NH_3 -TPD	1.126	(Bae <i>et al.</i> , 2009)
Co-H-FER	28.5	NH_3 -TPD	0.720	(Resini, 2003)
H-ZSM-5	30	NH_3 -TPD	0.700	
H-ZSM-5	50	NH_3 -TPD	0.440	(Rodríguez-González <i>et al.</i> , 2007)
H-ZSM-5	80	NH_3 -TPD	0.270	
H-ZSM-5	51	NH_3 -TPD	0.320	(Kubo <i>et al.</i> , 2014)
H-ZSM-5	200	NH_3 -TPD	0.083	
ZSM-5	280	NH_3 -TPD	0.063	(Al-Dughaiter & de Lasa, 2014)
F.CP914C	20	NH_3 -TPD	1.407	This study
ZBV 23	23	NH_3 -TPD	1.110	This study
ZBV 30	30	NH_3 -TPD	0.785	This study
ZSM 55	50	NH_3 -TPD	0.569	This study
F.CP914	55	NH_3 -TPD	0.508	This study
ZBV 80	80	NH_3 -TPD	0.213	This study
ZSM 280	280	NH_3 -TPD	0.166	This study

Validating the results from this study with those from the literature has shown a good agreement existing between similar techniques. Both ferrierite samples with similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 20 and 25 produced values of 1.407 and 1.126 mol/kg respectively (Bae *et al.*, 2009). The ZSM-5 samples with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 30 also showed a distinct correlation resulting in values of 0.785 mol/kg for this study and 0.700 mol/kg in the literature (Rodríguez-González *et al.*, 2007). It is reassuring to notice that the results measured by the various research groups for similar zeolites with higher aluminium

contents were generally shown to have higher acid site concentrations (Al-Dughaiter & de Lasa, 2014; Bae *et al.*, 2009; Kubo *et al.*, 2014; Resini, 2003; Rodríguez-González *et al.*, 2007). This reemphasises the theory of zeolite acidities being proportional to their aluminium content. The trend that clearly exists in Table 6.6, whereby the acid site concentrations decrease with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ is as expected. Added to these results are plausible discoveries and analyses found in the literature that corroborate strong correlations between results measured for acid site determination using volumetric (TPD) and *in situ* techniques in line with FRT (Eigenmann *et al.*, 2000; Van Oers *et al.*, 2014).

6.1.2.3. Ammonia Sorption Dynamics

Having quantified the amounts of ammonia adsorbed and desorbed from the zeolite samples, it was possible to examine the ammonia sorption behaviour for each dynamic cycle and determine when the FRT system reached an equilibrium state. Once again it is important to consider the Langmuir adsorption model where the assumptions are made that all active sites are equally distributed, that the heat of adsorption is independent of coverage, that the rate of adsorption (desorption) is proportional to the number of empty adsorption sites, and that at adsorption equilibrium the rate of adsorption equals the rate of desorption (Holder, 2008). By analysing the *sorption ratio analysis*, defined as a parameter of the system that quantifies the ratio of desorbed ammonia to adsorbed ammonia within a fixed time period (r_d/r_a), it was possible to relate the sorption dynamics with respect to the zeolite surface coverage. When performing the ratio analysis, it was important to adhere to the following key principals and assumptions stipulated in previous studies (Palmer, 2010).

- The adsorption and desorption cycle times must be equal for both phases on the flux response profile.
- The *sorption time* is defined as an integration time and is consistent when analysing both adsorption and desorption peaks.
- The nature of the sorption peaks on the flux response profiles is such that a longer approach (asymptotic) to the baseline is observed for the desorption peaks. As a consequence of this and the fact that a specified sorption time limit exists, the area underneath the desorption peak is representative of an

imminently complete desorption phase while the area underneath the adsorption peak exhibits the *complete adsorption phase*.

Figure 6.20 – Figure 6.26 show the FRT ratio profiles for each of the zeolite samples. During the analysis of the samples, it was taken into consideration that the profiles would be examining the case of rapid adsorption and slow desorption ($r_d/r_a < 1$), eluded to earlier on in the results shown for the FRT dynamic cycle profile.

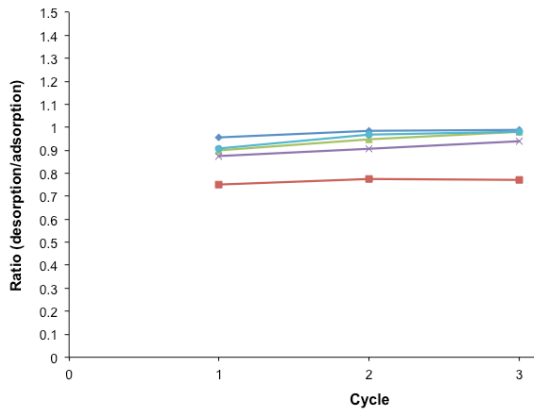


Figure 6.20: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for F.CP914C: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

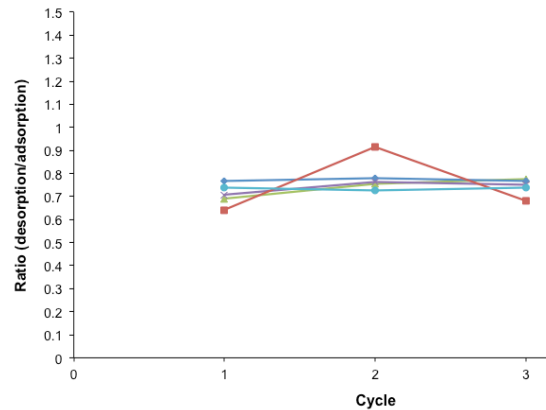


Figure 6.21: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for ZBV 23: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

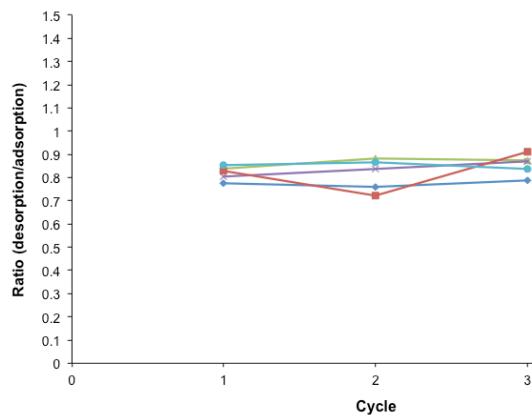


Figure 6.22: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for ZBV 30: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

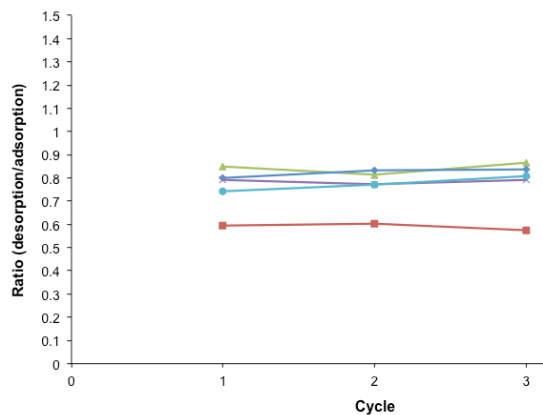


Figure 6.23: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for ZSM 55: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

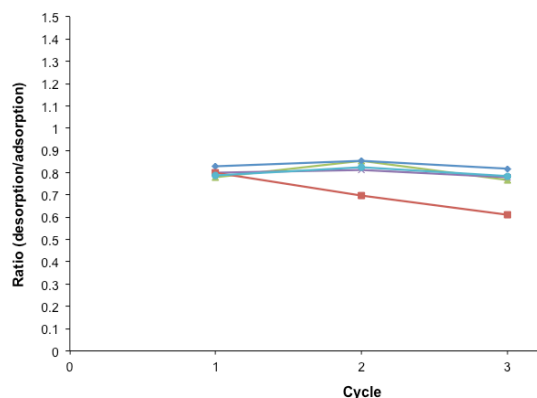


Figure 6.24: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for F.CP914: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

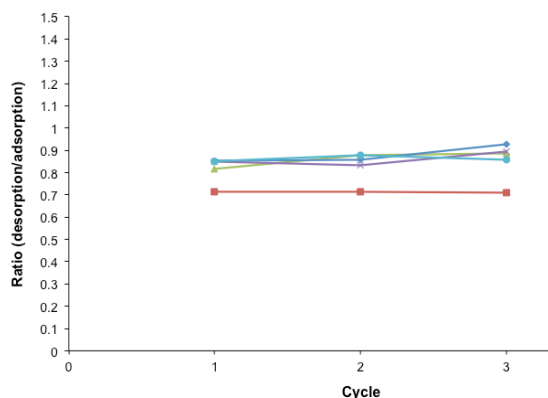


Figure 6.25: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for ZBV 80: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

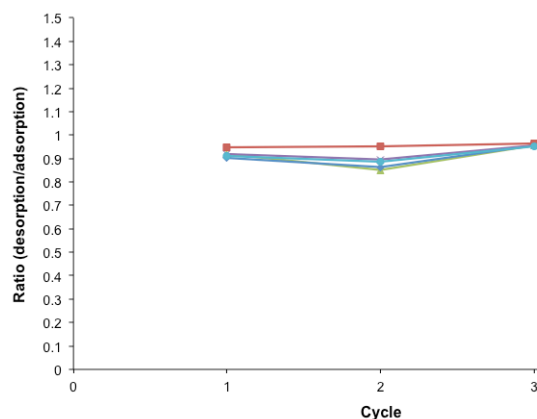


Figure 6.26: FRT ratio profiles showing sorption ratio against number of sorption cycles between 100 – 450 °C for ZSM 280: 100 °C (■), 200 °C (×), 300 °C (♦), 400 °C (▲), 450 °C (●)

The figures above exhibit the FRT adsorption-desorption processes for ammonia on zeolites. A state of pseudo-equilibrium is seen to be reached for all the samples at and above 200 °C. The average sorption ratio for the ZSM-5 zeolites were measured as being 0.75, 0.83, 0.80, 0.86, and 0.91 for ZBV 23, ZBV 30, ZSM 55, ZBV 80, and ZSM 280 respectively. An interesting observation here pertains to the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the samples. ZSM 280 with the highest sorption ratio also has the highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio meaning it has the least amount of acid sites. When the effect of temperature was analysed, the sorption ratio measurements displayed a standard deviation below 4 %, proving that the surfaces of the zeolites had achieved full coverage. It was encouraging to see the standard deviation of the sorption ratios above 100 °C for all samples varied

between 1 – 4 %. When analysing the sorption ratios at 100 °C, it is worth considering the strength of the acid sites within this temperature region. The NH₃-TPD experiments reported earlier showed the strength distribution of the acid sites for the zeolite samples. The results also indicated that the distribution of these sites favoured the strong acid sites and as such, it is not surprising to see the sorption ratio being lower at 100 °C for most of the zeolite samples.

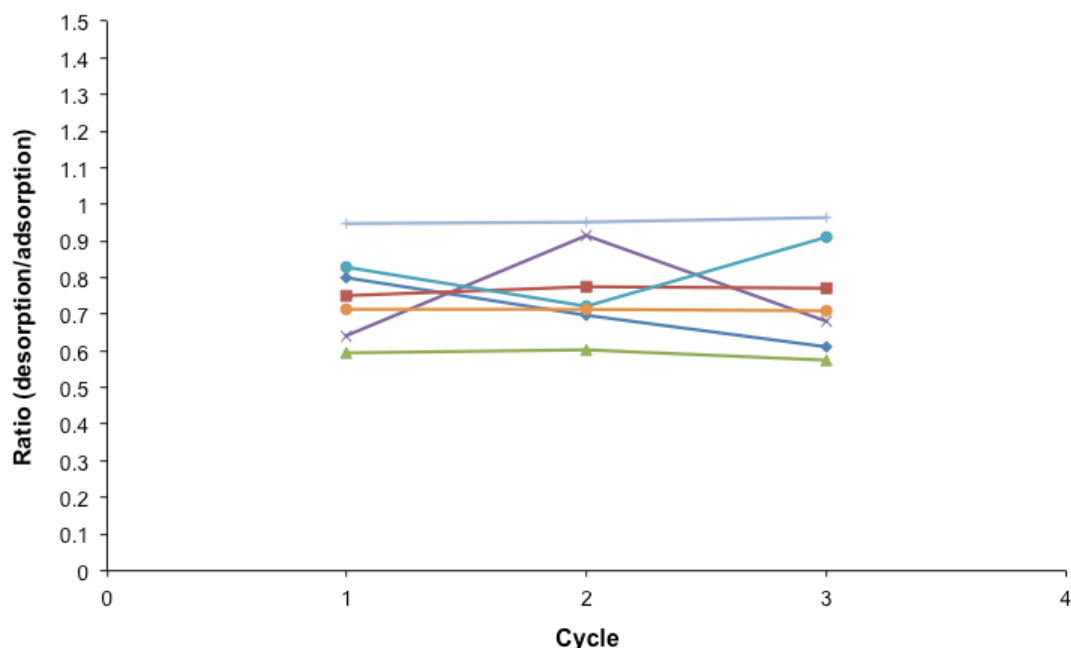


Figure 6.27: FRT results for average cycle analysis at 100 °C for F.CP914C (■), ZBV 23 (×), ZBV 30 (◆), ZSM 55 (▲), F.CP914 (◆), ZBV 80 (●), and ZSM 80 (+)

Figure 6.27 presents the sorption ratio profiles for each sample at 100 °C. The first observation shows the high sorption ratio that existed for ZSM 280. Once again this comes as no surprise due to the high silica content in this sample. As the total quantity of acid sites was considerably smaller than the other zeolite samples, it was safe to assume that the quantity and quality of the desorption expressed in the FRT desorption peaks would remain closer to the adsorption amounts. It can also be seen from Figure 6.27 that a steady state is reached in 4 of the 7 samples. Zeolites ZBV 23, ZBV 30, and F.CP914 show marked points of anomaly at one cycle point. The nature of the FRT setup leaves it susceptible to miniscule changes in its environment due to the sensitivity of the technique. As a result of this, experimental errors brought about through changes in the environment of the test sample or the FRT system can have an effect on the measurements. Although these anomalies exist, it is comforting to discover the standard

deviations were measured as being 15 %, 10 %, and 10 % for ZBV 23, ZBV 30, and F.CP914 respectively. The analysis of the sorption ratio parameter has also lead to additional significant implications concerning the steady-state kinetics of the ammonia sorption. With the calculations showing the sorption ratio being lower than 1 under normal operating conditions, it can be assumed that a state of pseudo equilibrium exists during the process of ammonia adsorption-desorption from zeolite surfaces. This conclusion has been echoed in the literature for ammonia adsorption-desorption on solid catalyst surfaces (Hesketh & Abraham, 2000; Krapivsky & Ben-Naim, 1994).

6.2. Summary

The analysis of the total acidity of commercially available zeolites using FRT and NH_3 as the probe molecule was successfully achieved. Earlier studies completed in measuring the quantity of acid sites present in zeolite samples was complemented with the addition of further samples as well as new research conducted into the strength and nature of the measured acid sites (Palmer *et al.*, 2011). A detailed analysis of the material and textural characteristics of the zeolite samples was carried out using TGA, solid state NMR, XRD, and XRF, which showed that the zeolite samples contained no extra framework aluminium. The FRT measured acid site quantities compared well with literature values while the TPD results gave a positive insight into the strength and nature of the acid sites.

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Chapter 7

FRT

Carbon Dioxide Sorption

Another equally important feature of zeolites in catalysis is the presence of basic centres that play a pivotal role in base-catalysed reactions. The oxygen atom in the Si-O-Al species bears a negative charge, which may generate a basic character. Zeolite basicity may also originate from basic hydroxyl sites, encaged oxide clusters, supported metals, reducing centres or associated with the acidity in acid-base pairs (Barthomeuf, 2003). A fundamental feature of zeolite chemistry concerns the acid-base behaviour occurring within the micropores of these materials. Zeolites can be considered as solid acid-base pairs as the protons and the exchangeable cations constitute the acid sites within the zeolite matrix, while the oxygen atoms within the lattice are the basic sites. By nature, the acid and base sites are not independent of each other in the zeolite structure due to their connection via the framework.

In line with the discussion delineated previously, it is understood that Lewis acidity and basicity have the same origin, appearing because of the ionicity of the element-oxygen bond. It is this synergy that couples the general association between Lewis acidity and surface basicity of zeolites (Bonenfant *et al.*, 2008; Fierro, 2005; Schoonheydt *et al.*, 2012). From this point of view, the use of FRT to suggest a better understanding and explanation of the acidobasic nature of zeolites is a requisite deployment of the technique.

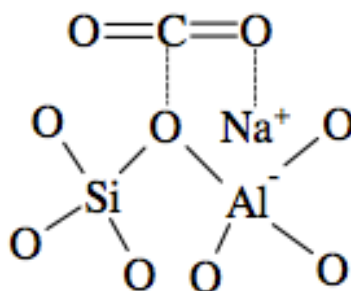


Figure 7.1: Schematic diagram of CO₂ adsorption on NaZSM-5

The use of a specific probe for the measurement of zeolite basicity has been less satisfactory when compared to the research carried out in acidity measurements. The use of probe molecule that would only interact specifically with basic sites has been a longstanding issue in the zeolite community (Anpo, 2000; Barthomeuf, 1996; Fierro, 2005; Weitkamp & Puppe, 1999). Carbon dioxide is a popular probe used for the investigation of basicity as it is small enough to penetrate and compensate for the oxygen anions (basic centres) created by the substitution of AlO₄ and SiO₄ tetrahedra due to its amphoteric nature (Araki *et al.*, 2012; Bonenfant *et al.*, 2008). However, it does suffer from the drawback that it also reacts with Lewis acid sites and forms different carbonates when interacting with zeolites. That being said, it has been acknowledged that the use of CO₂ as a probe for basic sites is not easy but when coupled with spectroscopic and theoretical data, can provide important information on the occurring phenomena (Fierro, 2005; Schoonheydt *et al.*, 2012). FRT was used to analyse the effective sorption capacities of CO₂ and determine the basicity/number of basic sites present within zeolites F.CP914C, ZSM 55, F.CP914, and ZSM 280.

7.1. Results and Discussion

7.1.1. Material Characterisation

7.1.1.1. FRT Profiles

The FRT profiles generated to determine the effective sorption capacities of CO₂ on the zeolite samples correlated well with the expected profile shown in Chapter 4.2, showing clear distinctions between sorption zones and viscosity phenomena. By measuring the

quantity of CO_2 molecules adsorbed in the successive dynamic cycles, the basicity/number of basic sites exposed could be calculated. The observed FRT profile shown in Figure 7.2 shows the CO_2 sorption effects that occurred while measuring sample F.CP914C at 50°C . The profile shows the CO_2 adsorption peak present; the viscosity effect caused by the CO_2 probe molecules being injected into the Ar carrier gas; the CO_2 partial desorption peak; and the viscosity effect caused by the composition change in the gas measured through the reactor from a CO_2/Ar mixture to the original Ar carrier gas stream. The complete set of dynamic cycles for all the zeolite samples can be found in Appendix D.

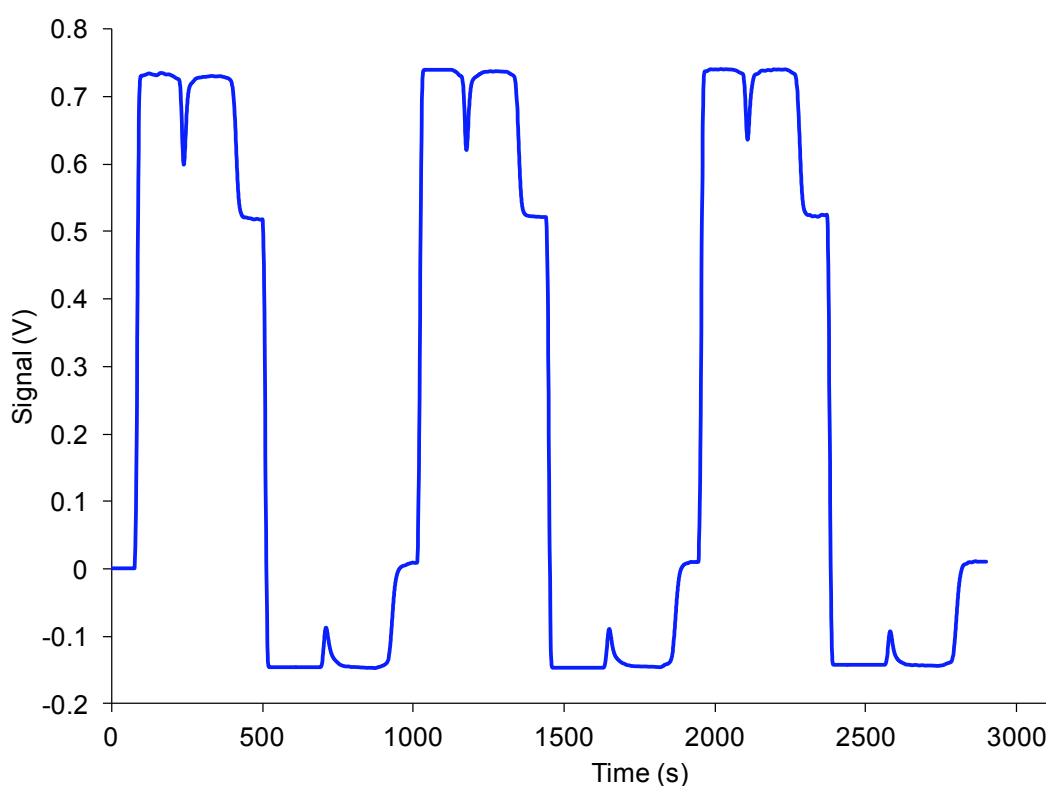


Figure 7.2: FRT profile for CO_2 sorption on F.CP914C at 50°C

To evaluate the adsorption capacities, the areas underneath the adsorption peaks were integrated with the aid of a curve fitting software. Both the evaluated results and Figure 7.2 showed a previously commented on observation exhibited in previous FRT results where the first adsorption cycle yields a higher adsorption capacity than subsequent cycles (Palmer *et al.*, 2011; Sasegbon & Hellgardt, 2012). This phenomenon might be explained by the fact that the CO_2 adsorption that follows the first adsorption cycle is limited by the adsorbate-adsorbate interactions that prevent the adsorption of new

molecules of CO₂ unto the pore wall sites that are thus occupied by other molecules of CO₂ that were not desorbed during the desorption cycle. This phenomena has been well documented in the literature and goes some way in explaining the competition of adsorption present in the FRT experiments (Barthomeuf, 1996; Hernández-Huesca *et al.*, 1999; Katoh *et al.*, 2000a; Yamazaki *et al.*, 1993).

7.1.1.2. Total Number of Basic Sites

Figure 7.3 shows the (quasi) equilibrium CO₂ adsorption capacities for the zeolite samples as a function of operating temperature. The first observation is the steep decrease in adsorption capacity noticed between 50 and 100 °C. Plausible explanations for this have been attributed to the possible loss of hydroxyl groups at increasing temperatures (Chester & Derouane, 2009; Palmer, 2010; van Bekkum *et al.*, 2001). This brings about an associated reduction in sorption capacity for all zeolites. It is also important to take into account the influence of the polarising power and distribution of the cations in the zeolites. All of the framework oxygens possess potential basic sites but only those that acquire the highest negative charge have a true basic character. Consider the two types of framework oxygens: O₃Si-O-SiO₃ and O₃Si-O-AlO₃. The presence of the Al³⁺ ions in the latter form is the most negative, therefore most basic. This negative charge is attributed to the negatively charged framework AlO₄⁻, interacting with a charge balancing cation, which indirectly influences the basicity of the oxygen. As a result of this, the stronger the acid (cation), the weaker the conjugate base (oxygen) (Auerbach *et al.*, 2003). The steep decline in adsorption capacity in the FRT results could therefore be an indication of the loss from weakly bound basic sites.

The second observation is an expected result where the zeolitic adsorption capacities increase with decreasing SiO₂/Al₂O₃ ratio; F.CP914C is shown to have the highest adsorption capacity (0.69, 0.66, 0.36, 0.08) mol · kg⁻¹ for CO₂ while ZSM 280 consequently exhibits the lowest capacity out of the four zeolite samples (0.45, 0.38, 0.14, 0.01) mol · kg⁻¹.

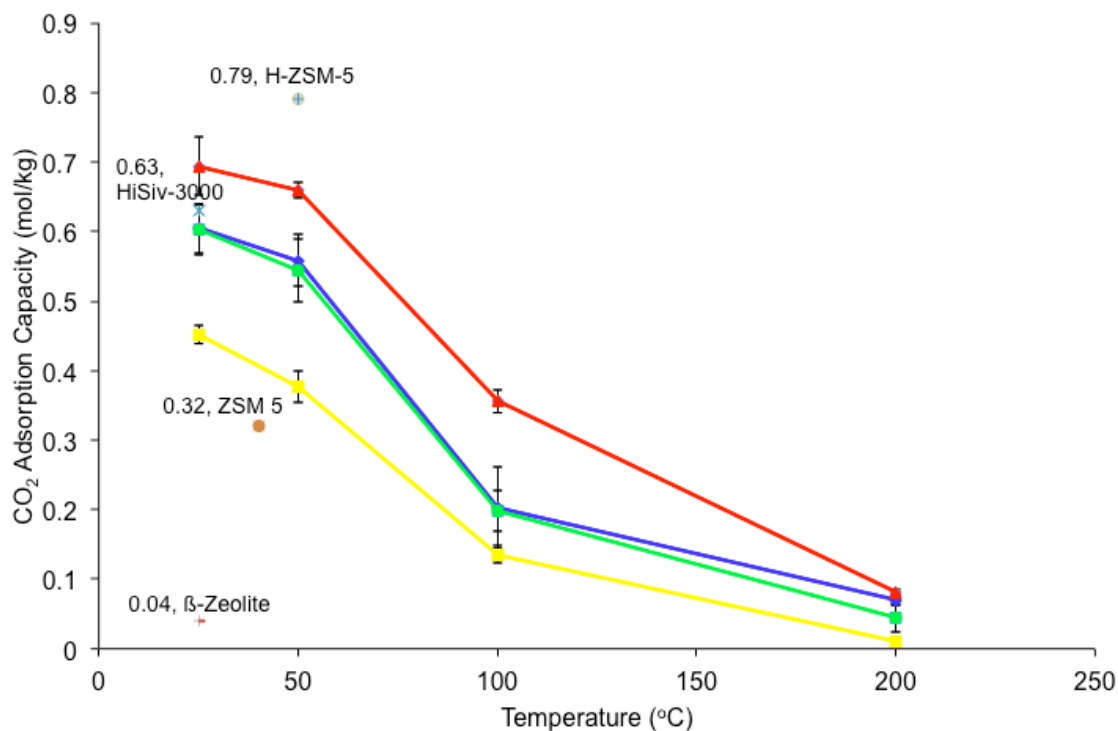


Figure 7.3: Effect of temperature on FRT CO₂ adsorption capacities of zeolites F.CP914C (▲), F.CP914 (◆), ZSM 55 (●), and ZSM 280 (■)

It has been shown repeatedly that selectivity and adsorption capacities of zeolites for polar molecules increase when the SiO₂/Al₂O₃ ratio decreases (Bonenfant *et al.*, 2008; Calleja *et al.*, 1998). One explanation for this phenomenon may be the increase of the electric field in zeolitic pores, induced by increasing number of charged sites present at the surface of the zeolites (Bonenfant *et al.*, 2008; Calleja *et al.*, 1998). Added to this, the basicity of the zeolite framework enhances with the content of Al³⁺ ions due to the presence of greater amounts of exchangeable cations (Laspéras *et al.*, 1996). Therefore, at low loading, the zeolites possessing the smallest SiO₂/Al₂O₃ ratios should have the best selectivity and adsorption capacity for polar molecules irrespective of operating temperature and this is indeed observed for the CO₂ adsorption capacities in Figure 7.3.

The FRT sorption results are summarised in Table 7.1, illustrating the close agreement of FRT derived data with literature values obtained using a variety of measurement techniques for similar zeolitic materials.

Table 7.1: Comparison of CO₂ adsorption capacities in zeolites

Zeolite	Method	T (°C)	SiO ₂ /Al ₂ O ₃ ratio	Adsorption capacity (mol kg ⁻¹)	Reference
Na-Ferr	Static volumetric	100	8.7	1.88	(Pulido <i>et al.</i> , 2009)
Na-ZSM 5	GC	30	23.8	0.75	(Samanta <i>et al.</i> , 2012)
HiSiv-3000 (Silicalite)	Static volumetric	25	46	0.63	(Bao <i>et al.</i> , 2011)
ZSM 55	FRT	25	50	0.61	This study
ZSM 5	GC	40	280	0.54	(Harlick & Tezel, 2003a)
ZSM 280	FRT	50	280	0.38	This study
H-ZSM 5	Step change response method	50	27	0.79	(Wirawan & Creaser, 2006)
F.CP914C	FRT	50	20	0.72	This study
β-Zeolite	Static volumetric	25	480	0.04	(Bao <i>et al.</i> , 2011)

It is also worth noting the influence of the size of the zeolite pores when analysing the capacity of CO₂ adsorption. This relationship is also directly dependent on the loading pressure of the adsorbate. At low pressures, the density of CO₂ is highest in the smaller pores while it is higher in the larger pores at high pressures (Samios *et al.*, 2000). The adsorbed molecules at the lower pressures have the tendency to occupy positions where the adsorbate-adsorbate interactions are less than the adsorbate-pore interactions. At higher pressures, the adsorbates are said to occupy the central region of the pores where an increase in their packing leads to a greater density (Quirke, 2005; Samios *et al.*, 2000). As the CO₂ molecules can interact with the pore wall of the zeolites, CO₂ adsorption could also be limited by the size of the pores at high pressures. Due to the CO₂-CO₂ interactions, the adsorption of new molecules of CO₂ into the pore wall sites already occupied by other CO₂ molecules might be prevented (Gargiulo *et al.*, 2014; Inglezakis & Zorpas, 2012; Katoh *et al.*, 2000). The FRT experiments were carried out with a low concentration of CO₂ in the perturbation stream to investigate the surface of the zeolites, which means the system should tend towards one favouring less adsorbate-adsorbate interactions. Table 7.2 gives the textural characterisation properties of the zeolite samples carried out using a Micromeritics Tristar 3000 Surface Analyser.

Table 7.2: Physical characterisation of zeolite test samples

Zeolite	SiO₂/Al₂O₃ ratio	S_{BET} (m²/g)	Pore size (×10⁻⁹ m)	Pore volume (cm³/g)
F.CP914C	20	296	2.87	0.21
F.CP914	55	282	2.97	0.21
ZSM 55	50	396	2.51	0.25
ZSM 280	280	386	2.20	0.21

When comparing the pore sizes to the adsorption capacity results, it follows in the same order as the adsorption capacities to a high degree. An interesting observation is noticed when analysing the adsorption capacity results of samples ZSM 55 and F.CP914 in Figure 7.3. Although the pore size of F.CP914 ($2.97 \times 10^{-9} \text{m}$) is shown to be the largest, its measured adsorption capacities were well below those measured for F.CP914C. It must be noted that this was an expected result due to the higher aluminium content of F.CP914C. Therefore, it would have been expected that a higher difference in the measured adsorption capacity between ZSM 55 and F.CP914 should have existed. A possible cause for the measured similarities in the adsorption capacities of ZSM 55 and F.CP914 could be as a result of the difference in their respective pore sizes, even though ZSM 55 has a higher SiO₂/Al₂O₃ ratio.

7.1.1.3. Carbon Dioxide Sorption Dynamics

The carbon dioxide sorption behaviour was investigated having quantified the amounts adsorbed and desorbed from the zeolite samples. It was also useful to analyse the diffusion coefficients of CO₂ in the zeolites to gain a better insight into the dynamics of CO₂ sorption. A unique feature of FRT is its ability to evaluate the adsorption capacities and the diffusion coefficients of CO₂ within the same experimental window. The dual-mode operation enables combined measurements and reduces experiment process times.

7.1.1.3.1. Sorption Behaviour

Figure 7.4 – Figure 7.7 show the sorption profile behaviour for CO₂ sorption on the zeolite samples. All four samples exhibit a constant behaviour with the number of cycles, thereby implying that the surfaces had reached full coverage: average of r_d/r_a at

each temperature = 0.91, 0.89, 0.94, 0.89 for F.CP914C; 0.94, 0.90, 0.87, 0.89 for ZSM 55; 0.96, 0.89, 0.91, 0.90 for F.CP914; and 0.98, 0.92, 0.93, 0.90 for ZSM 280.

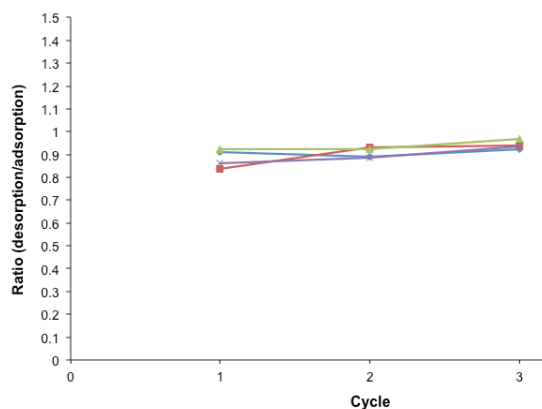


Figure 7.4: FRT ratio profiles showing sorption ratio against number of sorption cycles between 25 – 200 °C for F.CP914C: 25 °C (♦), 50 °C (■), 100 °C (▲), 200 °C (×)

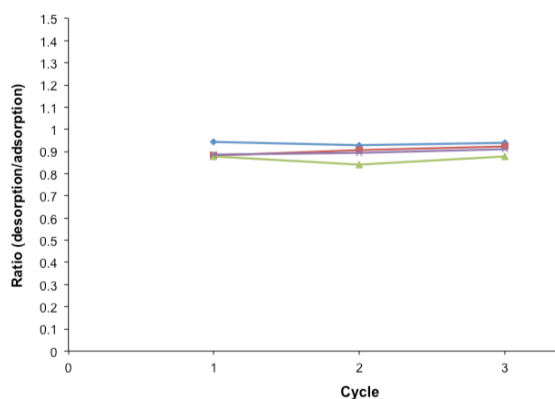


Figure 7.5: FRT ratio profiles showing sorption ratio against number of sorption cycles between 25 – 200 °C for ZSM 55: 25 °C (♦), 50 °C (■), 100 °C (▲), 200 °C (×)

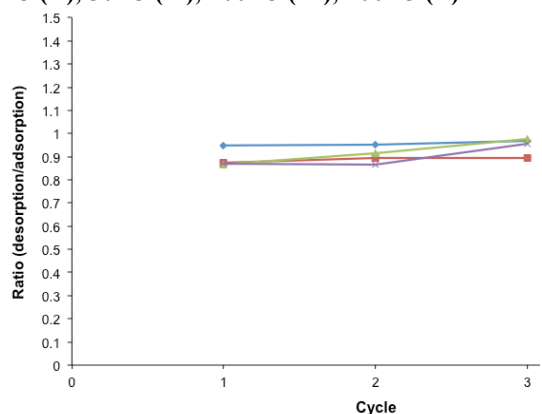


Figure 7.6: FRT ratio profiles showing sorption ratio against number of sorption cycles between 25 – 200 °C for F.CP914: 25 °C (♦), 50 °C (■), 100 °C (▲), 200 °C (×)

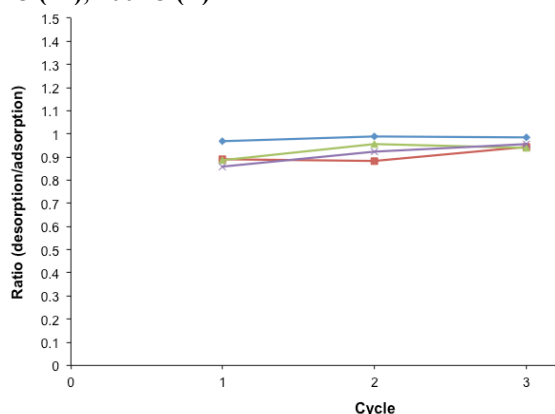


Figure 7.7: FRT ratio profiles showing sorption ratio against number of sorption cycles between 25 – 200 °C for ZSM 280: 25 °C (♦), 50 °C (■), 100 °C (▲), 200 °C (×)

This result is in accordance with the strength of the basic sites measured earlier on as the rate of desorption tends closer to that of the adsorption at low temperatures. The profiles indicate a low degree of chemisorption occurring at the basic sites with the degree of variability between each cycle for the four samples measured at an average standard deviation of 2.89 %. It is not surprising to notice this result as certain studies have indicated that by only varying the balancing cation of the oxygen, weakly basic zeolites are produced. Increasing the basic strength would require the occlusion of alkali metal oxides (Bonenfant *et al.*, 2008; Fierro, 2005; Galownia & Davis, 2005). Additional studies on CO₂ chemisorption to determine the relative basicity of HY and

KY zeolite catalysts also showed no chemisorbed amount up until the inclusion of iron content on the supports (Inui *et al.*, 1998).

7.1.1.3.2. Carbon Dioxide Diffusion in Zeolites

It is already well known that the effective CO₂ sorption capacity of zeolites as well as the diffusion of molecules inside their nanometre scale pores affects and controls their performance as suitable materials for CO₂ abatement (Ahn *et al.*, 2004; Dirar & Loughlin, 2013). Adapting the FRT-ZLC technique to analyse the effective diffusivity coefficients provided another measure of the sorption dynamics of carbon dioxide adsorption capacities outlined earlier.

Following the ZLC approach, it was necessary to normalise the FRT partial adsorption response curve to initial concentrations of CO₂ diffusing into the zeolite samples using equation 5.3 (Brandani, 2002; Ruthven & Brandani, 2000; Sasegbon & Hellgardt, 2012). The leading edge of the adsorption transient (highlighted as  in Figure 7.8) was used to analyse the diffusion coefficients. The transient shown in Figure 7.8 had to be flipped and mirrored in order to model the diffusion coefficients as operating from regions of high to low concentrations of CO₂. Figure 7.9 depicts the process of converting the FRT profile to the normalised curves applicable for ZLC analysis. The dispersion corrected FRT-ZLC curve depicting transport into the porous network is presented in Figure 7.10.

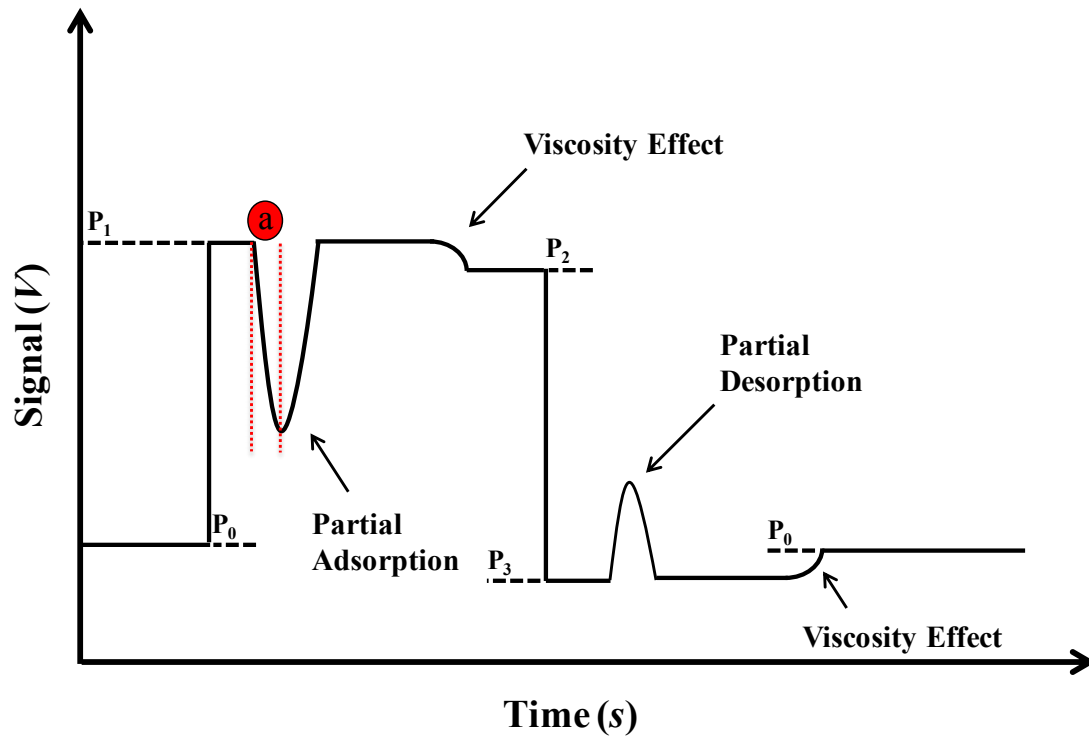


Figure 7.8: Schematic of expected flux response profile for CO₂ sorption under isothermal conditions

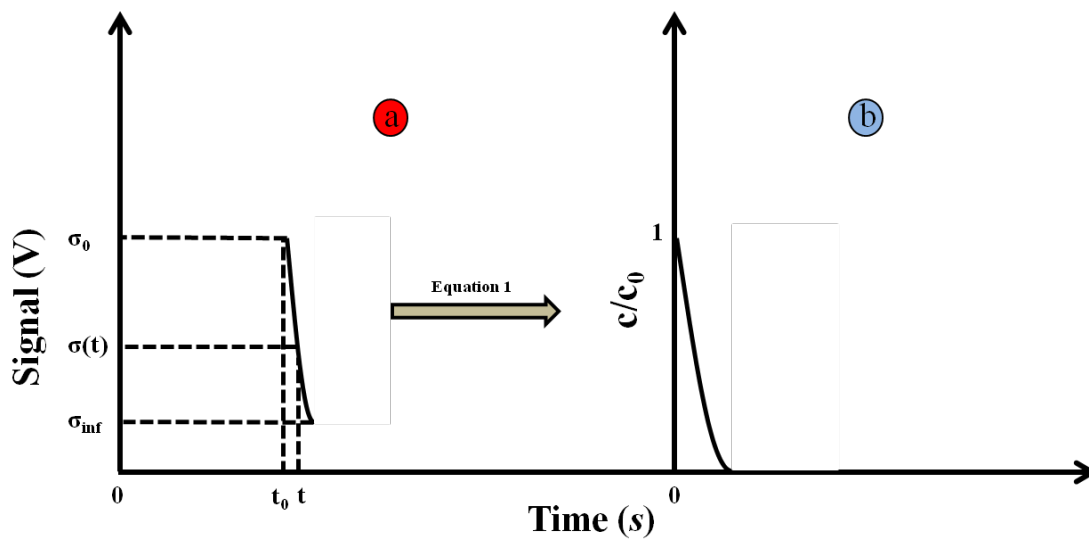


Figure 7.9: FRT adsorption transient response curve normalised and shown in part b

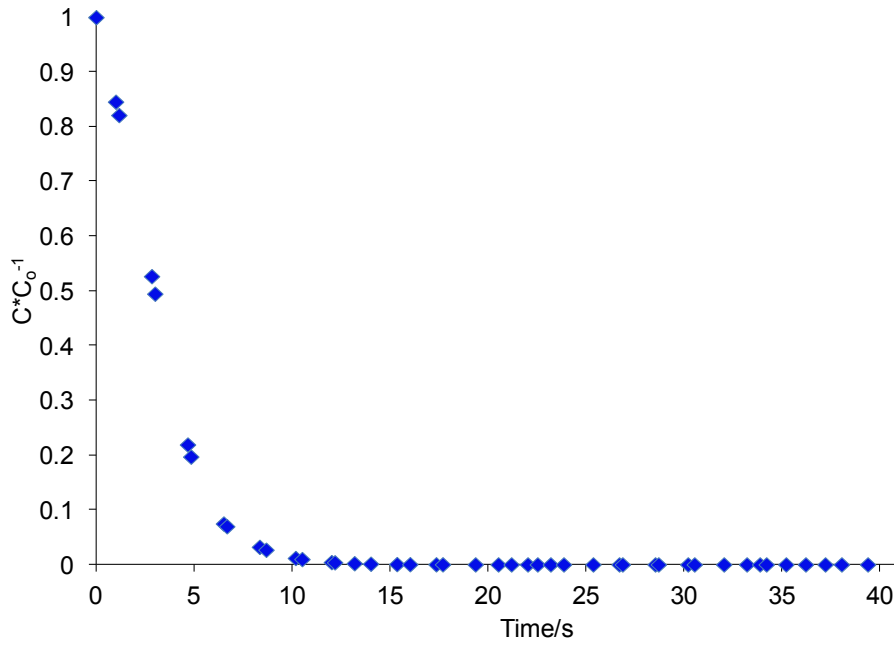


Figure 7.10: Experimental FRT-ZLC decay curve (CO_2 mole fraction, 0.3) of zeolite F.CP914C at 50°C

By using the LT analysis approach detailed earlier, semi-logarithmic plots of c/c_0 against t of the experimental FRT-ZLC decay curves were constructed to evaluate the ZLC parameters. Using the values of the slope and intercept combined with the transcendental equation 5.6 and solved analytically using Maple, it was possible to construct FRT-ZLC plots of the experimental decay curves with the ZLC model.

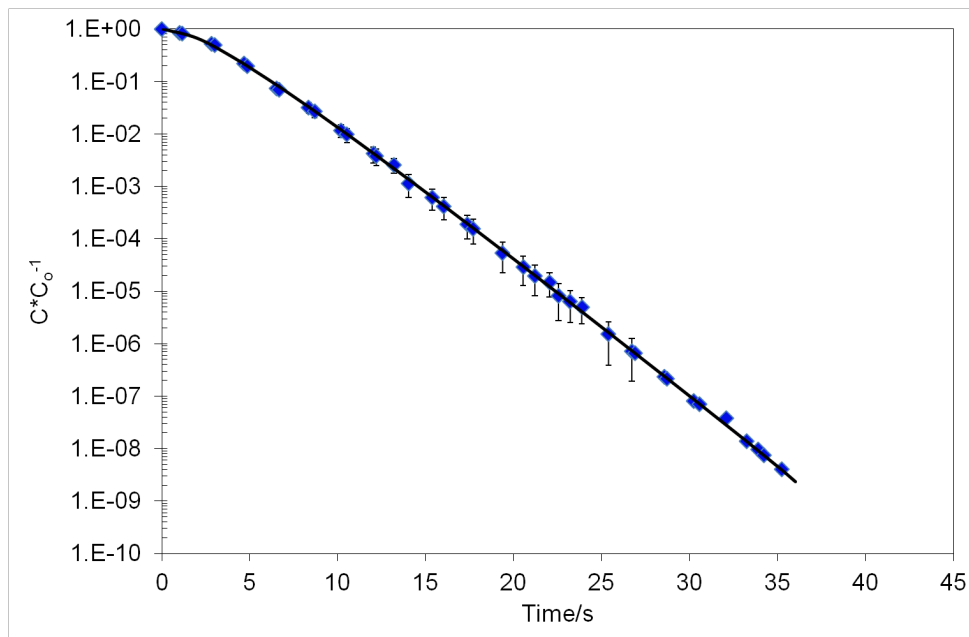


Figure 7.11: Generated FRT response curve for zeolite F.CP914C at 50°C with fitted ZLC curve

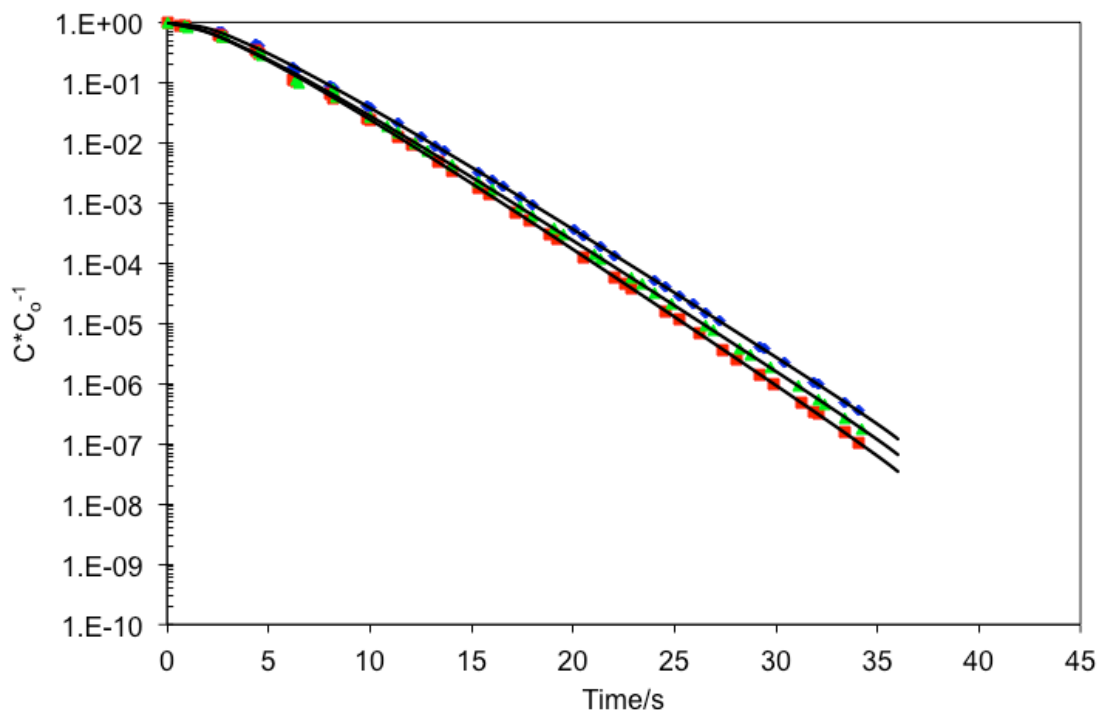


Figure 7.12: Experimental and fitted FRT-ZLC curves for ZSM 55 at 50 °C for all three cycles (1st - ▲, 2nd - ■, and 3rd - ◆)

Figure 7.11 shows the semi-log plot of zeolite F.CP914C at a temperature of 50 °C. A good agreement between the FRT generated response curve and the LT model for ZLC diffusion exists. Figure 7.12 illustrates the log-scale approach of the long time asymptote for all 3 cycles of zeolite sample ZSM 55 at 50 °C. It is clear that the asymptotes of these response curves are similar, with only a slight divergence exhibited between cycles. For a given temperature, the slopes of the asymptotes indicate how far removed from equilibrium the system is operating at. As the purge flowrate at each cycle was the same, it was expected that the generated asymptotes would be similar. A possible explanation of the slight difference in the asymptotes can be attributed to the packing procedure for the zeolite samples. Pieces of quartz wool were used to hold the samples in place within the quartz reactor. The amount of quartz wool used had to be sufficient in holding the zeolite in place while not exceeding an amount that would create a pressure drop within the system. The generated response curves show that during the repeat cycles, a perfectly consistent approach to the surface of the zeolite samples by the probe molecules was not achieved due to the packing.

The analysis of the adsorption capacities of the zeolite samples performed earlier in Chapter 7.2 also served the dual purpose of supporting the assumptions required for ZLC analysis. When fulfilling the requirement of operating within the linear range of the isotherm, it has been acknowledged that the satisfaction of this condition pertains to the change in concentration $c_0 - c_\infty$ being sufficiently small (Ei  *et al.*, 2002). In this limit of low concentration, the isotherm must converge to Henry’s law such that $q \ll q_m$, where q_m is the “monolayer capacity” (Schirarz & Contescu, 1999). Table 7.3 below outlines monolayer capacities of CO₂ isotherms on zeolites compared with the quantities of CO₂ adsorbed for the FRT-ZLC experiments at 30 *mol*-% and room temperature.

Table 7.3: FRT evaluated zeolite adsorption capacities at 25 °C compared with literature monolayer capacities

Zeolite	SiO ₂ /Al ₂ O ₃ ratio	Adsorption capacity (<i>mol kg</i> ⁻¹)	Zeolite	SiO ₂ /Al ₂ O ₃ ratio	Monolayer capacity (<i>mol kg</i> ⁻¹)	Ref
F.CP914C	20	0.69	Na-FERR	27.5	2.02	(Bul�nek <i>et al.</i> , 2010)
F.CP914	55	0.60	Li-FERR	27.5	1.96	
ZSM 55	50	0.60	ZSM-5	25	3.90	(Li <i>et al.</i> , 2013)
ZSM 280	280	0.44	ZSM 280	280	4.31	(Harlick & Tezel, 2003b)

As can be seen in Table 7.3, the adsorption capacities of the FRT derived zeolite samples at 30 *mol*-% CO₂ are at a range well within the evaluated monolayer capacities of zeolite samples with similar SiO₂/Al₂O₃ ratios in the literature.

Measurements were conducted for the different zeolite samples over a range of temperatures exhibited in Figure 7.13. The resulting plots for ZSM 280 show a consistent agreement with the ZLC LT model. The experiments carried out between 25 – 200 °C show the effect of temperature on the ZLC response curves, with a strong temperature dependence on the response times.

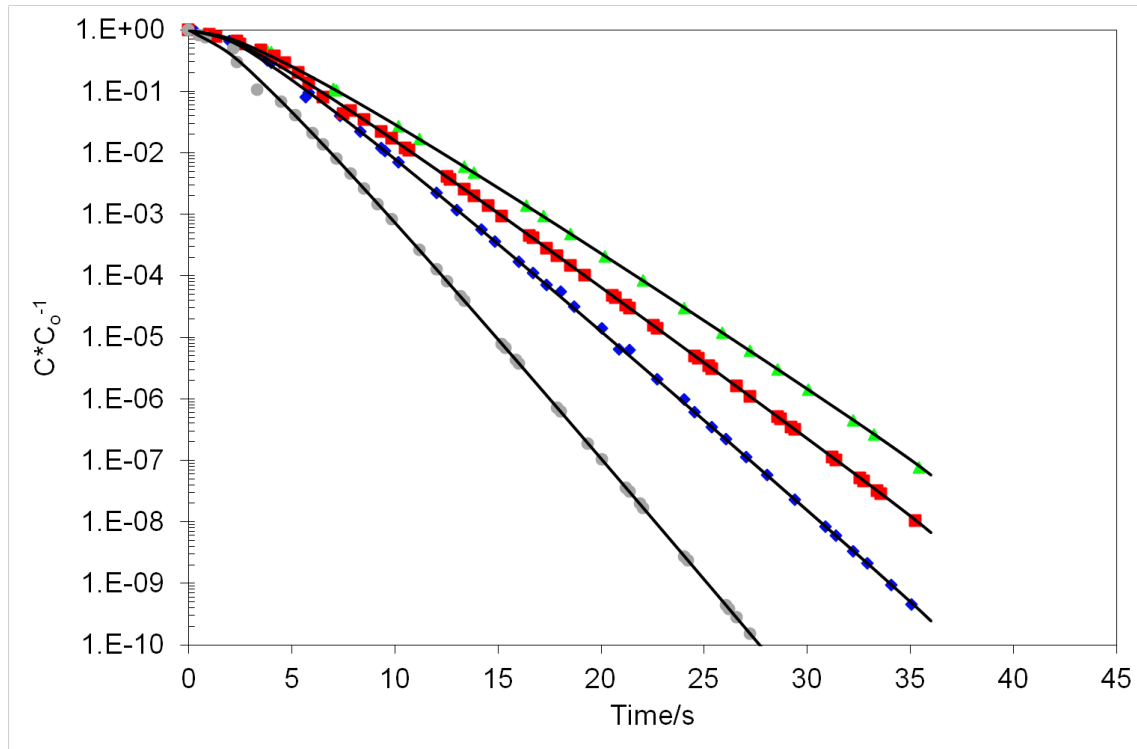


Figure 7.13: Effect of temperature on zeolite sample ZSM 280 at 25 °C ($\blacktriangle$), 50 °C ($\blacksquare$), 100 °C ($\blacklozenge$), and 200 °C ($\bullet$)

With the ZLC diffusion models confirming the validity of the experimental runs, it was possible to construct graphs of the diffusion coefficients for each of the zeolites plotted against temperature to evaluate the respective activation energies of diffusion. A clear linear trend in the expression of the diffusivity coefficients with respect to temperature is exhibited by each of the zeolite samples shown in Figure 7.14. It can also be observed that the diffusivity coefficients increase with temperature as would be expected (Kärger *et al.*, 2012). By comparing the structural differences unique to each zeolite shown in Table 5.2 with the graph in Figure 7.14, it can be deduced that the size of the pores of the zeolites influence the rate of diffusion. F.CP914 with the largest pore size, shown to have the highest diffusion coefficients across the temperature range compared to ZSM 280 with the smallest pore size and diffusion coefficients. It is thus observed that the diffusion coefficients of the zeolite samples decrease in the following order:

$$\text{F.CP914} > \text{F.CP914C} > \text{ZSM 55} > \text{ZSM 280}$$

The order of the diffusivity coefficients is further corroborated by the analytically derived Maple results shown in Table 7.4.

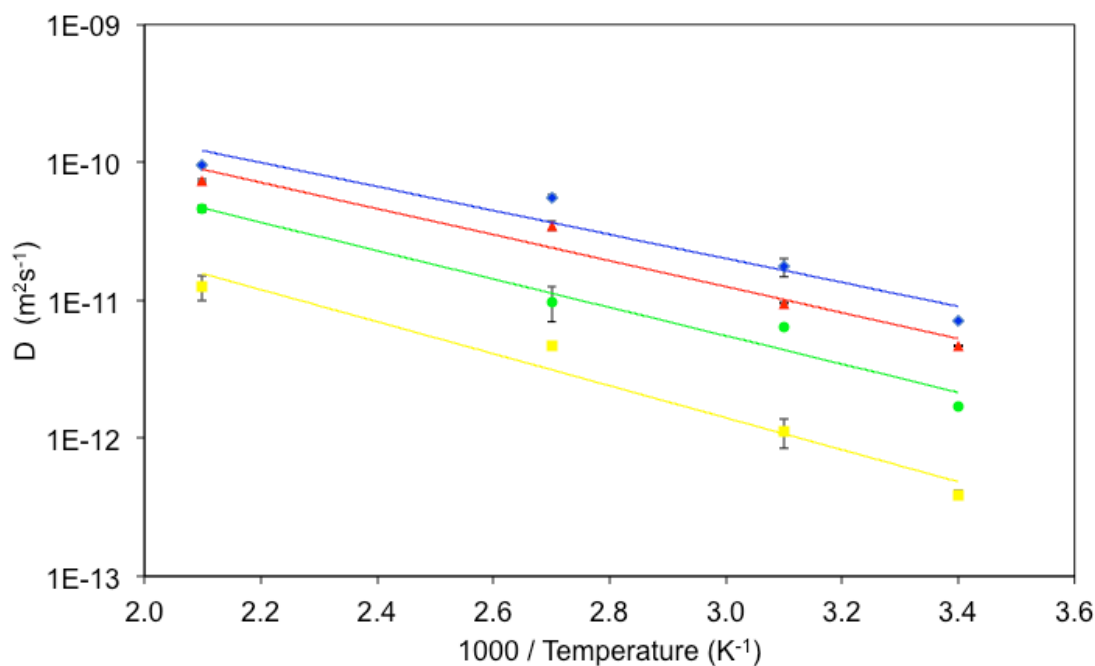


Figure 7.14: FRT Diffusion coefficients at temperatures between 25 - 200 °C for zeolite F.CP914 (♦), F.CP914C (▲), ZSM 55 (●), and ZSM 280 (■)

From the Arrhenius-plots developed in Figure 7.14, it was possible to calculate the activation energies and pre-exponential factors for diffusion. In Table 7.4, the activation energies for diffusion and the pre-exponential factors for all four zeolite samples are given. The activation energy of diffusion for the ZSM-5 zeolite samples was measured between 21.5 – 24.2 kJ mol^{-1} . These value are less than the literature value of 30.6 kJ mol^{-1} reported for tracer measurements of CO_2 diffusion in ZSM-5 at similar CO_2 molar concentration (Pitale *et al.*, 1988). This is an expected result as recent studies have shown that differences exist in diffusion parameters of complex zeolite systems where the substructure (defect structure) of the crystals offers a second diffusional resistance – a consideration detected by longer range (macro) measurements (Chmelik *et al.*, 2011; Maguire *et al.*, 2013).

Table 7.4: Diffusivity coefficients and activation energy (E_A) parameters of average FRT cycle

Zeolite	Temperature (K)	D ($m^2 s^{-1}$)	Pre-exponential factor ($m^2 s^{-1}$)	E_A ($kJ mol^{-1}$)
F.CP914	298	7.12×10^{-12}	6.82×10^{-9}	17.00 ± 0.50
	323	1.75×10^{-11}		
	373	5.62×10^{-11}		
	473	9.58×10^{-11}		
F.CP914C	298	4.67×10^{-12}	6.70×10^{-9}	18.00 ± 0.20
	323	9.50×10^{-12}		
	373	3.51×10^{-11}		
	473	7.38×10^{-11}		
ZSM 55	298	1.71×10^{-12}	5.51×10^{-9}	20.00 ± 1.50
	323	6.42×10^{-12}		
	373	9.79×10^{-12}		
	473	4.61×10^{-11}		
ZSM 280	298	3.91×10^{-13}	2.82×10^{-9}	22.00 ± 2.20
	323	1.11×10^{-12}		
	373	4.75×10^{-12}		
	473	1.24×10^{-11}		

When comparing diffusivity parameters of various techniques shown in the literature to those observed by FRT-ZLC measurements, it was promising to have established and exhibited similar results to other macroscopic techniques. Between 293 – 298 K, the activation energies predicted by Ahn *et al.*, based on Cahn electrobalance analysis of CO₂ diffusion in CaX as well as the gravimetric analysis of CO₂ diffusion into 5A studied by Kamiuto *et al.*, are approximately 16 and 30 $kJ mol^{-1}$ respectively (Ahn *et al.*, 2004; Kamiuto & Goubaru, 2006). These values compare well with the FRT-ZLC predicted measurements of 17 and 22 $kJ mol^{-1}$ for zeolites F.CP914 and ZSM 280 at similar temperatures. The results also compare well to the diffusivity coefficient results reported by Yucel and Ruthven who made use of the Cahn microbalance to measure CO₂ diffusion in zeolite 5A. Between the temperature range 298 – 373 K, their diffusivity coefficients were found to be between $1 - 3 \times 10^{-12} m^2 s^{-1}$ while the measured values for this study in the same temperature range for ZSM 55 were between $2 - 10 m^2 s^{-1}$ (Yucel & Ruthven, 1980).

Having evaluated the diffusion parameters analytically using Maple, it was possible to determine the Henry's constants in accordance with the mathematical model for ZLC analysis postulated by Crank (Crank, 1979). The temperature dependence of the Henry's constants for each zeolite can be observed from Figure 7.15. As is expected, the Henry's constants exhibit an inverse proportionality to the rise in temperature. Figure 7.15 also shows that the affinity of CO₂ to the zeolite samples is given by the following order:

$$\text{F.CP914} > \text{F.CP914C} > \text{ZSM 55} > \text{ZSM 280}$$

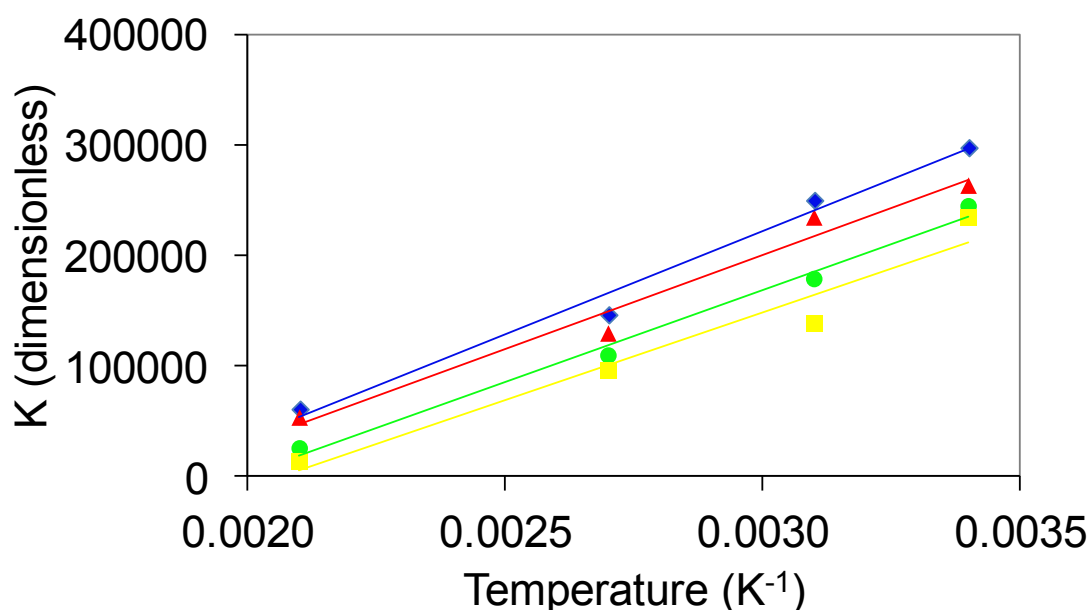


Figure 7.15: FRT Henry's constants over 25 – 200 °C temperature range for zeolite F.CP914 (♦), F.CP914C (▲), ZSM 55 (●), and ZSM 280 (■)

These results suggest that FRT is a viable method for the evaluation of CO₂ diffusivity within the zeolite pore network, as the measured diffusivity parameters compare favourably with those found in the literature.

7.2. Summary

A novel feature of the FRT system has been utilised to enable the measurements of sorption capacities and diffusion coefficients of CO₂, used to analyse the total basicity of commercially available zeolites in one experiment. The bi-modal operation of the FRT system was applied to analyse the total basic density of the zeolite samples by

measuring the total number of basic sites while the ZLC method was utilised once again to analyse the sorption dynamics of CO₂ and determine the diffusivity coefficients.

The adsorption capacities of the zeolites correlated with their SiO₂/Al₂O₃ ratios as was to be expected. The sensitivity of the FRT system was also able to determine the differences in the adsorption capacities of zeolites with similar SiO₂/Al₂O₃ ratios but varying physical characteristics. This same conclusion was to be found when measuring the diffusion coefficients of the various samples. The results for both analysis modes compared positively with the literature, suggesting further insights into FRT's ability to measure the strength and nature of the basic sites is required.

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Chapter 8

FRT

Development & Optimisation

8.1. FRT Surface Area Characterisation

The characterisation of particulate materials by way of understanding their surface properties is a fundamental area of fine particle engineering. Being able to quickly and accurately characterise surface properties such as porosity, particle size, and surface area, are key determinants for industrial scale production processes and the manufacture of a wide range of consumer goods. To date, the most widely employed technique for the investigation of the surface area and pore structure of porous materials lies with the static volumetric method of measuring nitrogen adsorption isotherms at cryogenic temperatures. Analysing sample materials is performed by measuring nitrogen adsorption and desorption at a constant temperature while incrementally dosing the sample to increase the nitrogen partial pressure. A review of the different techniques employed in surface characterisation of porous materials is given in Chapter 2.2. Previous studies of FRT surface area characterisation have also highlighted its ability in accurately measuring nitrogen sorption isotherms of low surface area materials below $2 \text{ m}^2 \text{ g}^{-1}$ – a well noted drawback of the static volumetric method is its inaccuracy in measuring such materials (Palmer *et al.*, 2011). As such, process optimisations of FRT surface area measurements were investigated to increase the accuracy and efficiency of the technique.

Chapter 8.4 compares and contrasts the data of the surface area measurements of intermediate and high surface area aluminium oxide with static volumetric, nominal, previous FRT, and optimised FRT values.

8.1.1. FRT Process Optimisation

8.1.1.1. Temperature Effect

The modification of the FRT experimental setup for the measurement of surface areas was undertaken to minimise the temperature fluctuations that occurred in previous studies. In the past, even with the presence of a dummy reactor, some of the experiments experienced temperature fluctuations between the gas lines submerged in the liquid nitrogen dewar due to the evaporation of liquid nitrogen. Being able to refill and control the liquid nitrogen level during experimentation was deemed impractical and needed addressing as a weakness of the technique. It was also found that the improper insulation of the gas lines connected to the system affected the accuracy of the generated response profiles. Such temperature fluctuations play a significant part in the viscosity of the gas streams running through the flux response apparatus. Ever since the pioneering work of Maxwell on kinetic theory, experimental results have confirmed the dependency on the viscosity of a gas to its absolute temperature (Viswanath *et al.*, 2006).

$$\eta \propto \left(\frac{MT}{\sigma^2} \right)^{1/2} \quad 8.1$$

Equation 8.1 shows the relationship between the viscosity and temperature of a gas where, η is the viscosity of the gas, M is the molecular mass, T is the absolute temperature, and σ is the hard sphere diameter. As the temperature increases, the frequency of intermolecular collisions are increased, which in turn increases the random motion of the gaseous molecules. The stronger the random motion, the stronger the resistance to the bulk motion of flow. Thus the viscosity of gases increase as temperature increases and is approximately proportional to the square root of temperature (Group, 2005).

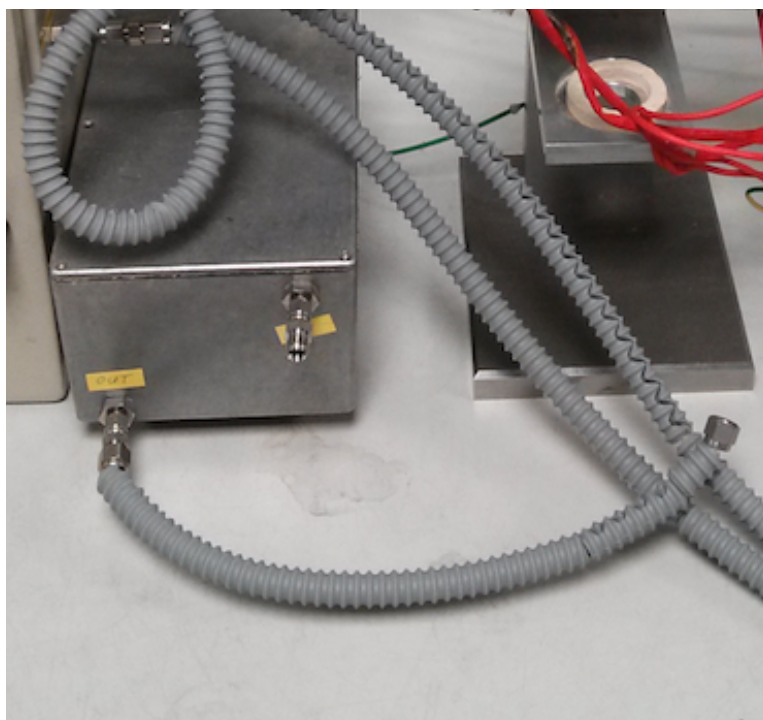


Figure 8.1: Modified silicone oven shelf guards used to insulate FRT gas lines

Figure 8.1 shows the insulating material used as a thermal jacket for the gas lines. The silicone tubes aided the reduction of the thermal noise exhibited in FRT profiles by insulating the gas lines connected to the system apparatus and providing a stable temperature boundary between the atmospheric temperature and cryogenic temperature for the gas lines at the entrance and exit of the dewar.

8.1.1.2. Viscosity Effect

The viscosity phenomena exhibited in FRT profiles when two different gas species are introduced into one stream is a unique feature of the technology and has been used in the past as a technique in perturbation viscometry. In the present study, modifications to the experimental setup were undertaken to investigate FRT's ability in performing fast turnaround measurements of sorption isotherms accurately. In order to establish the mode of operation whereby a quick succession of perturbations (dosing) could be performed across the entire isotherm range, the viscosity effect would need to be minimised. Previous FRT surface area measurements ran with 3 – 5 dynamic cycles, each lasting for 20 mins. Taking into consideration that the dynamic cycles needed to be performed at at least five partial pressures, the total run time excluding the time taken to regenerate the samples after each cycle would end up lasting over 8 hours. Reducing the

impact of the viscosity effect was a key feature that led to the application of step-wise perturbations and the improvement in process turnarounds.

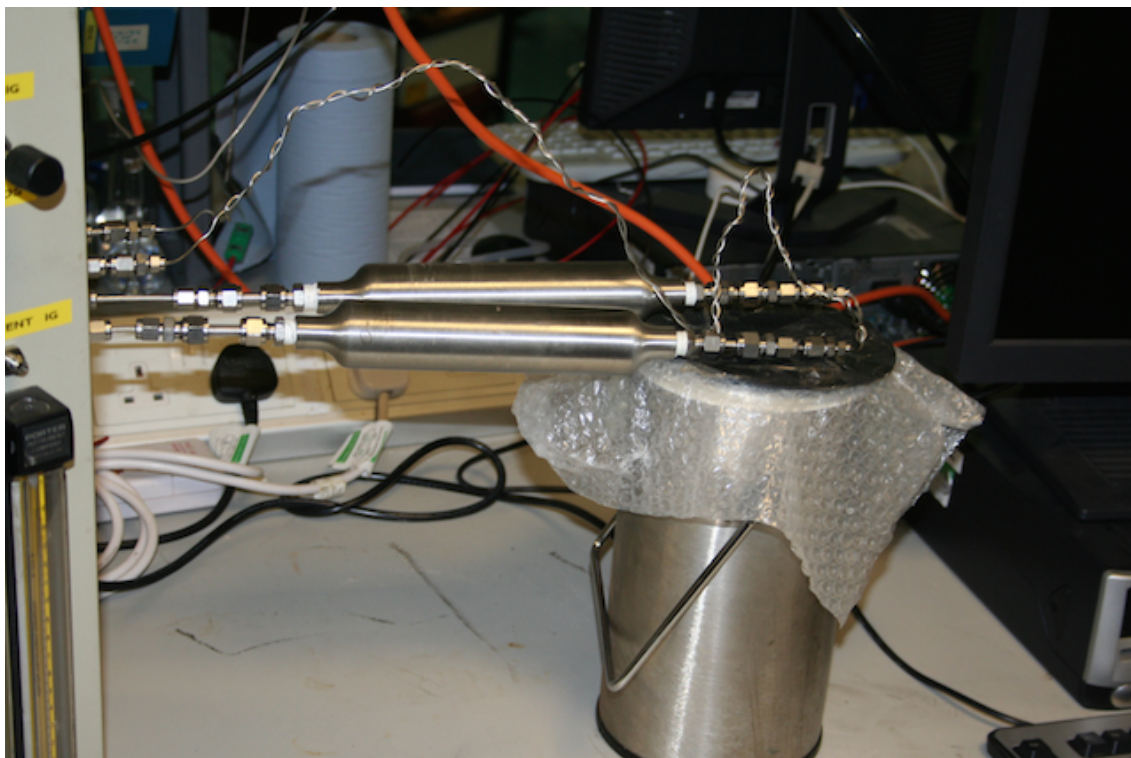


Figure 8.2: FRT surface area system modification with sample cylinders attached for the minimisation of the viscosity effect

Figure 8.2 displays the sample cylinders used in the minimisation of the viscosity effect. The purpose of the vessels was to create a dead volume to effectively dilute the gas mixture. As a consequence of this, the diluted viscosity effect would be measured as a drift in the baseline detected by the DPT. Process turnaround times for the entire composition range were shown to last between 25 – 42 mins dependent on the number of step-wise perturbations carried out.

8.1.2. Material Characterisation

8.1.2.1. Static Volumetric Method

A Micromeritics Tristar 3000 surface analyser was used to investigate and compare the nitrogen adsorption isotherms at 77 K with the values measured using the FRT techniques. It was also possible to compare the analysed data with the nominal values provided by the sample manufacturer. Appendix E contains the measured adsorption

isotherms of the aluminium oxide samples. A noticeable conclusion from the data was the classification of the samples as being Type IV isotherms. The region attributed to unrestricted monolayer-multilayer adsorption typically between nitrogen partial pressures of 0.2 – 0.5 was exhibited, along with the hysteresis loop in the high partial pressure region between 0.5 – 1.0. Analysis of the shape of the hysteresis loop also showed that the steepness of the desorption branch decreased with decreasing surface area, a common result reported on in the literature (Sing, 1985). Table 8.1 summarises the surface area results of the aluminium oxide samples.

Table 8.1: Surface properties of aluminium oxide measured by the static volumetric method

Sample	$S_{\text{BET}} (m^2/g)$	$S_{\text{Langmuir}} (m^2/g)$
Aluminium oxide – Intermediate (I-Al)	102.17	140.93
Aluminium oxide – High (H-Al)	192.85	265.65

8.1.2.2. FRT Profiles

Investigation of the aluminium oxide samples was carried out using the standard step approach shown in previous studies alongside the viscosity minimising approach for ultra fast isotherm measurements. Both methods involved a dynamic approach to the measurement of sorption isotherms at cryogenic temperatures. The first approach consisted of carrying out a series of step perturbations for a number of dynamic cycles. Determining the experimental parameters needed to carry out the investigation was concluded upon completion of a set of preliminary experiments. These parameters included the determination of the sorption times, nitrogen partial pressures and the number of dynamic cycles. The sorption times for each dynamic cycle consisted of the addition of the nitrogen perturbation gas for 8 *mins* to analyse the partial adsorption and the removal of the same gas for 12 *mins* to analyse the partial desorption. The second approach involved the successive step-wise dosing of the sample with the nitrogen perturbation gas through the BET composition range. Preliminary experiments carried out to determine the length of time required for each dosing cycle indicated that 3 *min* cycles were sufficient to investigate the aluminium oxide surface properties. Equation 8.2 details the BET equation needed to transform the isotherm points to be able to work out the surface area,

$$\frac{1}{W[(P_o/P) - 1]} = \frac{1}{W_m C} + \frac{(C - 1)}{W_m C} \frac{P}{P_o} \quad 8.2$$

where, W is the weight of nitrogen adsorbed at a given partial pressure, W_m is the weight of gas to give monolayer coverage, and C is a constant related to the heat of adsorption. A linear relationship between $1/W[(P_o/P) - 1]$ and P_o/P is required to obtain the quantity of nitrogen adsorbed. Experimental data has shown that this linear portion of the curve is restricted to a limited portion of the isotherm, generally between 0.05 – 0.30 (Lowell *et al.*, 2004). Consequently, the dynamic experiments were carried out at five nitrogen partial pressures within the stated range of operation.

Classic FRT

An expanded view of the partial adsorption and desorption in the first dynamic cycle of the high surface aluminium oxide measurements is shown in Figure 8.3. The full set for the N_2 partial pressure in question can be seen in Figure 8.4. The key effects are, the nitrogen partial adsorption peak; the resultant viscosity effect caused by the nitrogen perturbation into the helium carrier gas; the nitrogen partial desorption peak; and finally, the viscosity effect caused by the composition change of the switch from a nitrogen/helium mixture to purely helium gas.

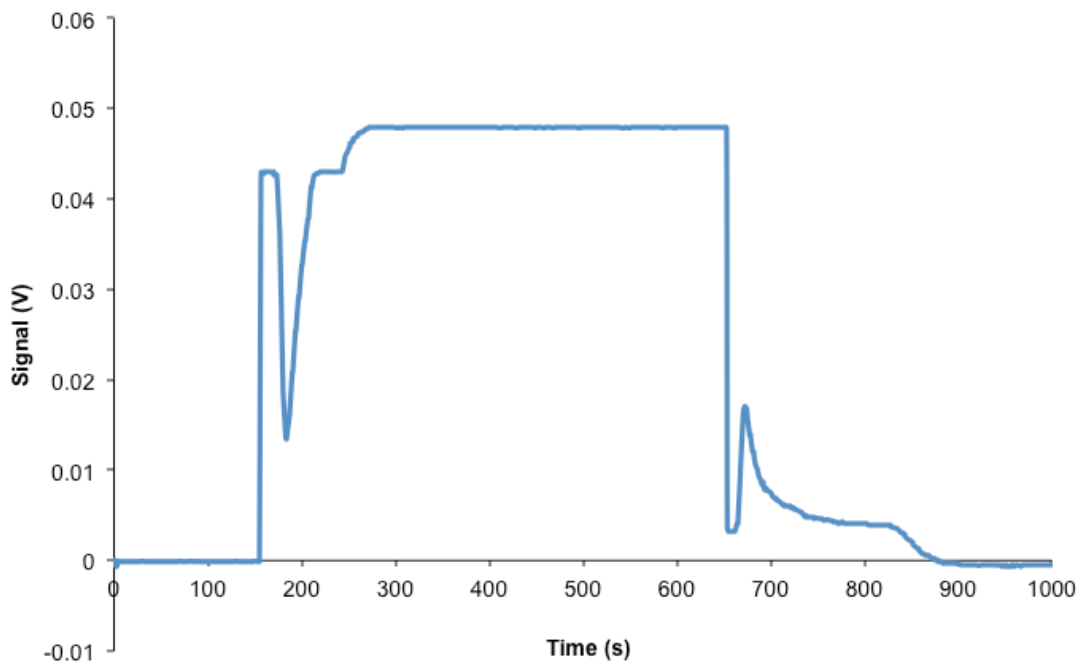


Figure 8.3: FRT profile of first dynamic sorption cycle for N_2 sorption on aluminium oxide at 77 K

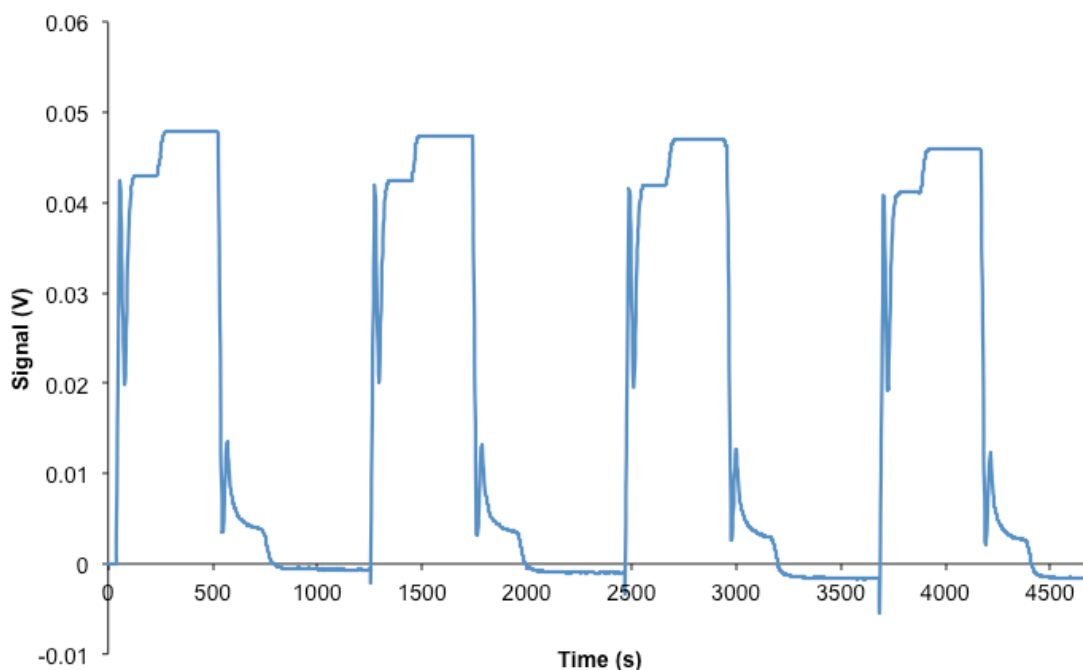


Figure 8.4: Complete FRT profile for N_2 sorption on high surface area aluminium oxide at 77 K

On addition of the nitrogen perturbation stream, a sharp downward spike in the flux response signal is noticed as is shown in Figure 8.4. The pressure regulators in the apparatus govern these signal spikes. The spike below the baseline is attributed to the under-pressurisation of the BPR for the perturbation gas. Conversely, a spike in the opposite direction above the step change would be attributed to an over-pressurisation of the BPR. A minor shift in the baseline after each dynamic cycle is also observable. This is due to a minor imbalance in the Wheatstone bridge of the FRT apparatus. Such imbalances can be caused by the way in which the test sample is held in place in the reactor; the over-tightening of fittings; incorrectly setting the pressure regulators upstream and downstream to name but a few of the possibilities. These are small imbalances within the apparatus, however, it should be noted that the peaks above or below the perturbation step change and the baseline drift pose insignificant in displacing the accuracy of the sorption profiles. Experimental modifications have been undertaken to negate such effects. The effect of thermal noise caused by the temperature gradient and fluctuations between ambient (298 K) and cryogenic (77 K) temperatures as a result of the evaporation of liquid nitrogen from the dewar was minimised by interlocking the system and reference side gas lines and insulating the lines using silicone thermal

guards. The opening to the dewar was also covered with bubble wrap and a Viton® rubber sheet to minimise the temperature fluctuations experienced by the reactor.

The sorption profiles obtained from the flux response profiles are extremely valuable and useful in evaluating the moles of gas adsorbed and desorbed during the test runs. The sorption phenomenon was quantified by calculating the area of the sorption peaks, representative of the number of moles of adsorptive gas involved in the sorption process. Determining the areas under the partial adsorption and desorption peaks was carried out using curve-fitting software (CurveExpert 1.4). By converting the number of moles to a volume per mass of adsorbent, an adsorption isotherm could be constructed. The number of moles of the sorption peaks was calculated using equation 8.3,

$$\frac{N_x}{N_o} = \frac{A_x}{A_o} \quad 8.3$$

where, N_o is the moles of adsorbent gas produced by a known perturbation, A_o is the area produced by the known perturbation, N_x is the moles of the sorption peak, and A_x is the area of the sorption peak. Altogether, the dynamic sorption profiles are able to represent the amount of sorption against the number of dynamic cycles, thereby displaying the sorption behaviour specific to each individual cycle as well as displaying the dynamic equilibrium present within a set of dynamic sorption cycles.

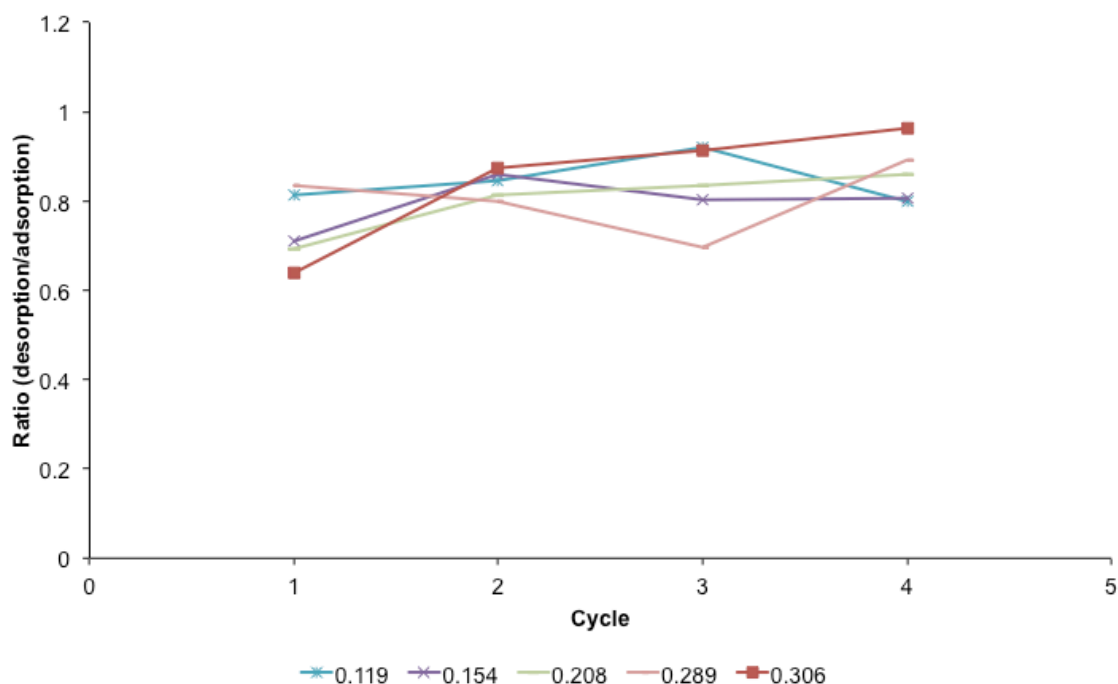


Figure 8.5: Dynamic sorption profile for high surface area aluminium oxide at specified N_2 partial pressures

Figure 8.5 illustrates the dynamic sorption profile for the high surface area aluminium oxide that represents the ratio of the quantity of nitrogen desorbed to the quantity adsorbed for each cycle. The profile is extremely useful in showing the sorption process in real time. When analysing the extent of adsorption and desorption, it was observed that the ratios remained relatively consistent across the cycle range. This suggests that the system was able to reach a quasi-steady state equilibrium. Analysis of the relative standard deviation also showed an average of only 8.4 %. The slight variation in the ratios across the composition range shown in Figure 8.5 highlights this fact.

Figure 8.6 shows the adsorption and desorption profiles of the test runs carried out at the specified partial pressures. The sorption values are shown to increase with increasing nitrogen partial pressure as is expected. The profiles also indicate that the surface coverage of the aluminium oxide approaches a steady state value as the experiment reaches the final cycle, implying complete coverage of the sample.

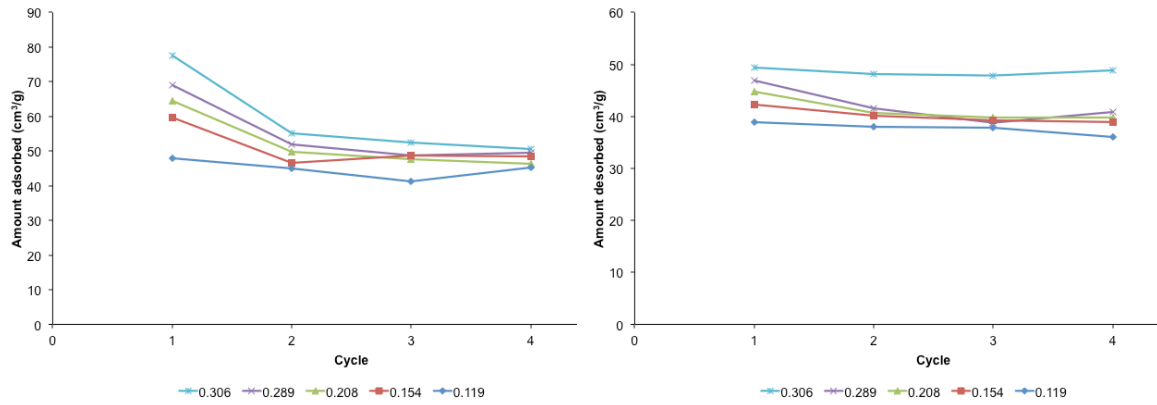


Figure 8.6: Comparison of sorption profiles for high surface area aluminium oxide at specified N₂ partial pressures.

From the adsorption profile in Figure 8.6, it is clearly shown that the values for the first cycle were significantly larger than the values for subsequent cycles. In understanding these phenomena, it is important to first consider the assumptions of the Langmuir model and the subsequent developments with particular emphasis placed on the Temkin adsorption isotherm. The assumptions of the Langmuir model stipulate that the adsorbate is localised on the surface of the adsorbant without lateral interactions and that adsorption takes place on a homogeneous crystal surface exhibiting only one kind of ‘elementary space’ i.e. a region of uniform adsorption energy (Kumar *et al.*, 2010). The limitation of the Langmuir model has constricted its usefulness in describing a real surface, as the uncertainty of the effect of ignoring lateral interactions is a major concern. The Temkin adsorption isotherm offers a solution to the series of results shown in FRT.

Temkin postulated that a fall in the heat of adsorption was apparent in the adsorption of gases onto heterogeneous surfaces. The isotherm was developed from the Langmuir isotherm, showing that the heat of adsorption decreased linearly with surface coverage. This effect was based on the repulsive forces on a uniform surface or from surface heterogeneity (Group, 2005). Research conducted by Rudzinski *et al.* found that the heat of adsorption curves calculated for the Temkin equation showed a decreasing function when plotted versus the adsorbed amount (Rudzinski *et al.*, 1996). Equation 8.4 is illustrative of the Temkin isotherm:

$$\theta = (RT/\alpha) \ln (AP) \quad 8.4$$

where, θ is the surface coverage, R is the universal gas constant, T is the absolute temperature, α and A are isotherm constants, and P is the pressure of the gas. The Temkin isotherm assumes adsorption sites have an intrinsic distribution of adsorption energies and an increasing electrostatic interaction is present between the dipoles at the interface with increasing concentration (Bockris *et al.*, 2001; Eriksson *et al.*, 1997; Yang, 1993). Equation 8.4 is derived by dividing the adsorbant surface into a number of uniform elements, on each of which the heat of these elements obeys the Langmuir isotherm (Group, 2005).

Incorporating these findings in the analysis of nitrogen adsorption isotherms and surface area determination of adsorbents, two methods of analysis were prescribed in analysing the experimental data. One method used the experimental data from the first cycle alone while the second method involved using the average of cycles 2 to 4.

Ultra fast FRT

An example of the flux response profile for the successive step-wise dosing of the aluminium oxide with N_2 perturbations is presented in Figure 8.7. Minimising the viscosity effect was key to the new investigatory technique. The empirical evidence strongly correlates with the schematic profile generated for the investigation of ultra fast isotherms reported earlier in Chapter 5.4. Five successful perturbation doses were performed between the BET composition range. The small spikes shown in the sorption profile upon switching in of the perturbation can be attributed to the over pressurisation of the BPR. Highlighted in Figure 8.7 are the measured adsorption peaks that were integrated to provide the moles of N_2 adsorbed onto the surface of the test sample required for the construction of the N_2 isotherm and the evaluation of the total surface area.

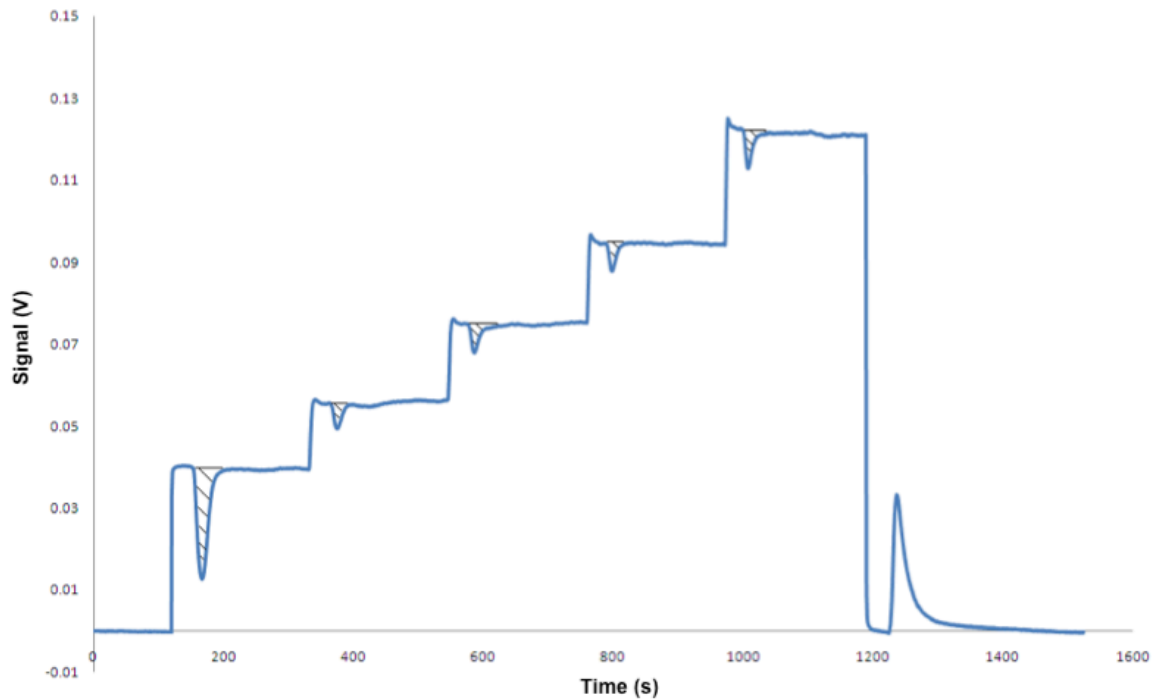


Figure 8.7: 5-step N_2 isotherm measurement of intermediate surface area aluminium oxide

Being able to accurately control the successive perturbation steps was performed easily through the use of the EMFCs. The digital controllers provided a clear advantage in the speed of process turnover and were pivotal in the actualisation of the process. The length of the entire process lasted no more than 25 mins.

8.1.2.3. Surface Area Determination

First cycle and average cycle analysis for the classic FRT system were used to evaluate the surface area of aluminium oxide. The ultra fast mode of operation took into account the total adsorption value from the measurement of all cycles. The result of the analysis was compared to the nitrogen adsorption isotherms determined through the use of the static volumetric method. A Micromeritics Tristar 3000 surface analyser was used for this comparison. Figure 8.8 shows a comparison, based on first cycle analysis, of the nitrogen isotherms for aluminium oxide using the FRT and static volumetric method. Figure 8.9 shows the same comparison but using the FRT method of average cycle analysis this time.

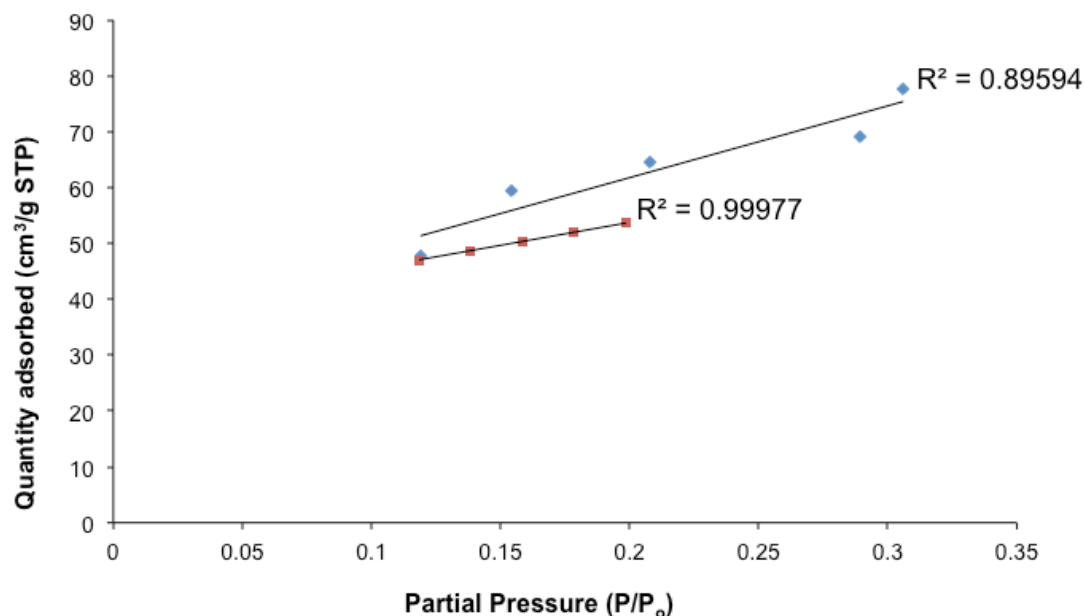


Figure 8.8: Comparison of FRT based 1st cycle analysis of N₂ adsorption isotherms at 77 K with the static volumetric method – FRT (♦), Micromeritics Tristar 3000 (■)

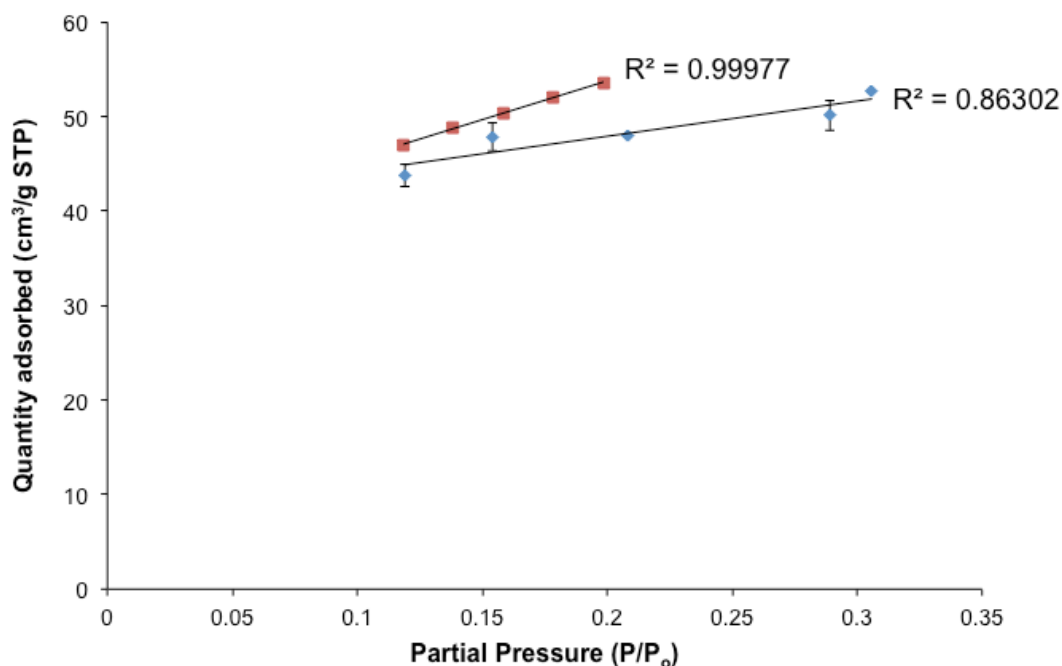


Figure 8.9: Comparison of FRT based average cycle analysis of N₂ adsorption isotherms at 77 K with the static volumetric method – FRT (♦), Micromeritics Tristar 3000 (■)

Figure 8.8 shows the FRT measured nitrogen isotherms are higher than those measured by the static volumetric method. The opposite is observed in the case of the average cycle analysis in Figure 8.9. Here, the FRT measured isotherms show a greater

consistency with the results from the static volumetric method. This observation is expected, as the levels of nitrogen uptake, shown in the dynamic profiles in Figure 8.6 are consistent over cycles two through till four. This consistency has been attributed to the system reaching a state of quasi-equilibrium. Such results would compare more favourably to the static volumetric method than the levels obtained from the first cycle alone. Thus, it would be expected and is not surprising that the data from the first cycle would generate an isotherm above that measured by the static volumetric method. Research presented in the literature into the differences between static and dynamic techniques for the measurement of nitrogen adsorption isotherms at 77 K yielded some interesting conclusions, similar to the present study when reviewing the FRT derived experimental results. Data from comparing the carrier gas method to the static method showed that the results of the adsorption isotherms for adsorbents with narrow micropore structures are positioned lower for the dynamic method in comparison to the static (González-González *et al.*, 2009). This is an important observation when analysing the process procedures and the differences therein for both techniques. It is worth considering that commercial static volumetric systems operate under ultra high vacuum conditions while FRT operates *in situ*. The differences in both techniques shall be highlighted further when analysing the BET derived surface areas.

The BET models for the nitrogen adsorption isotherms at 77 K of both FRT systems are shown in Figure 8.10 and Figure 8.11. Figure 8.10 shows the single cycle data while Figure 8.11 shows the multipoint data. Although both figures displayed a high linear regression for their respective BET models, a distinct advantage in the process control and overall accuracy of the experiment is displayed for the multipoint method where digital EMFCs were utilised. The classic FRT method suffers from lower flowrate control of the N₂ perturbations when using the MFCs, with its R² coefficient being equal to 0.9742 in contrast to 0.9969 displayed for the multipoint technique.

The high linear regression displayed by both methods corroborates the previously stipulated assumption of the presence of multilayer adsorption on the surface of the test sample as is expected for Type IV isotherms. Using these results, it was possible to derive the BET parameters needed to calculate the BET surface areas to compare with previous studies and the static volumetric method.

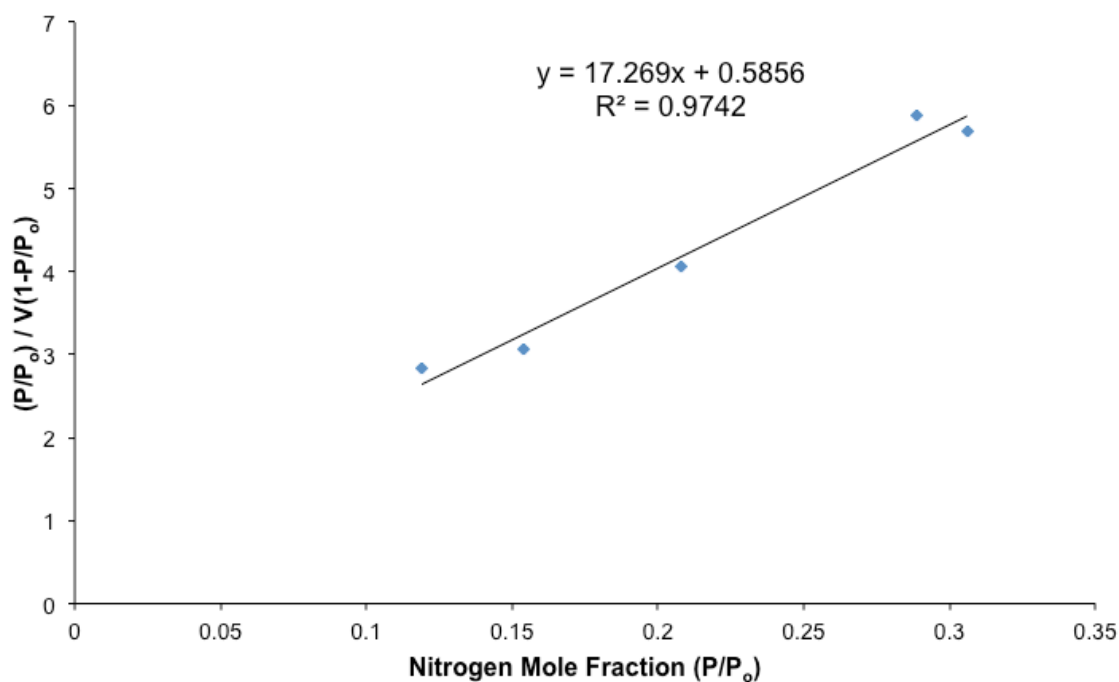


Figure 8.10: BET Model – Single cycle analysis of high surface area aluminium oxide at 77 K

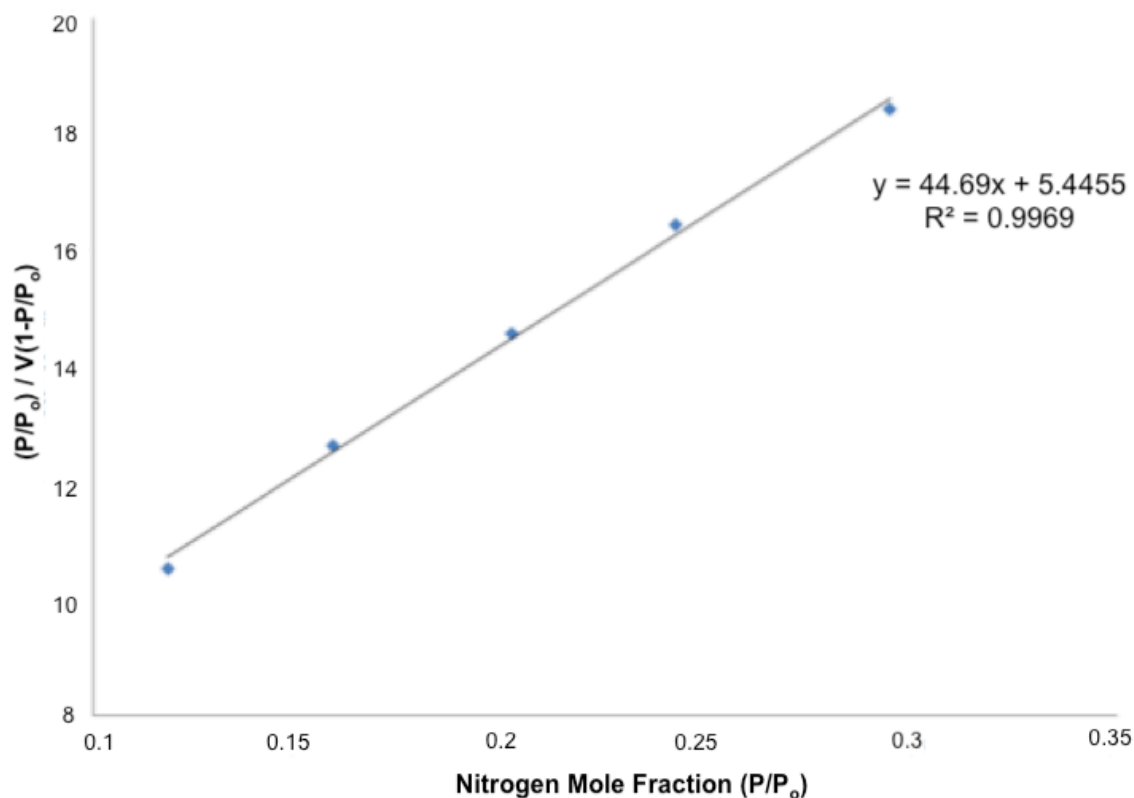


Figure 8.11: BET Model – Multipoint analysis of intermediate surface area aluminium oxide at 77 K

Table 8.2 gives the evaluated BET surface areas for the aluminium oxide samples for the various techniques. The measurement technique and the analytical method used by the manufacturer to obtain the nominal surface area are unreported.

Table 8.2: Comparison of BET surface areas

Aluminium Oxide Sample	Classic FRT Single Cycle S_{BET} (m^2/g)	Multipoint FRT S_{BET} (m^2/g)	Static Volumetric S_{BET} (m^2/g)	Nominal Surface Area (m^2/g)
I-Al	93.44	100.63	102.17	100.00
H-Al	243.84	257.95	192.85	255.00

A strong agreement is found between the FRT derived surface areas and the nominal surface area of the test samples as is shown in Table 8.2. It is also reassuring to find that the progress made in the ultra fast FRT experimental technique yielded positive results with excellent correlations to the nominal values. Measuring the intermediate and high surface area aluminium oxide samples with the multipoint method resulted in surface areas of 100.63 and 257.95 m^2/g in comparison with the nominally derived values of 100.00 and 255.00 m^2/g . When comparing the manufacturer's data with the surface areas measured using the static volumetric technique, there is less of an agreement between the values. It is useful to revisit the underlying features of the various methodologies to obtain a better understanding of the results.

The main difference between the static and dynamic techniques of surface area determination consists within the time interval of operation. Consequently, both methods work on a different equilibrium basis. Commercial static volumetric systems operate at an equilibration point defined as being when the pressure change per equilibration time interval is less than 0.01 % of the average pressure during the interval (Micromeritics TriStar 3000) and are said to develop fully equilibrated isotherms. FRT measures the partial sorption on the surface of the adsorbent by operating under the assumption of a continuous equilibrium (dynamic). This allows for quicker analysis of test materials under industrial conditions. With the adoption of the multipoint adsorption technique with the continuous adsorption cycles, the process time is sped up considerably. The shift from static to dynamic methods of analysis has become more important over the years as a result of the inherent advantages that exist in comparison to static methods (Thielmann, 2004). A key advantage in the use of FRT other than its ability to analyse *in situ* measurements is that the system needs no calibration, thereby

reducing causes for error in experimental approaches that directly affect the accuracy of the quantity of the gas adsorbed or desorbed. Static volumetric techniques require precise calibrations of the manifold temperature and volume that play a direct role in effecting the accuracy of the calculated gas sorption quantities. Criticisms of the FRT experiment are focused on the temperature control of the system stemming from the control of the liquid nitrogen level in the dewar. The modification of the system with the silicone insulation tubes attempted to minimise the temperature fluctuations experienced by the system gas lines.

8.2. FRT Dynamic Parallel Performance Testing (DPPT)

Further developments to the FRT technique were explored to develop a working system capable of providing comparative measurements of test materials operating simultaneously. To build the DPPT system, it was necessary to modify the perturbation switching procedure to incorporate the additional reactor required for the parallel performance. A modified two position injector six port valve was used to carry out the experiments. The modification to the experimental configuration of the perturbation switching valve was necessary to be able to interrogate the reference side of the Wheatstone bridge assembly alongside the system. Figure 8.12 and Figure 8.13 illustrate the construction of the modified valve and the derived flow path of the gaseous fluids. Considering the schematic of the experimental setup for the DPPT experiment detailed previously in Chapter 4.5, it is possible to understand the development of the technique.

The flow path presented in Figure 8.13 applies to the experimental gases used in the procedure. Ports 1 and 4 are open to the reactors present on both sides of the Wheatstone bridge. Ports 3 and 6 are connected to the NH_3 electronic mass flow controllers while 2 and 5 are open to the vent. Switching in the NH_3 perturbation stream was carried out following the progression of Position A to Position B shown in Figure 8.13. At Position A, the surfaces of the samples in the reactors are exposed to the argon carrier gas only as the perturbation streams' flow paths are directed towards the vent. Upon switching to Position B, the ammonia gas is directed towards the reactors where it is diluted by the carrier gas. At this point, the interrogation of the samples has begun

and ports 2 and 5 are open to the vent. A schematic illustration of the procedure is shown in Figure 8.14.

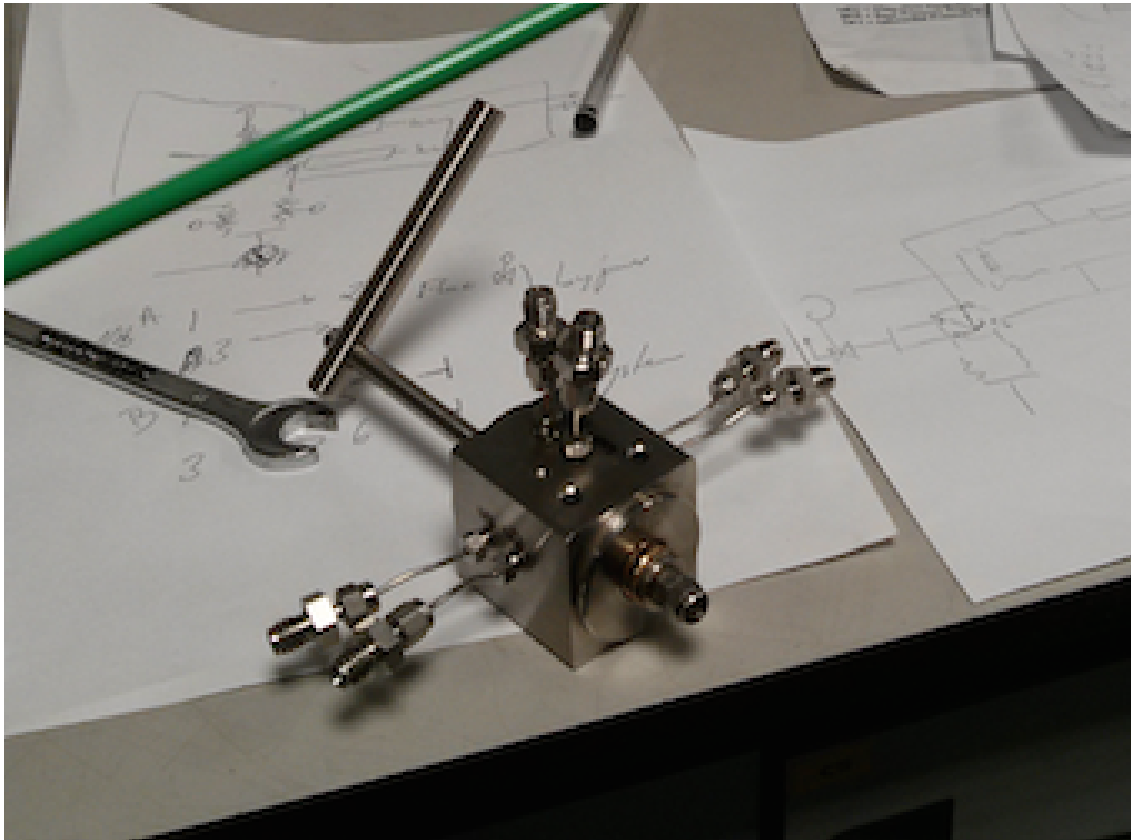


Figure 8.12: Modified switching valve

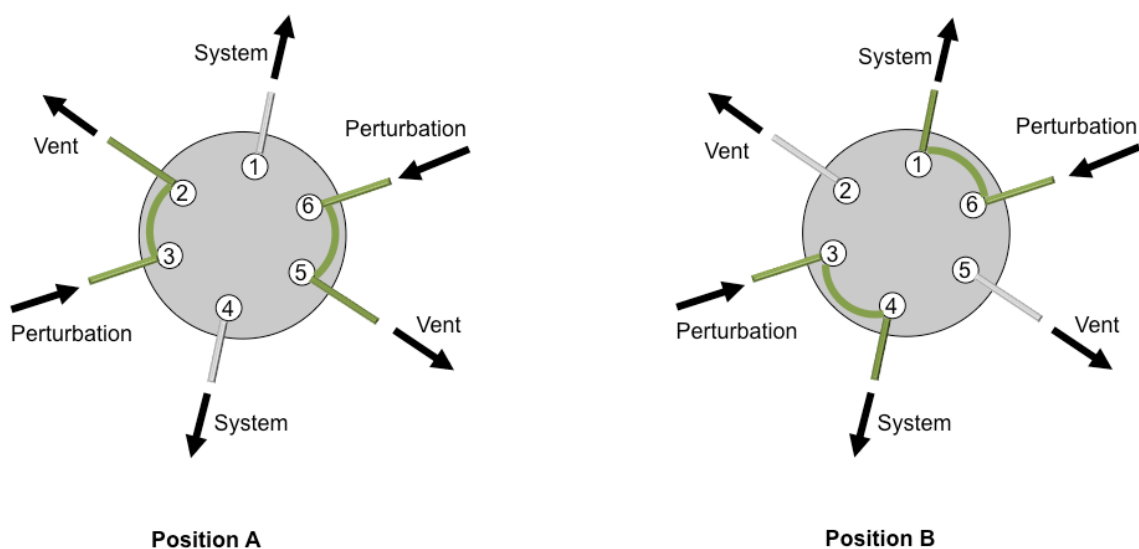


Figure 8.13: Switching valve flow diagram

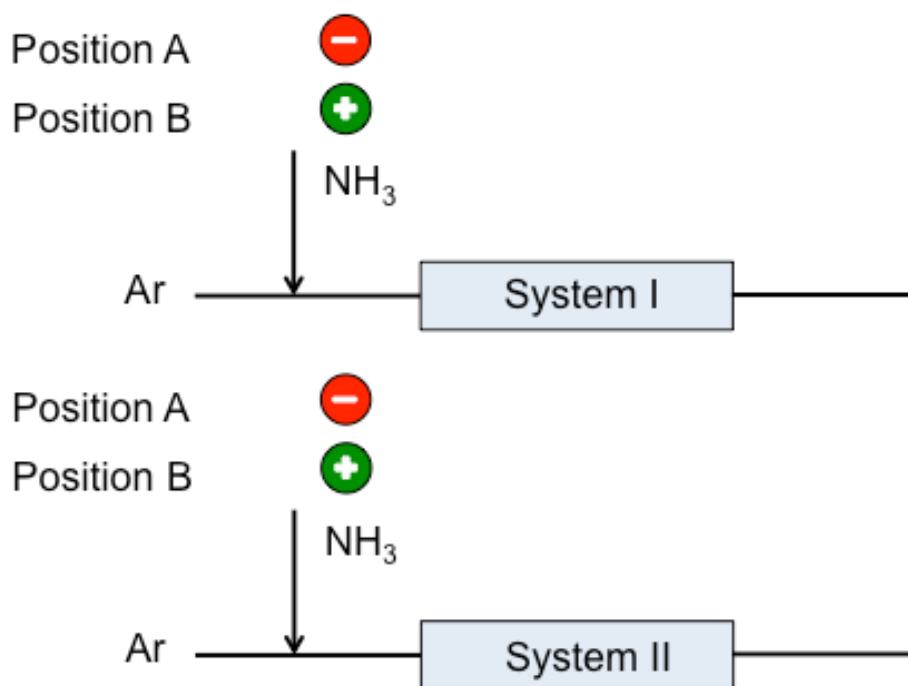


Figure 8.14: Schematic representation of perturbation switch

For the preliminary experiments reported here, a constant flowrate of ammonia was added to both sides of the system.

8.2.1.1. FRT Profiles

The results of balancing the new system are presented below. It is worth noting again that an equal flowrate between both sides of the bridge is an essential prerequisite for the system to operate. It was possible to make do with slight variations in the past as only fluctuations on one side of the bridge required accurate monitoring. Figure 8.15 depicts the flux response profile of the DPPT system with the same test samples. Both reactors were loaded with identical weights of zeolite sample ZSM 55 and subjected to 30 *mol-%* perturbation streams during the experimental interrogation. To achieve reputable data, one would expect a balanced profile to exhibit a straight line through the switching procedure.

In the case shown in Figure 8.15, the system yielded an unfavourable response to the perturbation switch. The increased signal during the perturbation signalled an unbalanced flowrate between the sides of the bridge. The necessary steps to correct the

balance of the system required injections of known flowrates into each side of the bridge to continually check the flux response.

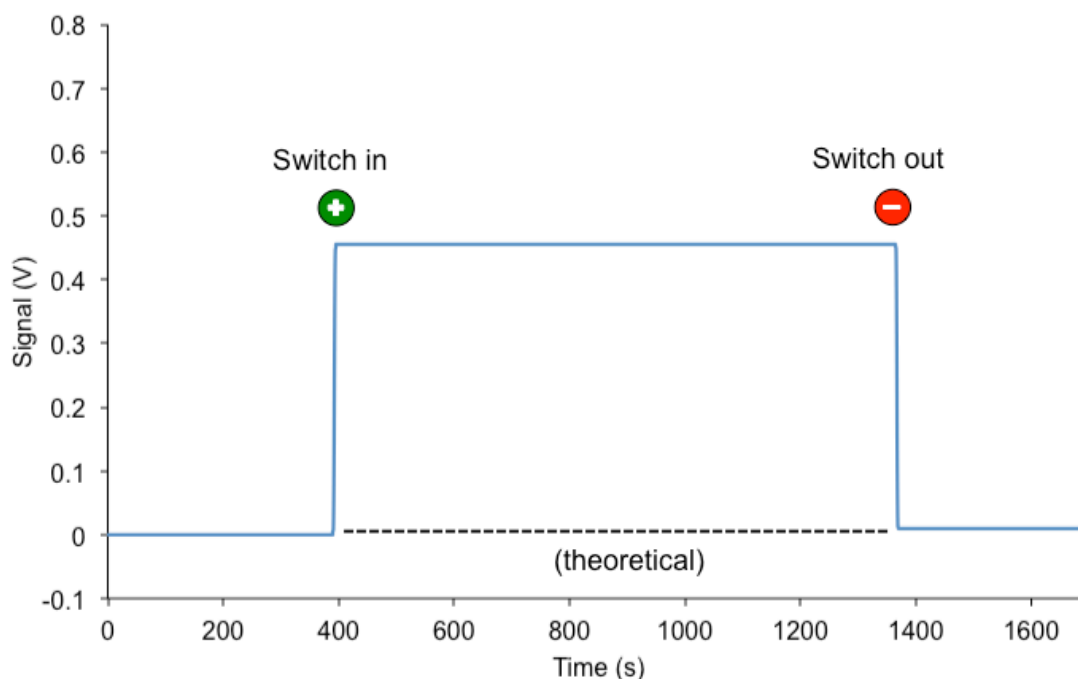


Figure 8.15: DPPT flux response profile showing the response to the perturbation switch

Possible sources of the error in the system can be attributed to a range of complications including; errors in the configuration of the modified switch valve, errors brought about by irregularities in the gas plumbing network, errors perpetuated from capillary irregularities within the up and downstream blocks, as well as dead volume errors within the system configuration. These errors all affect the flowrates between the bridge and consequently the Wheatstone balance, the critical driver behind the successful operation of the apparatus.

8.3. Summary

Optimisations carried out to increase the range and capabilities of FRT were explored and successfully implemented in the characterisation of surface areas of porous materials. Accessing the BET derived surface areas of aluminium oxide has been conducted in the past with a high degree of success (Palmer *et al.*, 2011). The advancement of the procedure necessitated for greater thermal precision when operating the FRT apparatus to offset system temperature fluctuations. Minimising the

temperature effects on the FRT measurements was embarked upon with greater control of the system temperature achieved through the insulation of the gas lines connected peripheral to the system casing. The second optimisation explored targeted the minimisation of the viscosity effect witnessed in flux response profiles during the mixing of gas species. The new apparatus was successfully constructed by implementing sample cylinders to provide the required dead volume, allowing for the complete measurement of the porous samples through the BET isotherm range in one experiment. This novel approach to surface area determination facilitated the progression of an ultra fast isotherm characterisation technique in FRT's modes of operation. The FRT derived surface areas compared well with the nominal surface area values provided by the manufacturer.

The significant capability of being able to directly compare the activities of two catalysts operating parallel to each other in one FRT experiment was proposed and explored as the final optimisation process. Building the new FRT rig included the incorporation of a modified 6-port switch in valve to control the perturbation flows to both reactors on each side of the system. Future studies into the development of the DPPT process are required to showcase the unique ability FRT offers in being able to compare and contrast different catalytic materials at the same time and in one experiment.

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Chapter 9

Conclusions and Future Work

9.1. Conclusions

The studies carried out in this thesis were aimed at characterising physicochemical properties through sorption measurements in order to build a fast, practical, efficient, and real time analytical tool for use as a bolt-on technology in catalytic material screening processes. As a characterisation tool, Flux Response Technology places itself as a robust *in situ* perturbation method capable of functioning competently at measuring a wide range of gaseous chemical reactions. The technique is based on a pneumatic Wheatstone bridge assembly made up of flow setting and sensing capillaries, and a very sensitive differential pressure transducer that conducts differential measurements between two gas lines. It is possible to apply the technique for use in any gaseous reaction involving a volumetric change in flowrate. The method is advantageous in its simplicity – measurements require no prerequisite system calibrations; experiments are conducted within defined reactor geometries; there are no limitations on sample masses; and the cost of construction is extremely inexpensive. The FRT method also utilises its unique ability in being able to analyse the composite chemical effects of the dual measurements of changes in the volumetric flowrate (pressure) and surface composition (molar concentration) carried out by the system, through the implementation of precise ‘delay lines’. Altogether, the efforts undertaken during the duration of the study were geared towards helping to bridge the pressure and materials gap present within catalyst characterisation.

Fulfilling the aims of this PhD were realised by addressing five applications of FRT, namely; applying and developing the Zero Length Column model to produce the FRT-ZLC technique of measuring diffusion in lab synthesised cordierite monoliths (Chapter 5); investigating the total acidity of commercially available zeolites of differing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios through the application of NH_3 sorption measurements (Chapter 6); exploring the co-current measurements of the basic properties and diffusion coefficients of commercially available zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios using CO_2 as a

probe molecule (Chapter 7); modifying the flux response system to minimise the viscosity effect, thus enabling ultra rapid measurements of nitrogen sorption on commercially available aluminium oxide at 77 K for surface area determination and modifying the flux response system to enable the dynamic parallel performance testing of catalysts operating simultaneously (Chapter 8). Overall, a high degree of success was achieved in accomplishing the aims and objectives of this study.

9.1.1. FRT-Zero Length Column (ZLC) Diffusion Studies

The modification and commission of the FRT-Zero Length Column diffusivity apparatus was successfully achieved in line with Objective I. The study of the diffusion coefficients of propane in the washcoat of cordierite monoliths is presented in Chapter 5. The method involved the analysis of the adsorption and desorption transients in the FRT dynamic cycle profiles and applying the ZLC method to evaluate the curves and extract the diffusion coefficients.

- i. The propane diffusion coefficients within the alumina/CeZrOx washcoat were successfully modelled using the FRT-ZLC method. The analysed sorption transients were evaluated and the diffusion coefficients showed a linear trend being directly proportional to temperature as would be expected. It was reassuring to observe the measured diffusivities of propane in similar materials by different techniques compared well with the FRT-ZLC method. At 373 K, the diffusivity within the cordierite washcoat was measured as $2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the FRT-ZLC (Sasegbon & Hellgardt, 2012). Molecular dynamic simulations of propane diffusion in 13X zeolite at 373 K were reported as being equal to $2.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for propane in silicalite-1 using the Wicke-Kallenbach method at 334 K (Granato *et al.*, 2010a; Sun *et al.*, 1996a).
- ii. By observing the dispersion corrected decay curves of the adsorption transient, FRT was able to measure the transport kinetics of the washcoat material without interfering concurrent desorption. Brandani *et al.*, observed that propane diffusivity in 13X is much smaller when measured with the ZLC approach as compared to PFG-NMR (Brandani *et al.*, 1995). Banas *et al.*, suggest that this may be due to the PFG-NMR technique returning intra-

crystalline diffusivities whereas ZLC experiments result in the observation of combined diffusion and desorption processes (Banas *et al.*, 2005). The FRT-ZLC technique appeared to yield satisfactory results as the dispersion corrected adsorption parameters of diffusivity compare particularly well with other macroscopic techniques (Karger & Ruthven, 1992).

- iii. The activation energies and pre-exponential factors for propane diffusion were determined from the generated Arrhenius-plots. The reported values show that the activation energies of diffusion for the adsorption transient were lower than those of the desorption transient. This is an expected result as the activation energies of the adsorption process are nearly always smaller than those of desorption (Ranke & Joseph, 2002). The activation energies for diffusion determined by other techniques to compare with this study displayed large variations between the measured values dependant on whether the technique operated microscopically or macroscopically in nature (Eic & Ruthven, 1989; Granato *et al.*, 2010b; Sun *et al.*, 1996b). The microscopic techniques generally result in high diffusivities and low activation energies for diffusion. Conversely, the macroscopic techniques generally have high activation energies for diffusion and diffusivity values as much as five orders of magnitude lower when compared with the microscopic techniques. It was reassuring to observe that the calculated activation energy for propane diffusion in alumina/CeZrO_x (extracted from the Arrhenius plot of diffusivities measured at different temperatures) compared well to that predicted by Granato *et al.*, based on theoretical molecular dynamics simulations of propane diffusion in 13X, and pulse field gradient nuclear magnetic resonance (PFG-NMR) data by Schwartz *et al.*, (Granato *et al.*, 2010b; Sasegbon & Hellgardt, 2012; Schwarz *et al.*, 1995).
- iv. The FRT-ZLC derived Henry's constants of the cordierite samples exhibited an inverse proportionality to temperature as was to be expected. The Henry's constants showed the affinity of propane to the samples followed the order where Sample 3 > Sample 4 > Sample 1 > Sample 2.
- v. A comparison of the diffusion coefficients for all the cordierite washcoat samples as determined by FRT showed a similar trend to that found using the Temporal Analysis of Products (TAP) methodology, however, it was evident that the values differed by approximately an order of magnitude – TAP results

of cordierite Sample 2 at 353 K were measured as being equal to $1.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ while FRT results for the similar material was determined to be equal to $1.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Maguire *et al.*, 2013). To evaluate the limits of effective diffusivity in the cordierite samples shown by both techniques, the sensitivities of the two methodologies were considered. TAP measurements are sensitive to the slowest diffusing species, operating within the Knudsen regime where the translational mobility of individual species is dominant. In the FRT-ZLC measurement of diffusivity, Fickian diffusion dominates and the transport diffusion coefficient accounts for the motion of species under the influence of a concentration gradient.

- vi. A marked advantage of the new technique is that FRT measures the diffusivity into the washcoats of the monoliths at the instance of propane reaching the bed of the material thereby reducing the error margins suffered by other chromatographic techniques in which dispersion through the column affects the accuracy of such results.

9.1.2. FRT Ammonia Sorption

The first part of Objective II was the analysis and determination of the total acidity of a set of commercially available zeolites, which was successfully achieved by investigating the dynamics of ammonia sorption using FRT and TPD results shown in Chapter 6 (Palmer *et al.*, 2011). The ability of FRT to measure the adsorption and desorption dynamics in the same experiment enabled the characterisation of the nature of the acid sites when compared with the TPD results. The total number of acid sites was quantified by evaluating the zeolite acid site densities. The experimental approach followed the administration of successive dynamic sorption cycles to measure the quantities of ammonia adsorbed and desorbed within a preset cycle time frame. The study determined the following conclusions:

- i. The integration of the areas underneath the FRT sorption peaks provided an accurate measure of the quantity of acid sites present at various temperatures. Evaluating the adsorption and desorption processes within the same experimental run also provided an accurate measure of the NH_3 sorption dynamics present within the system.

- ii. The effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios on the total number of acid sites was accurately described using FRT. The total number of acid sites was shown to decrease with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, where F.CP914C with the lowest ratio was measured to have the highest acid site quantity, while ZSM 280 with the highest ratio had the lowest measured acid site quantity. The acid site density of the zeolite samples depend on the availability of unoccupied sites, sites that become more prevalent as the aluminium content within the zeolite framework increases (Contescu & Schwarz, 1999).
- iii. The acid site quantity was measured with a high degree of accuracy for each zeolite sample using FRT. The results yielded reassuring comparisons with NH_3 -TPD results. The total acid site density for ZBV 23 was measured at 1.788 mol/kg using the FRT single cycle approach. TPD results for the same material produced an acid site density of 1.720 mol/kg . Zeolite ZBV 30 was also determined to possess acid sites of 1.637 and 1.423 mol/kg measured by FRT and TPD respectively.
- iv. A new method of determining the nature of the acid sites was successfully developed using FRT adsorption and desorption results coupled with NH_3 -TPD. A strong correlation existed between the strongly adsorbed FRT acid sites (correspondent to Brønsted-acid sites) and the desorption results from the TPD h -peak. Comparisons with the literature showed equally strong correlations between the FRT-TPD methodology and NH_3 -TPD. For example, ZSM 23 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$) was evaluated to contain strongly adsorbed acid sites equivalent to 0.786 mol/kg . Co-H-FER ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28.5$) was reported to have a value of 0.720 mol/kg (Resini, 2003). F.CP914 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 55$) with a value of 0.379 mol/kg compared well with H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 51$) with a value of 0.320 mol/kg (Kubo *et al.*, 2014). A positive correlation was also shown between ZBV 30 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) with a measurement of 0.619 mol/kg and H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) with a reported value of 0.700 mol/kg (Rodríguez-González *et al.*, 2007).
- v. The graph of the FRT evaluated acid site quantities were shown to level off to a constant value above 300°C . The approach to a constant value may represent the dehydroxylation of the hydroxyl groups in the zeolite samples to form Lewis acid sites. Similar studies in the literature have brought about comparable conclusions (Chen, 1996; Chen *et al.*, 1996).

9.1.3. FRT Carbon Dioxide Sorption

Having reported on the acid properties of the zeolite samples, it was deemed necessary to explore their basic properties using CO₂ as the probe molecule to complete the final part of Objective II. A second FRT system was successfully augmented for the measurement of CO₂ sorption dynamics across the zeolite range. The total number of basic sites was measured by analysing the basic site densities following the FRT successive dynamic cycle approach to measure sorption values within a set time period and is situated in Chapter 7. A unique and advantageous feature of FRT was also exhibited where the adsorption, desorption, and diffusivity parameters could all be measured within the same experimental window. As yet, other characterisation techniques cannot perform measurements to detect the adsorption, desorption, and diffusivity of material systems under isothermal conditions in the same experiment run. The key conclusions are as follows:

- i. The FRT measurements corroborated with the widely held view of the selectivity and adsorption capacities of zeolites for polar molecules being indirectly proportional to their SiO₂/Al₂O₃ ratio (Bonenfant *et al.*, 2008; Calleja *et al.*, 1998). The adsorption values of CO₂, relative to the basicity of the zeolite framework, were shown to be enhanced with the content of Al³⁺ ions due to the presence of a greater amount of exchangeable cations (Gargiulo *et al.*, 2014; Laspéras *et al.*, 1996). F.CP914C is shown to have the highest adsorption capacity (0.69, 0.66, 0.36, 0.08) *mol · kg⁻¹* for CO₂ while ZSM 280 consequently exhibits the lowest capacity out of the four zeolite samples (0.45, 0.38, 0.14, 0.01) *mol · kg⁻¹*.
- ii. The FRT quantified basic sites were measured with a high degree of accuracy and compared well with literature values for a variety of experimental techniques. The FRT derived values for F.CP914C (SiO₂/Al₂O₃ ratio = 20) at 50 °C, ZSM 280 (SiO₂/Al₂O₃ ratio = 280) at 50 °C, and ZSM 55 (SiO₂/Al₂O₃ ratio = 50) at 25 °C were measured at 0.72, 0.38, and 0.61 *mol/kg* respectively. Close agreements between FRT and a variety of techniques are shown where 0.79, 0.54, and 0.63 *mol/kg* were reported values for H-ZSM-5 (SiO₂/Al₂O₃ ratio = 27) at 50 °C, ZSM 5 (SiO₂/Al₂O₃ ratio = 280) at 40 °C, and HiSiv-3000

- (SiO₂/Al₂O₃ ratio = 46) at 25 °C for a step change response, gas chromatographic, and static volumetric method respectively (Bao *et al.*, 2011; Harlick & Tezel, 2003; Wirawan & Creaser, 2006).
- iii. A steep decrease in the adsorption capacities was observed between 50 and 100 °C that may be attributed to the loss of hydroxyl groups at increasing temperatures (Chester & Derouane, 2009; Palmer, 2010; van Bekkum *et al.*, 2001). Another possible explanation could be the loss of weakly bound CO₂-basic site complexes. Considering all the framework oxygen atoms possess potential basic sites but only those that acquire the highest negative charge have a true basic nature, two types of framework oxygens exist: O₃Si-O-SiO₃ and O₃Si-O-AlO₃. The stronger the cation, the weaker the conjugate oxygen and because the presence of Al³⁺ ions in the latter form of the framework produces a negatively charged framework of AlO₄⁻ to interact with a charge balancing cation, the decline in the adsorption may be as a result of losses from the weaker complex (Auerbach *et al.*, 2003).
 - iv. The influence of the size of the zeolite pores and the relationship with the loading pressure of the adsorbate in the FRT experiments facilitated an experimental setup whereby less adsorbate-adsorbate interactions existed and the adsorption capacities compared well with the order of the pore sizes. The CO₂ adsorption capacities could be limited by the size of the pores at high pressures as the CO₂ molecules could interact with the pore wall of the zeolites. Due to the CO₂-CO₂ interactions, the adsorption of new molecules of CO₂ into the pore wall sites already occupied by other CO₂ molecules might be prevented (Gargiulo *et al.*, 2014; Inglezakis & Zorpas, 2012; Katoh *et al.*, 2000). The pore size of F.CP914 (2.97×10^{-9} m) was shown to be the largest, although its measured adsorption capacities were well below those measured for F.CP914C. This was an expected result due to the higher aluminium content of F.CP914C.
 - v. The sorption behaviour of CO₂ was evaluated successfully using the FRT derived adsorption and desorption results. The relative rates of adsorption and desorption were analysed with all four zeolite samples showing a consistent behaviour with the number of cycles, implying that the surfaces had reached full coverage: average of r_d/r_a at each temperature = 0.91, 0.89, 0.94, 0.89 for F.CP914C; 0.94, 0.90, 0.87, 0.89 for ZSM 55; 0.96, 0.89, 0.91, 0.90 for

- F.CP914; and 0.98, 0.92, 0.93, 0.90 for ZSM 280. The FRT system was shown to operate within a state of pseudo-equilibrium. The dynamics of CO₂ adsorption were further evaluated by analysing the CO₂ diffusion coefficients.
- vi. The effective CO₂ diffusion coefficients within the commercially available zeolite samples were well characterised using the FRT-ZLC method. Adapting the FRT-ZLC technique to analyse the effective diffusivity coefficients provided another measure of the sorption dynamics of carbon dioxide.
 - vii. A comparison of the diffusivity parameters of various techniques shown in the literature to those observed by FRT-ZLC measurements yielded encouraging results when compared to other macroscopic techniques. Between 293 – 298 K, the activation energies predicted by Ahn *et al.*, based on the Cahn electrobalance analysis of CO₂ diffusion in CaX as well as the gravimetric analysis of CO₂ diffusion into 5A studied by Kamiuto *et al.*, are approximately 16 and 30 kJ mol⁻¹ respectively (Ahn *et al.*, 2004; Kamiuto & Goubaru, 2006). These values compare well with the FRT-ZLC predicted measurements of 17 and 22 kJ mol⁻¹ for zeolites F.CP914 and ZSM 280 at similar temperatures. The results also compare well to the diffusivity coefficient results reported by Yucel and Ruthven who made use of the Cahn microbalance to measure CO₂ diffusion in zeolite 5A. Between the temperature range 298 – 373 K, their diffusivity coefficients were found to be between $1 - 3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ while the measured values for this study in the same temperature range for ZSM 55 were between $2 - 10 \text{ m}^2 \text{ s}^{-1}$ (Yucel & Ruthven, 1980).
 - viii. The results suggest that FRT is a viable method for the evaluation of CO₂ diffusivity within the zeolite pore network, as the measured diffusivity parameters compared favourably with those found in the literature.

9.1.4. FRT Surface Area Characterisation

A novel approach to the determination of the surface areas of high surface and intermediate surface area aluminium oxides was successfully realised by incorporating an FRT system modification to enable ultra fast nitrogen isotherm measurements at 77 K. In order to establish the new sorption mode, a critically important alteration to the FRT system was introduced to dampen the viscosity effect measured during the mixing of gas streams of differing species. The inclusion of twin sample cylinders to both sides of the Wheatstone bridge provided the necessary dead volume required to dilute the gas

streams, minimise the viscosity effect, and achieve the objectives set out in Objective III. The experimental approach for the ultra fast isotherms involved the successive step dosing of the aluminium oxide samples over the BET composition range. The method was compared with FRT surface area results of aluminium oxides determined using the classic prototype whereby the experimental approach involved the use of successive sorption cycles to measure the quantities of nitrogen adsorbed and desorbed on the samples during a specific time period. Both results were compared further with the static volumetric technique, the most widely used tool for the determination of surface areas of microporous materials. The key achievements and conclusions illustrated in Chapter 8 are summarised as follows:

- i. The augmentation of the classic FRT prototype was successfully achieved to minimise the process turnaround time required to run surface area characterisation experiments. The classic FRT surface area measurements ran with 3 – 5 dynamic cycles, each lasting for 20 mins. Bearing in mind that the dynamic cycles needed to be performed at at least five partial pressures, the total run time excluding the time taken to regenerate the samples after each cycle lasted for a minimum of 8 hours. By reducing the impact of the viscosity effect using the new FRT prototype, it was possible to reduce the process turnaround times for the entire isotherm composition range to last between 25 – 42 mins dependent on the number of step-wise perturbation doses carried out.
- ii. The sorption behaviour of the high surface area aluminium oxide was determined using the classic FRT approach to relate the quantities of N₂ adsorbed and desorbed for each dynamic cycle and N₂ partial pressure. The ratio of the quantity of nitrogen desorbed to the quantity adsorbed for each cycle was analysed to determine the extent of adsorption and desorption. It was observed that the ratios remained relatively consistent across the cycle range. This suggests that the system was able to reach a quasi-steady state equilibrium. Analysis of the relative standard deviation across the cycles also showed a low average deviation between the measured values of 8.4 %.
- iii. The BET models for the nitrogen adsorption isotherms at 77 K of both FRT systems displayed an excellent linear regression for their respective BET models. A distinct advantage in the process control and overall accuracy of the

experiment is displayed for the multipoint ultra fast method where digital EMFCs were utilised. The classic FRT method suffers from lower flowrate control of the N₂ perturbations when using the MFCs, with its R² coefficient being equal to 0.9742 in contrast to 0.9969 displayed for the multipoint technique. The high linear regression displayed by both methods corroborates the previously stipulated assumption of the presence of multilayer adsorption on the surface of the test sample as is expected for Type IV isotherms.

- iv. A strong agreement was found between the FRT derived surface areas and the nominal surface area of the test samples. It was also reassuring to find that the progress made in the ultra fast FRT experimental technique yielded positive results with excellent correlations to the nominal values. Measuring the intermediate and high surface area aluminium oxide samples with the multipoint method resulted in surface areas of 100.63 and 257.95 m²/g in comparison with the nominally derived values of 100 and 255 m²/g. When comparing the manufacturer's data with the surface areas measured using the static volumetric technique, there was less of an agreement between the values, with the measured surface areas equal to 102.17 and 192.85 m²/g for the intermediate and high surface area aluminium oxides respectively.
- v. The main difference between the static and dynamic techniques of surface area determination consists within the time interval of operation. Consequently, both methods work on a different equilibrium basis. Commercial static volumetric systems operate at an equilibration point defined as being when the pressure change per equilibration time interval is less than 0.01 % of the average pressure during the interval (Micromeritics TriStar 3000). FRT measures the partial sorption on the surface of the adsorbent by operating under the assumption of a continuous equilibrium. This allows for quicker analysis of test materials under industrial conditions.

9.1.5. FRT Dynamic Parallel Performance Testing (DPPT)

Building the FRT Dynamic Parallel Performance Testing system was explored in Chapter 8 to provide a novel technique of investigating the catalytic properties of test materials simultaneously. This would provide the perfect platform to be able to rapidly screen and compare the activities of a pair of catalysts operating side by side. The

critical modification required to build the new system was a new perturbation switching procedure to incorporate the additional reactor required for the parallel performance. A modified two position injector six port valve was used to carry out preliminary experiments. The modification to the experimental configuration of the perturbation switching valve was necessary to be able to interrogate the reference side of the Wheatstone bridge assembly alongside the system.

- i. Attempts to balance the new system with the modified perturbation switch were unsuccessful, altogether limiting the advancement of the technique. In the past, it was possible to make do with slight variations in flow between both sides of the bridge as only fluctuations on one side of the bridge required accurate monitoring.
- ii. With the critical driver behind the DPPT technique being the balance between the Wheatstone bridge, it is imperative to be able to operate the system by circumventing sources of errors including, errors in the configuration of the modified switch valve, errors brought about by irregularities in the gas plumbing network, errors perpetuated from capillary irregularities within the up and downstream blocks, as well as dead volume errors within the system configuration.

9.2. Future Work

The experiments and improvements to the FRT system that were explored in this thesis have contributed significantly towards an improved understanding of catalytic and gas sorption measurements. The present studies have showcased FRT as a dynamically powerful *in situ* and online characterisation method, which can be used to measure very small changes in flowrate, easily facilitating measurements of complete molar balances. The system operation is independent of analysis volume and requires no calibration when working with any gas at any temperature. Coupled with the low capital cost of the machinery and the inherent advantages of the technique, it is necessary to continue to improve upon the technique in order to qualitatively embody the FRT method to both academic and industrial communities. Future upgrades to the system require a specific focus on overcoming current setbacks encountered when operating the FRT systems including:

- i. In order to qualitatively analyse the composition of product streams to increase the accuracy of FRT measurements, it is suggested that all future experiments should be combined with mass spectrometry (MS). A simple addition such as this would enable more conclusive data to be extracted from present FRT experiments such that the typical flux response profile inferences could be assessed with higher degree of reliability. Typical examples where the present study would have benefited from the inclusion of MS results are shown in the FRT ammonia sorption and carbon dioxide sorption studies where the possibility of dehydroxylation in the zeolite samples across an increased temperature range existed. Being able to analyse the effluent streams leaving the reactor across the specific temperature ranges shown in the flux response profiles would be extremely advantageous in aiding in the explanation of these profile results. Coupling both techniques presently would allow for a deeper level of understanding in the interpretation of flux response profiles as well as adding a secondary level of analytical data. It must be noted however that any addition to the process inventory adds an additional source for errors, which must be taken into account when building the apparatus.
- ii. Modifications were made to the FRT systems to address the level of insulation required to minimise temperature fluctuations occurring during the running of the process. The effect of thermal noise was mitigated by the application of silicone tubing to the gas lines but further improvements need to be addressed in order to possess greater temperature control of the apparatuses. Having such control is needed to mitigate the temperature fluctuation effects such as those experienced in the surface area characterisation studies due to the evaporation of liquid nitrogen. The use of a thermal jacket and a modified liquid nitrogen dewar to seal the reactors in place during experimentation would limit evaporation and facilitate a more stable temperature boundary between room and cryogenic temperatures.
- iii. A marked advancement in the FRT technique would be the adaptation of a high-pressure flux response rig to measure catalytic materials at elevated pressures. This would bring experimental results closer in line with industrial conditions and increase the range and flexibility of the technology. Currently, advances are being made in the setup of such a system with preliminary

experiments being run to develop an apparatus capable of operating at above 10 *bar*. A significant amount of attention is required in the design of the system, as a great deal of care is needed to preserve the integrity of the delicate Wheatstone bridge assembly. The design and working of the backpressure regulators will be proven pivotal in eventual operations.

- iv. Advancements in FRT process automation have already shown improvements in flow control and flux response accuracy through the implementation of electronic mass flow controllers. Upgrading the technology further to incorporate more automated fittings would aid system operations and improve the end-user experience by making the technology easier to use. Being able to build a system with automated pressure regulators would drastically reduce the process times and increase user flexibility to be able to operate FRT systems remotely and within set schedules. Due to the fact that the method requires a significant level of understanding in several factors that each play a part in the ability of the systems to attain a steady balance (such as effects caused by the addition and removal of experimental fittings, thermal expansions, imbalanced pressures and flowrates, as well as dead volumes), an optimisation that could be engineered to address these factors and increase the automation would be extremely valuable and should be sought after.
- v. When investigating the ultra fast nitrogen isotherms, it was determined that the surface area characterisations correlated well with the nominal values provided by the manufacturer. Another step towards the advancement of the method would be an investigation into possible effects on the FRT results brought about by reducing the viscosity effect and to what extent such an effect would impact the accuracy of the measured values. Introducing experiments to review the new technique is essential in order to improve the reliability of the method. Comparing the data from simple experiments to quantify the adsorption capacities on a reference material pre and post minimisation is the first step required to establish the method.
- vi. Developing the DPPT system to engage and compare catalytic materials running side by side is an essential requirement for further studies. The challenge here is to develop an alternative experimental approach to nullify the imbalances experienced when switching perturbations of dual gas streams into both reactors on opposite sides of the Wheatstone bridge. This development

could focus on the modified perturbation switch and the control required therein not to affect the balance of the bridge while still being able to switch perturbations in and out. An option here would be to focus on installing another perturbation switch with a higher number of ports to enable the required switching configuration to be achieved where all four gas lines (carrier and perturbation) run through the switch in valve. A different development could focus on modifying the DPPT rig to alter the experimental setup to incorporate a reference stream between two system reactors, similar to the classic FRT setup.

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Appendix A:

Maple source code for Zero Length Column analysis

Maple was used as the mathematical solver of choice to determine the ZLC parameters required to calculate the effective diffusion coefficients from the FRT derived response profiles. Maple provides one of the world's most powerful mathematical computation engines used to implement solutions in scientific research. Appendix A presents the source code and sample calculation used to derive the diffusivity coefficients from the slope and intercept of the FRT-ZLC curves.

Maple Code

Digits := 5

5

By combining the equation for the intercept,

$L/(\beta)$ equation 1

with the root of transcendental equation β ,

$\beta \cot \beta + L - 1 = 0$ equation 2

Substitute for L in equation 1

x substituted for β

$b := 2 \cdot x \cdot \cot(x) - 2$

$$\begin{aligned}
 & 2x \cot(x) - 2 \\
 c &:= x \cdot (\cot(x) - x - x \cdot \cot(x)^2) \\
 & x (\cot(x) - x - x \cot(x)^2) \\
 d &:= \frac{b}{c} = \text{intercept} \\
 & \frac{2x \cot(x) - 2}{x (\cot(x) - x - x \cot(x)^2)} = \text{intercept} \\
 & \text{evalf}(d) \\
 & \frac{2 \cdot x \cot(x) - 2}{x (\cot(x) - 1 \cdot x - 1 \cdot x \cot(x)^2)} = \text{intercept} \\
 sold &:= \text{fsolve}(d, x, x = 0 .. \pi) \\
 e &:= L = 1 - sold \cdot \cot(sold) \\
 & L = 1 - sold \cot(sold) \\
 sole &:= \text{fsolve}(e, L)
 \end{aligned}$$

In order to obtain D/r^2 and D , substitute for B in slope equation

Equation of slope -

$$S = -B^2(D/r^2)$$

where K is (D/r^2)

$$\begin{aligned}
 f &:= \text{slope} = -sold^2 \cdot K \\
 & \text{slope} = -sold^2 K
 \end{aligned}$$

$$solf := \text{fsolve}(f, K)$$

$$\begin{aligned}
 g &:= D = r^2 \cdot solf \\
 & D = r^2 solf
 \end{aligned}$$

where r is the radius of the particle

$$solg := fsolve(g, D)$$

The equation of the ZLC line is as below

$$\ln(c/c_0) = \ln\{2L/[\beta^2 + L(L-1)]\} - \beta^2(D/r^2)$$

Having established all ZLC parameters, the theoretical plot for each experiment is shown below

$$h := \ln(y) = -x \cdot solf \cdot sold^2 + \ln\left(\frac{2 \cdot sole}{sold^2 + sole \cdot (sole - 1)}\right)$$

$$\ln(y) = -x solf sold^2 + \ln\left(\frac{2 sole}{sold^2 + sole (sole - 1)}\right)$$

Appendix B:

Mathematical concept of tension splines

The curve fitting software Curve Expert was used to analyse flux response profiles and determine the integrals of the various sorption peaks. When fitting the curves, the tension spline was used to analyse the experimental data.

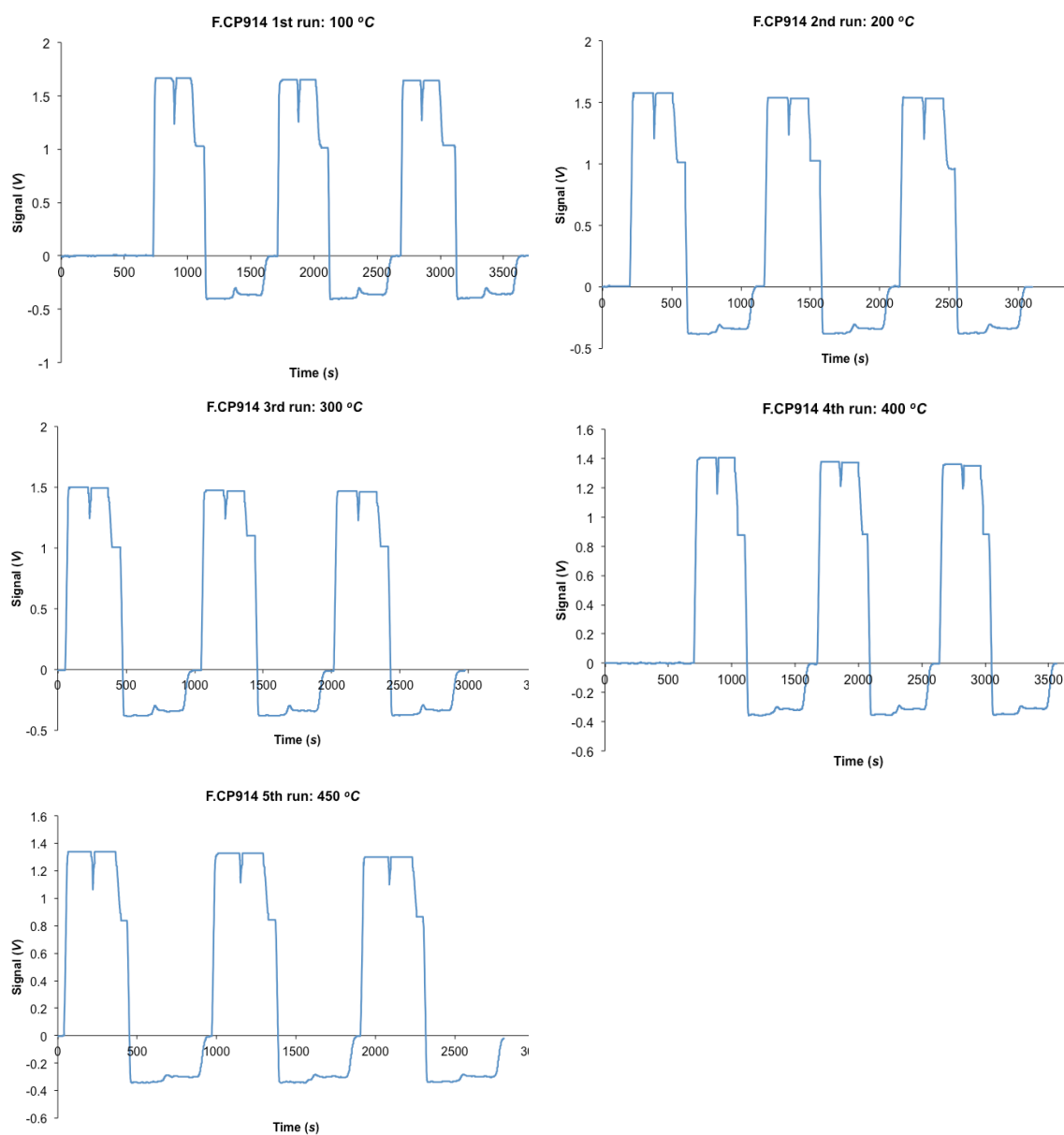
A tension spline $s(x)$ is a continuous function for which $s''(x) - \sigma s(x)$ is given by a straight line on $[\lambda_i - \lambda_{i+1}]$. For all $\sigma = 0$, it is reduced to a cubic spline, whereas if all $\sigma_i = 0$, it becomes a piecewise linear function. Increasing the tension factor employs a local stretching effect on the curve which may be used to prevent unwanted oscillations (Dierckx, 1995).

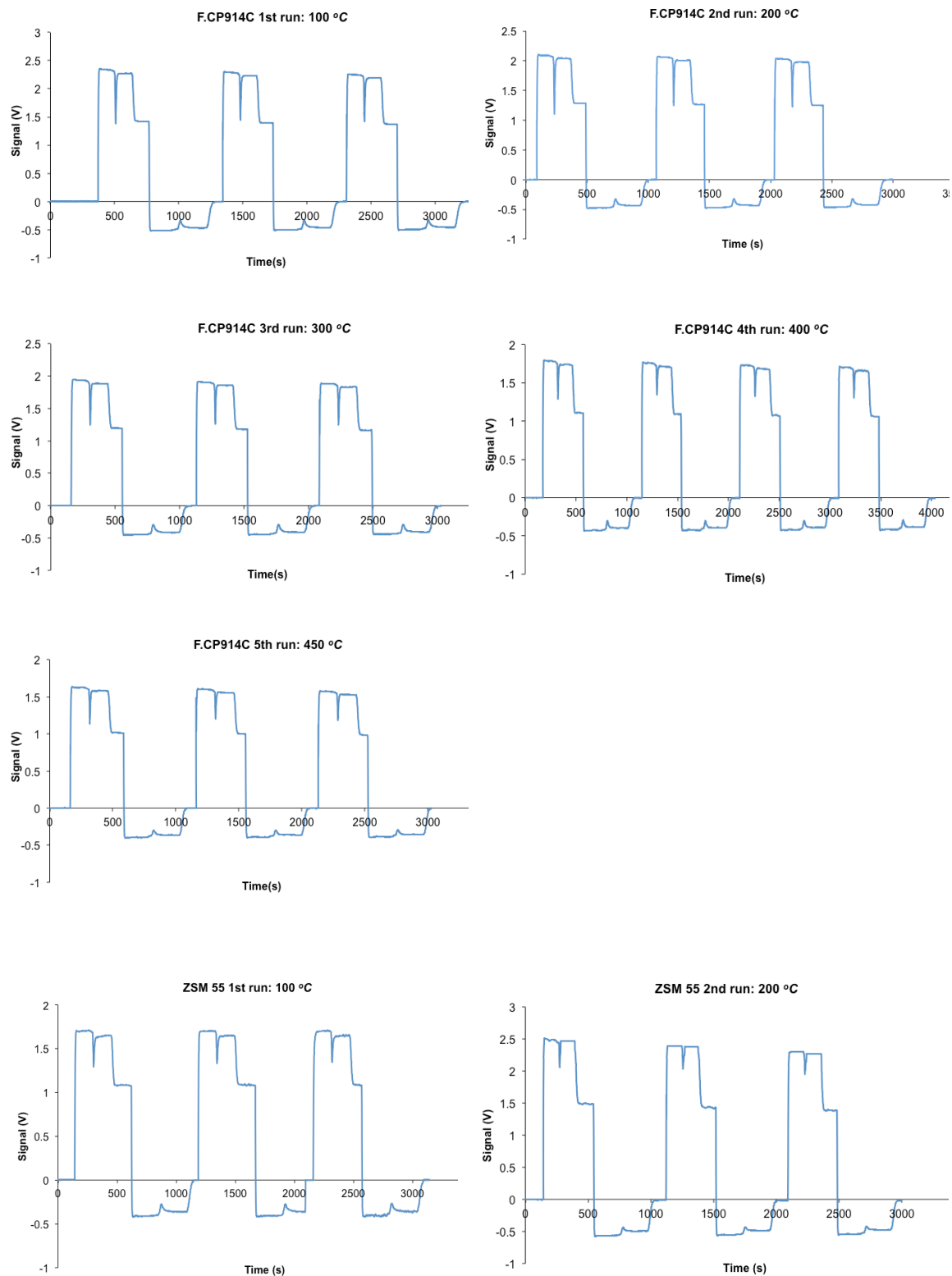
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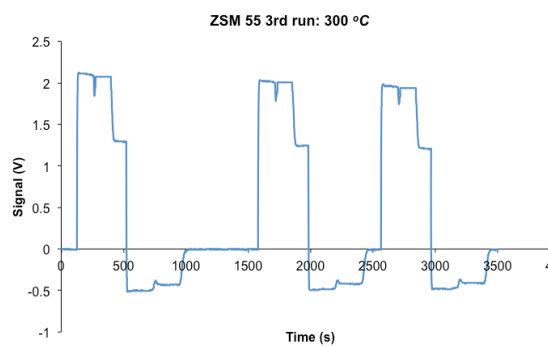
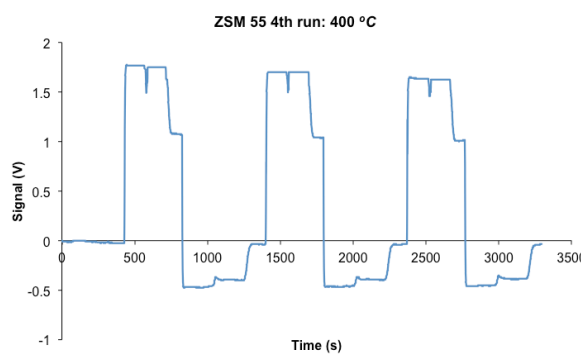
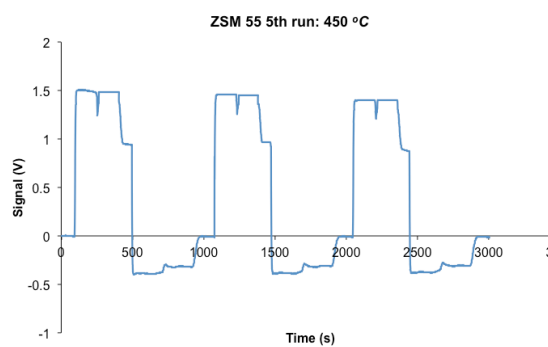
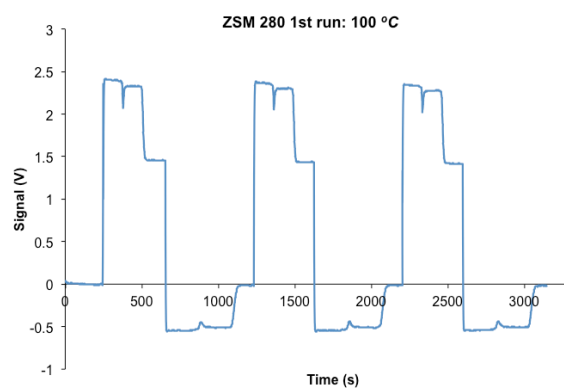
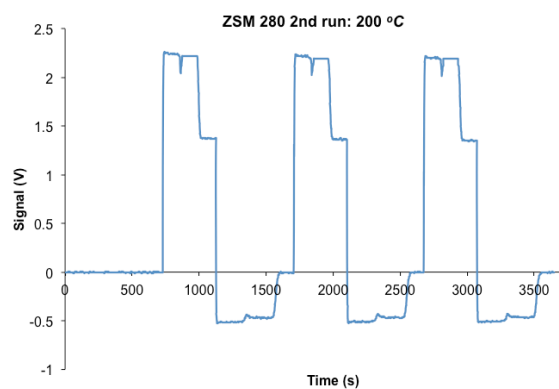
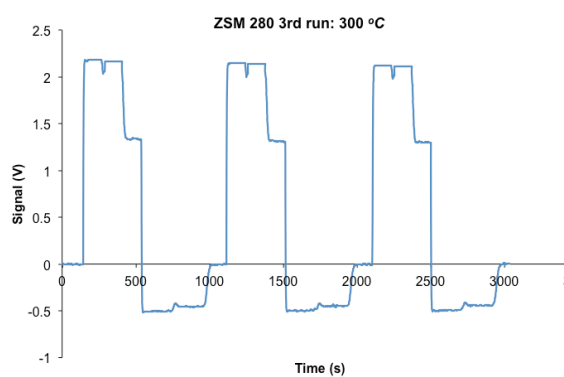
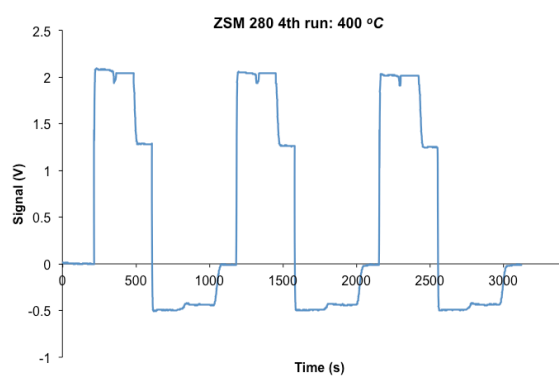
Dierckx, P. (1995). *Curve and Surface Fitting with Splines: Monographs on numerical analysis Numerical mathematics and scientific computation Oxford science publications* (p. 285). Clarendon Press, Oxford.

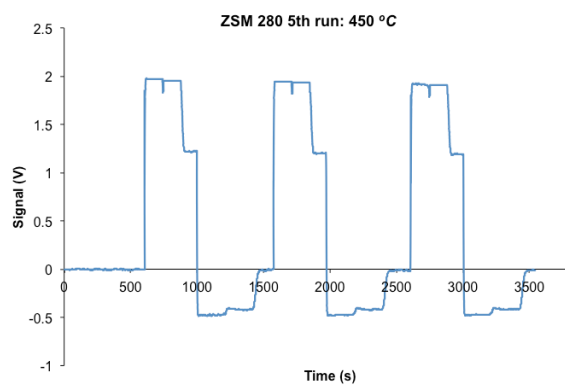
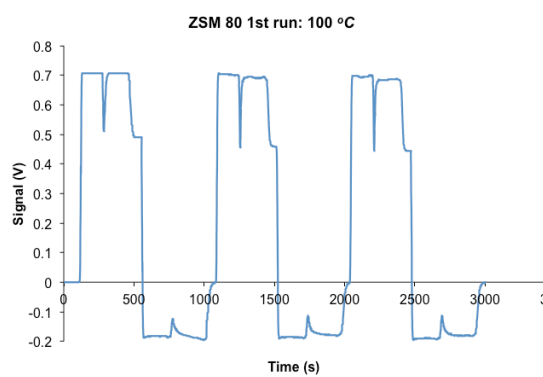
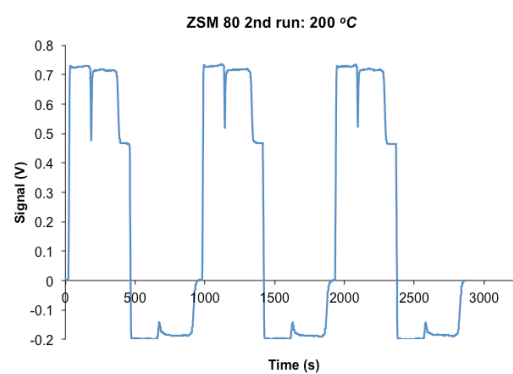
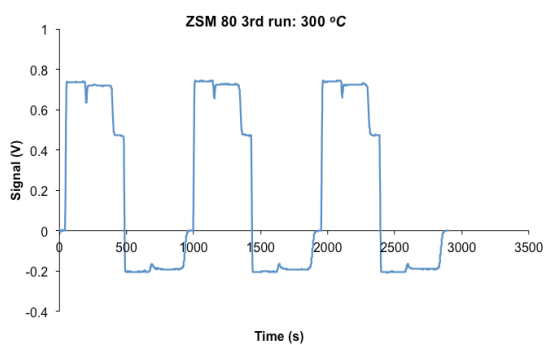
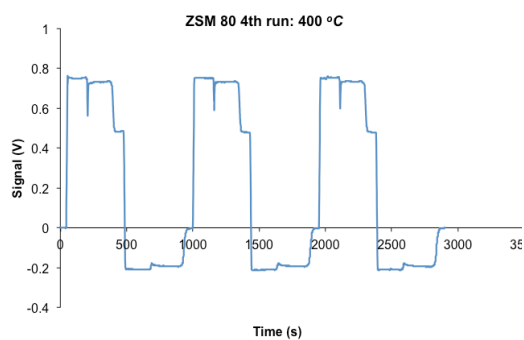
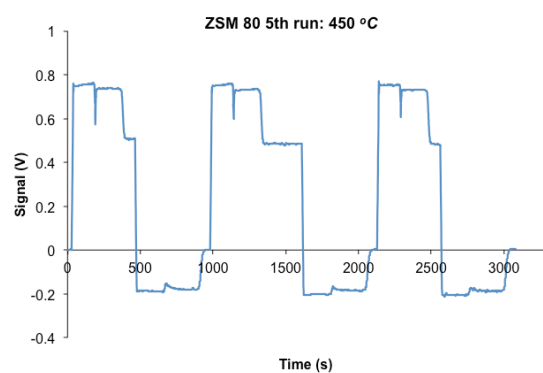
Appendix C: FRT cycles for NH_3 sorption on zeolites with varied $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios

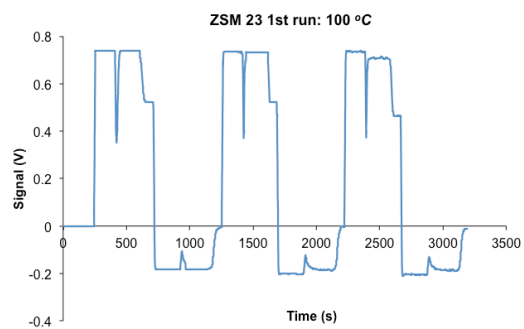
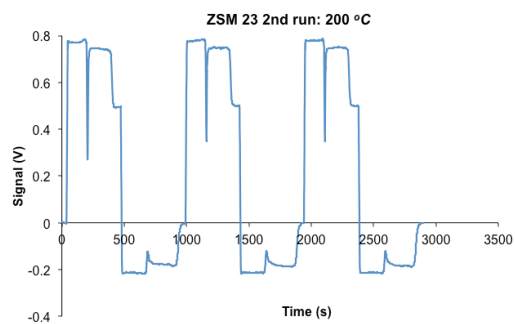
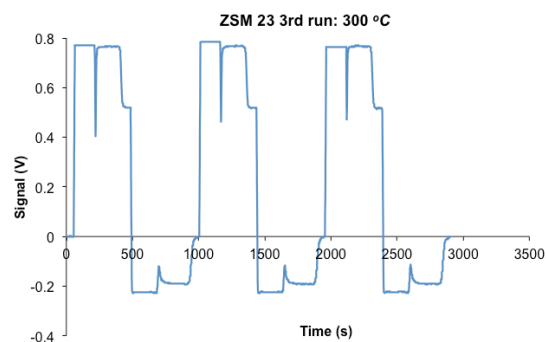
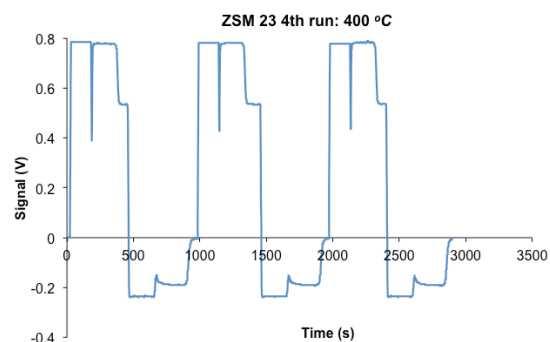
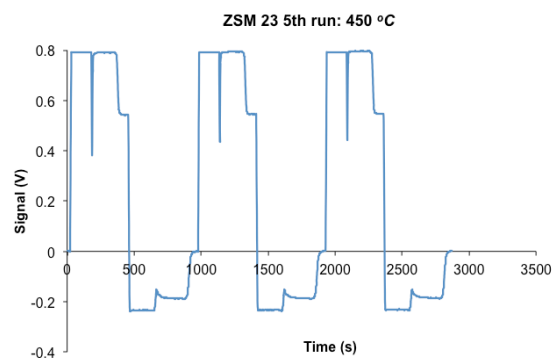
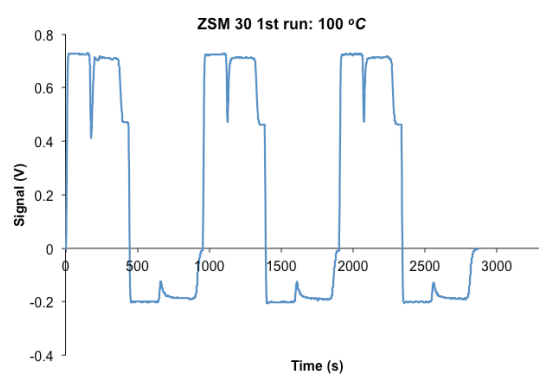
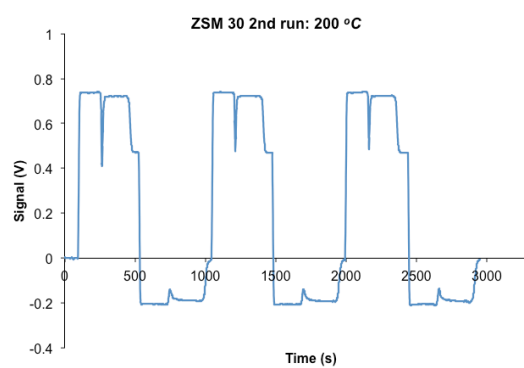
Presented in Appendix C are the flux response profiles that were measured at 30 *mol-%* of NH_3 running through the system reactor during perturbation injections. The NH_3 perturbations were made into a constantly flowing stream of argon carrier gas.

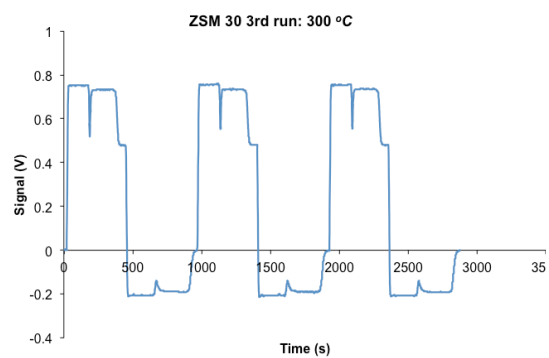
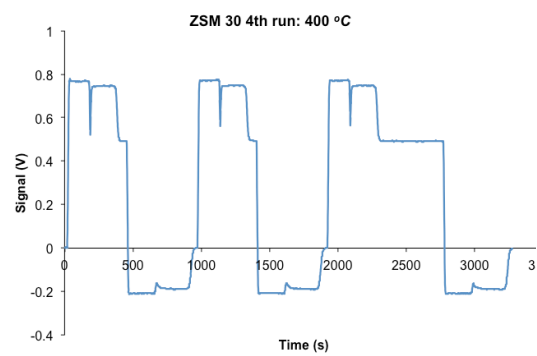
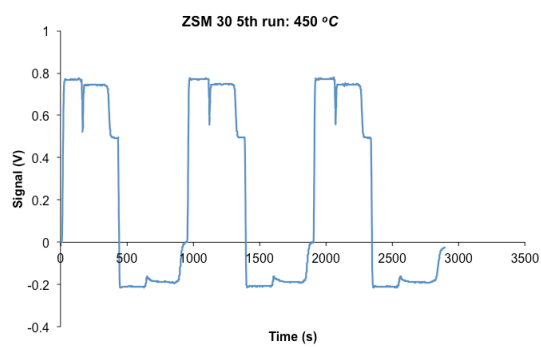






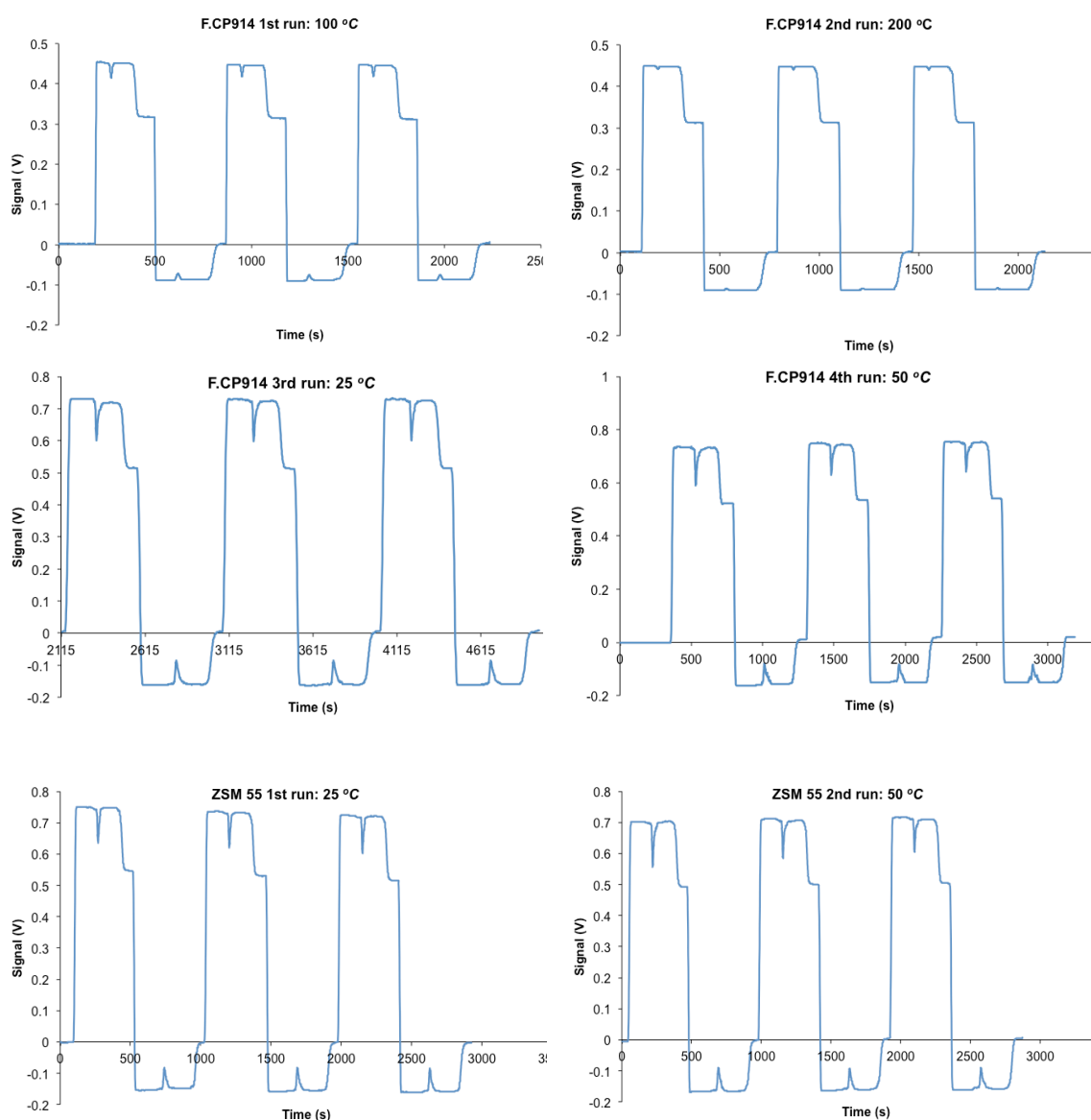


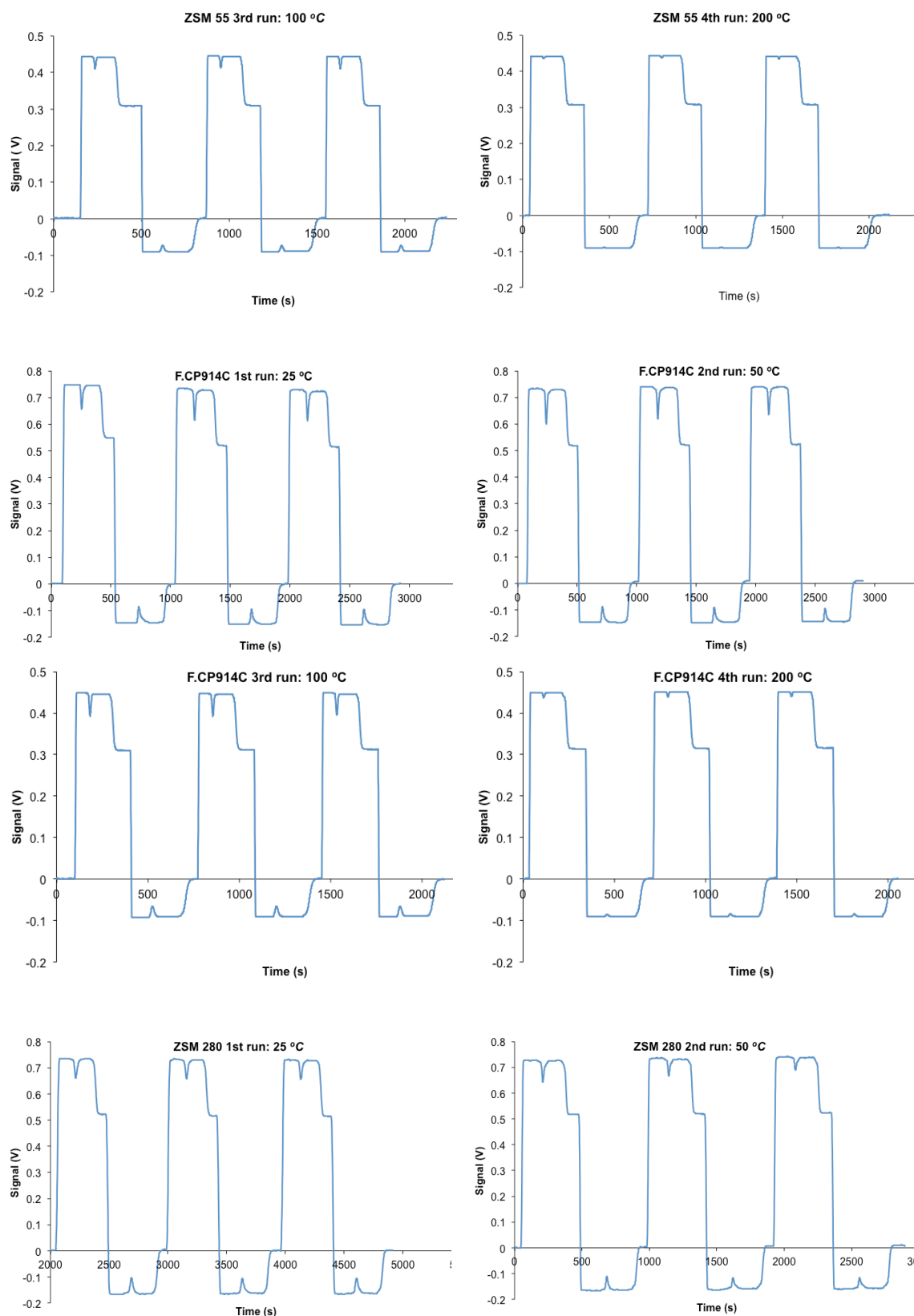


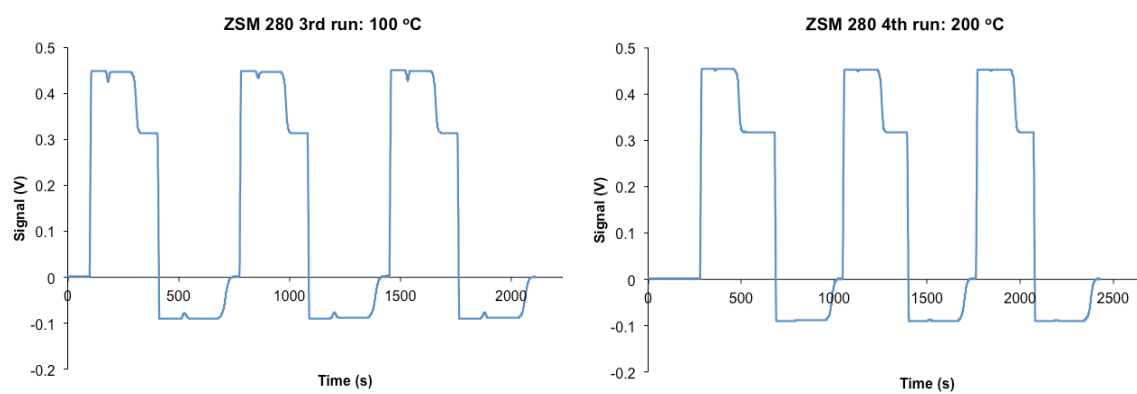


Appendix D: FRT cycles for CO₂ sorption on zeolites with varied SiO₂/Al₂O₃ ratios

Presented in Appendix D are the flux response profiles that were measured at 30 mol-% of CO₂ running through the system reactor during perturbation injections. The CO₂ perturbations were made into a constantly flowing stream of argon carrier gas.







Appendix E:

FRT adsorption isotherms for N₂

derived surface areas of aluminium oxide

Appendix E features examples of FRT derived N₂ adsorption isotherms of aluminium oxide used to calculate the BET surface areas at 77 K. The flux response profiles were measured at different mole fractions of N₂ in He by adjusting the flowrate of nitrogen in a constantly flowing carrier gas stream of He.

Table 1: FRT derived N₂ sorption quantities on high surface area aluminium oxide

Mass of sample (g)	0.012				
1st run					
Sorption time / s	56.000				
N ₂ partial pressure	0.118				
Measured flowrate / ml/min	2.600				
Calibrated flowrate / ml/min	2.608				
Calibrated N ₂ partial pressure	0.119				
Cycle	1	2	3	4	Average
Adsorption/Vs -Tension	0.562	0.529	0.485	0.531	0.515
Desorption/Vs - Tension	0.456	0.446	0.446	0.424	0.439
Difference/Vs - Tension	0.106	0.082	0.039	0.108	0.076
Adsorption/ cm ³ /g - Tension	47.810	44.969	41.243	45.176	43.796
Desorption/ cm ³ /g - Tension	38.809	37.975	37.903	36.029	37.302
Difference/ cm ³ /g - Tension	9.001	6.994	3.340	9.146	6.493

2nd run					
Sorption time / s	56.000				
N ₂ partial pressure	0.155				
Measured flowrate / ml/min	3.400				
Calibrated flowrate / ml/min	3.397				
Calibrated N ₂ partial pressure	0.154				
Cycle	1	2	3	4	Average
Adsorption/Vs -Tension	0.698	0.546	0.570	0.566	0.561
Desorption/Vs - Tension	0.496	0.470	0.459	0.456	0.462
Difference/Vs - Tension	0.202	0.076	0.112	0.110	0.099
Adsorption/ cm ³ /g - Tension	59.573	46.578	48.677	48.335	47.863
Desorption/ cm ³ /g - Tension	42.297	40.089	39.162	38.919	39.390
Difference/ cm ³ /g - Tension	17.277	6.488	9.514	9.416	8.473

3rd run	
Sorption time / s	56.000
N ₂ partial pressure	0.205
Measured flowrate / ml/min	4.500
Calibrated flowrate / ml/min	4.590
Calibrated N ₂ partial pressure	0.208
Cycle	1 2 3 4 Average
Adsorption/Vs -Tension	0.755 0.583 0.557 0.541 0.560
Desorption/Vs - Tension	0.523 0.475 0.465 0.465 0.468
Difference/Vs - Tension	0.232 0.108 0.092 0.075 0.092
Adsorption/ cm ³ /g - Tension	64.595 49.927 47.637 46.262 47.942
Desorption/ cm ³ /g - Tension	44.772 40.664 39.755 39.810 40.077
Difference/ cm ³ /g - Tension	19.823 9.263 7.882 6.452 7.866

4th run	
Sorption time / s	56.000
N ₂ partial pressure	0.282
Measured flowrate / ml/min	6.200
Calibrated flowrate / ml/min	6.360
Calibrated N ₂ partial pressure	0.289
Cycle	1 2 3 4 Average
Adsorption/Vs -Tension	0.806 0.607 0.568 0.579 0.585
Desorption/Vs - Tension	0.547 0.485 0.452 0.477 0.471
Difference/Vs - Tension	0.259 0.122 0.116 0.102 0.113
Adsorption/ cm ³ /g - Tension	69.114 52.045 48.741 49.640 50.142
Desorption/ cm ³ /g - Tension	46.885 41.554 38.784 40.920 40.419
Difference/ cm ³ /g - Tension	22.229 10.491 9.957 8.721 9.723

5th run	
Sorption time / s	56.000
N ₂ partial pressure	0.291
Measured flowrate / ml/min	6.400
Calibrated flowrate / ml/min	6.733
Calibrated N ₂ partial pressure	0.306
Cycle	1 2 3 4 Average
Adsorption/Vs -Tension	0.905 0.642 0.610 0.589 0.614
Desorption/Vs - Tension	0.577 0.561 0.558 0.569 0.563
Difference/Vs - Tension	0.328 0.080 0.053 0.021 0.051
Adsorption/ cm ³ /g - Tension	77.612 55.055 52.372 50.566 52.664
Desorption/ cm ³ /g - Tension	49.471 48.160 47.860 48.777 48.266
Difference/ cm ³ /g - Tension	28.141 6.895 4.512 1.789 4.399

Table 2: FRT derived N₂ sorption quantities on intermediate surface area aluminium oxide

1st run					
Sorption time / s	40.000				
N ₂ partial pressure	0.279				
Measured flowrate / ml/min	6.200				
Calibrated flowrate / ml/min	6.700				
Calibrated N ₂ partial pressure	0.302				
Cycle	1	2	3	4	Average
Adsorption/Vs - Tension	0.440	0.418	0.408	0.411	0.412
Desorption/Vs - Tension	0.350	0.364	0.377	0.362	0.368
Difference/Vs - Tension	0.091	0.053	0.031	0.049	0.044
Adsorption/ cm ³ /g - Tension	29.725	28.196	27.545	27.744	27.828
Desorption/ cm ³ /g - Tension	23.606	24.607	25.472	24.457	24.845
Difference/ cm ³ /g - Tension	6.119	3.589	2.073	3.287	2.983
2nd run					
Sorption time / s	40.000				
N ₂ partial pressure	0.256				
Measured flowrate / ml/min	5.700				
Calibrated flowrate / ml/min	5.864				
Calibrated N ₂ partial pressure	0.264				
Cycle	1	2	3	4	Average
Adsorption/Vs - Tension	0.392	0.266	0.256	0.254	0.258
Desorption/Vs - Tension	0.261	0.248	0.254	0.240	0.247
Difference/Vs - Tension	0.131	0.017	0.002	0.013	0.011
Adsorption/ cm ³ /g - Tension	25.694	17.387	16.764	16.605	16.919
Desorption/ cm ³ /g - Tension	17.116	16.255	16.603	15.730	16.196
Difference/ cm ³ /g - Tension	8.578	1.132	0.160	0.875	0.722
3rd run					
Sorption time / s	40.000				
N ₂ partial pressure	0.216				
Measured flowrate / ml/min	4.800				
Calibrated flowrate / ml/min	4.939				
Calibrated N ₂ partial pressure	0.222				
Cycle	1	2	3	4	Average
Adsorption/Vs - Tension	0.281	0.195	0.193	0.210	0.199
Desorption/Vs - Tension	0.167	0.179	0.183	0.174	0.179
Difference/Vs - Tension	0.113	0.016	0.010	0.036	0.021
Adsorption/ cm ³ /g - Tension	18.904	13.146	12.975	14.105	13.409
Desorption/ cm ³ /g - Tension	11.267	12.044	12.327	11.688	12.020
Difference/ cm ³ /g - Tension	7.637	1.102	0.648	2.417	1.389

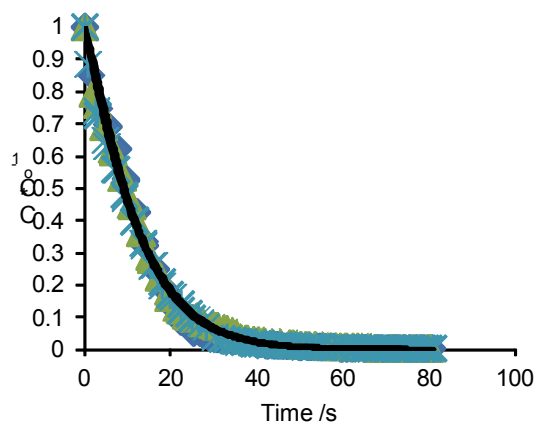
4th run						
Sorption time / s	40.000					
N₂ partial pressure	0.191					
Measured flowrate / ml/min	4.200					
Calibrated flowrate / ml/min	4.190					
Calibrated N₂ partial pressure	0.189					
Cycle	1	2	3	4	Average	
Adsorption/Vs - Tension	0.151	0.084	0.079	0.097	0.087	
Desorption/Vs - Tension	0.081	0.079	0.079	0.088	0.082	
Difference/Vs - Tension	0.070	0.005	0.001	0.009	0.005	
Adsorption/ cm³/g - Tension	10.476	5.812	5.509	6.713	6.012	
Desorption/ cm³/g - Tension	5.603	5.460	5.455	6.103	5.673	
Difference/ cm³/g - Tension	4.874	0.352	0.054	0.610	0.339	

Appendix F: FRT-ZLC curves modelling diffusivity coefficients

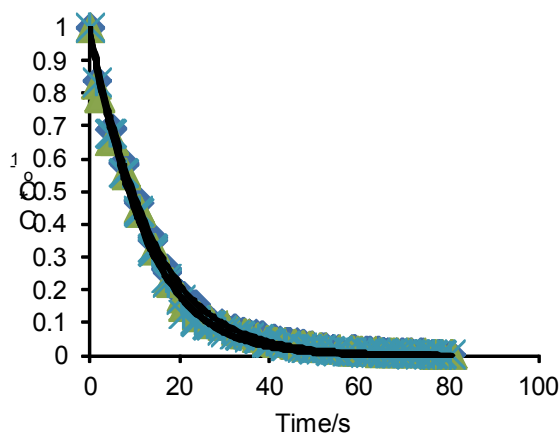
Appendix F contains examples of the FRT-ZLC profiles of the experimental data used in analysing the diffusivity coefficients of propane and CO₂ in cordierite washcoats and zeolites respectively.

Complete cycle of FRT experimental (1st cycle - ◆, 2nd cycle - ▲, 3rd cycle - ×) and fitted (solid lines) desorption curves for Sample 1 using propane (mole fraction of 0.5) at (a) 25 °C (b) 40 °C (c) 60 °C (d) 80 °C and (e) 100 °C.

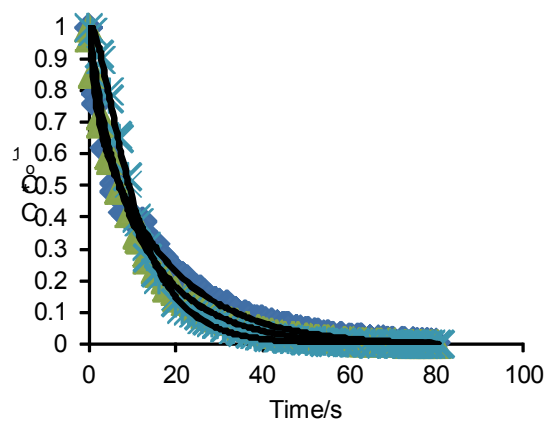
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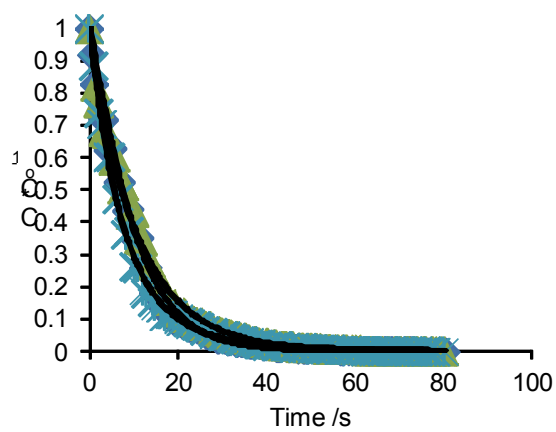
(b)



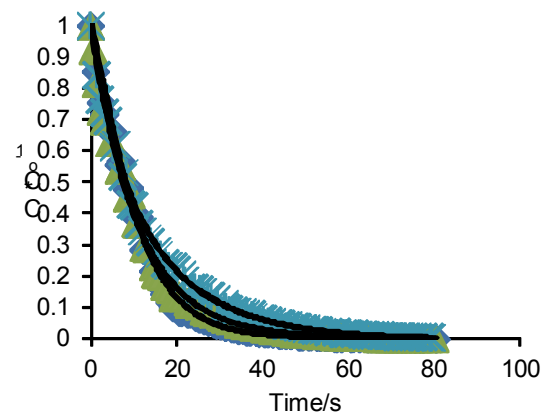
(c)



(d)

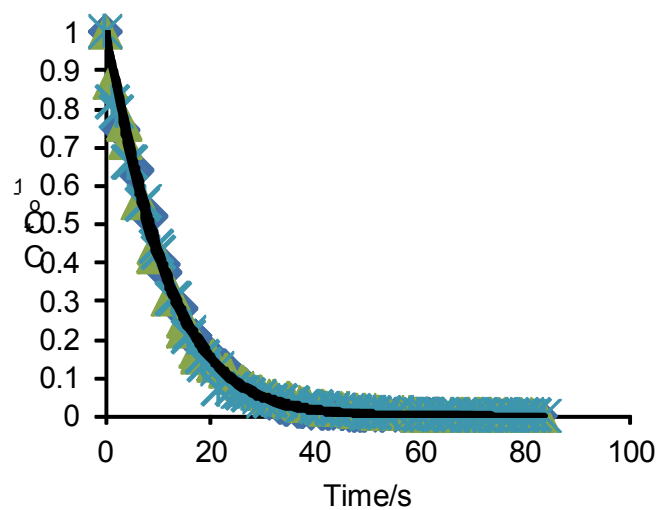


(e)

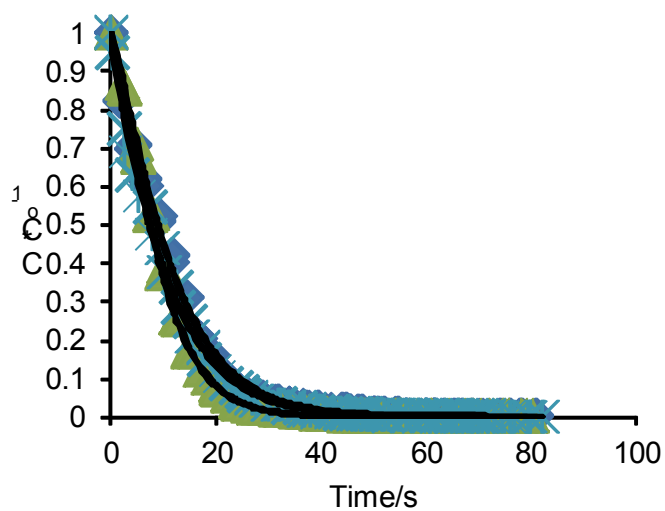


Complete cycle of FRT experimental (1st cycle - ◆, 2nd cycle - ▲, 3rd cycle - ×) and fitted (solid lines) desorption curves for Sample 2 using propane (mole fraction of 0.5) at (a) 25 °C (b) 40 °C (c) 60 °C (d) 80 °C and (e) 100 °C.

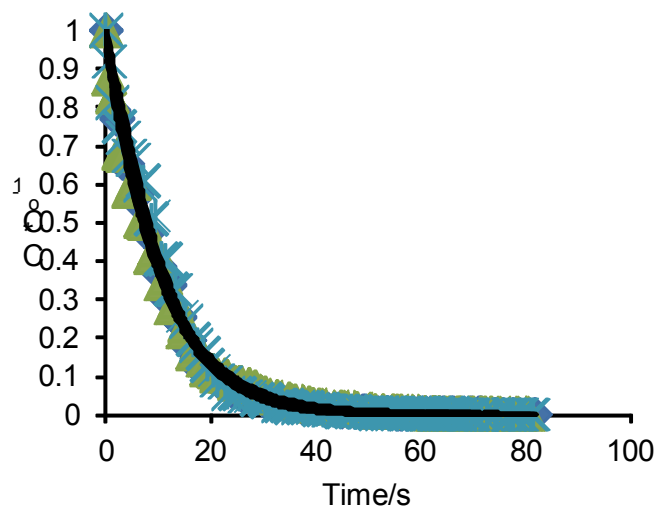
(a)



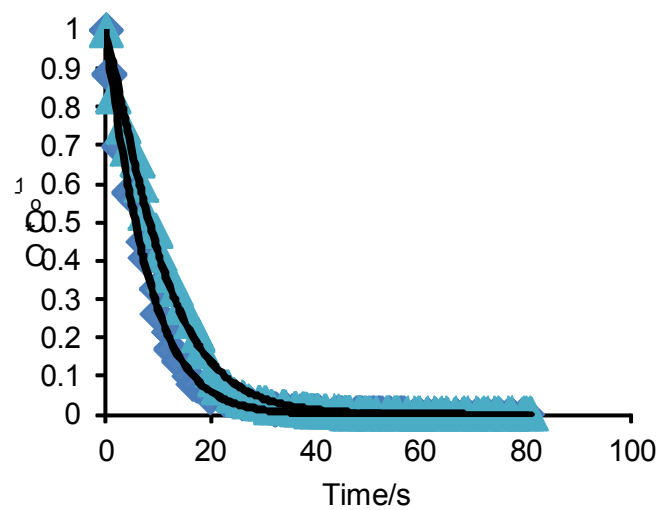
(b)



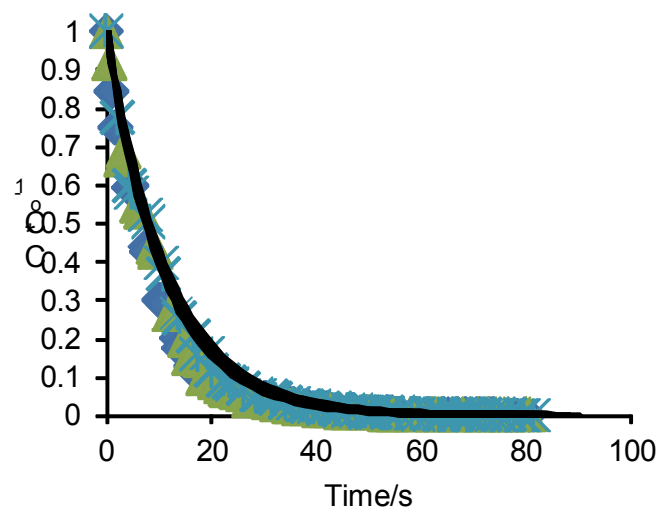
(c)



(d)

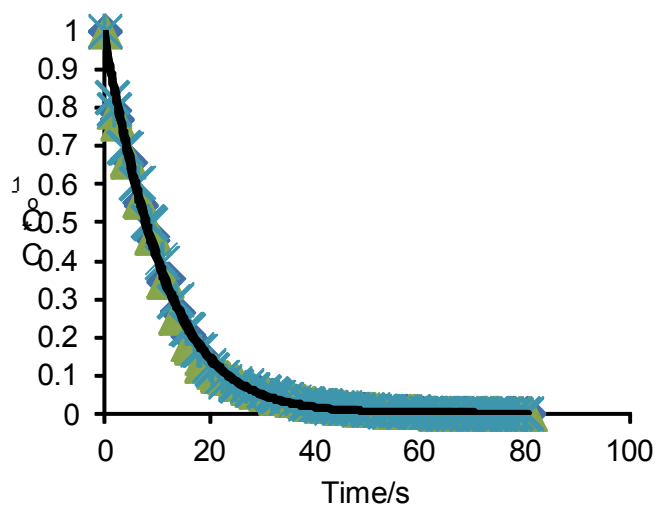


(e)

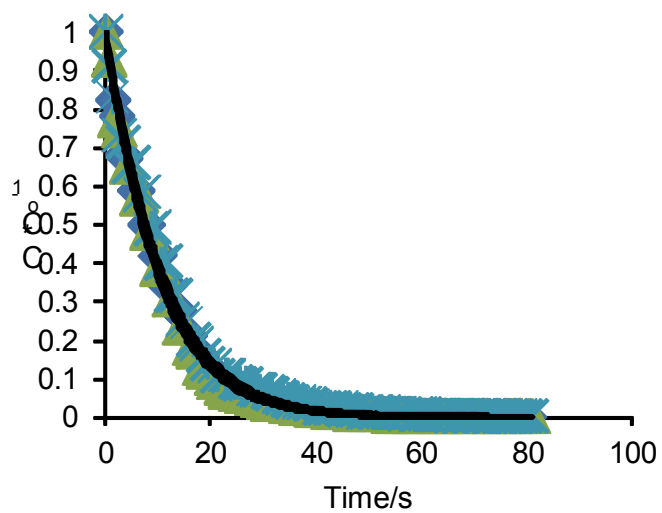


Complete cycle of FRT experimental (1st cycle - ◆, 2nd cycle - ▲, 3rd cycle - ×) and fitted (solid lines) desorption curves for Sample 4 using propane (mole fraction of 0.5) at (a) 25 °C (b) 40 °C (c) 60 °C (d) 80 °C and (e) 100 °C.

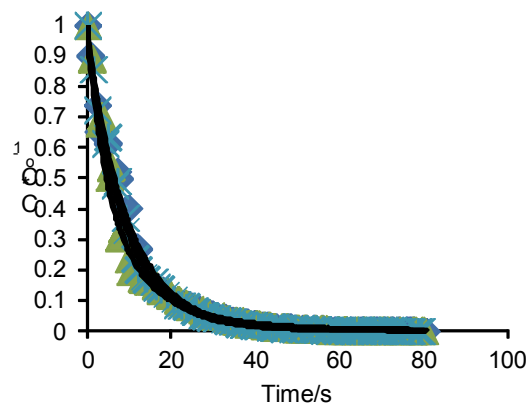
(a)



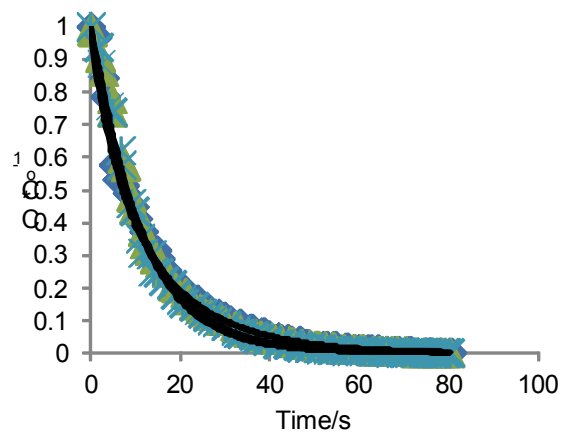
(b)



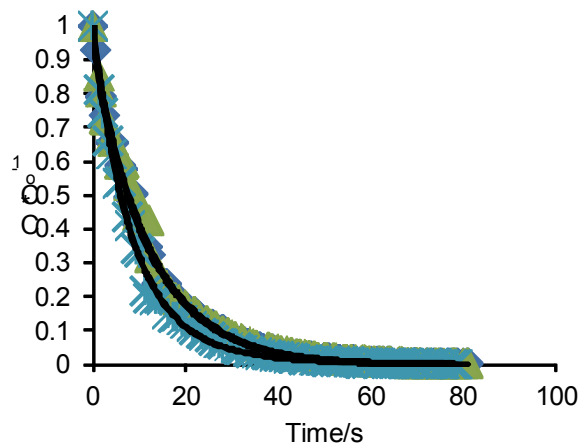
(c)



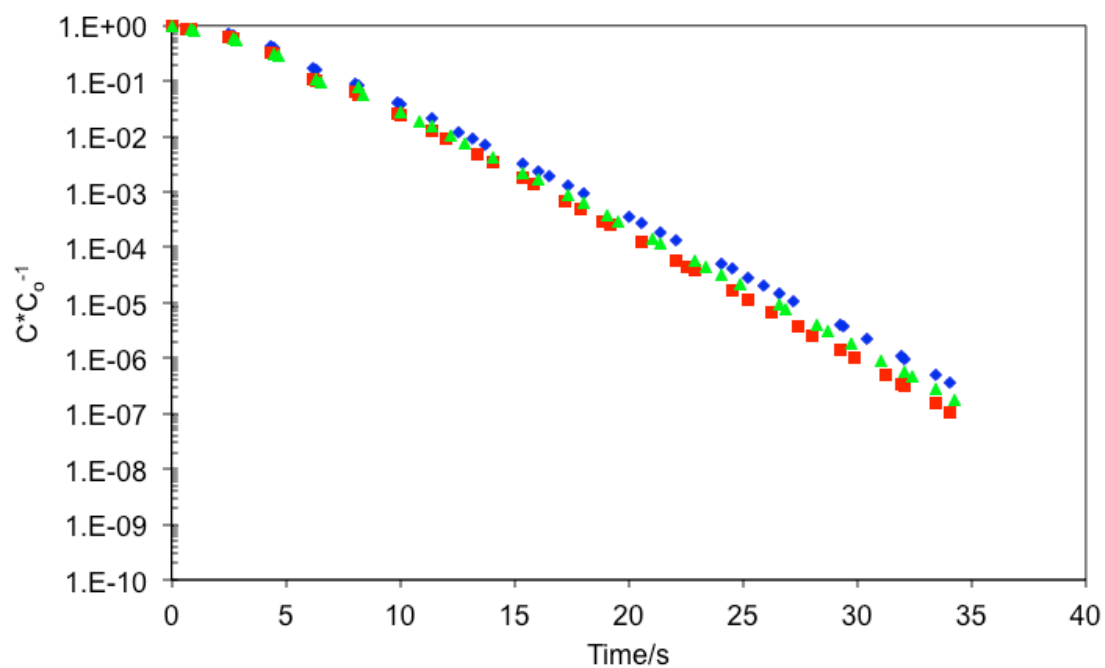
(d)



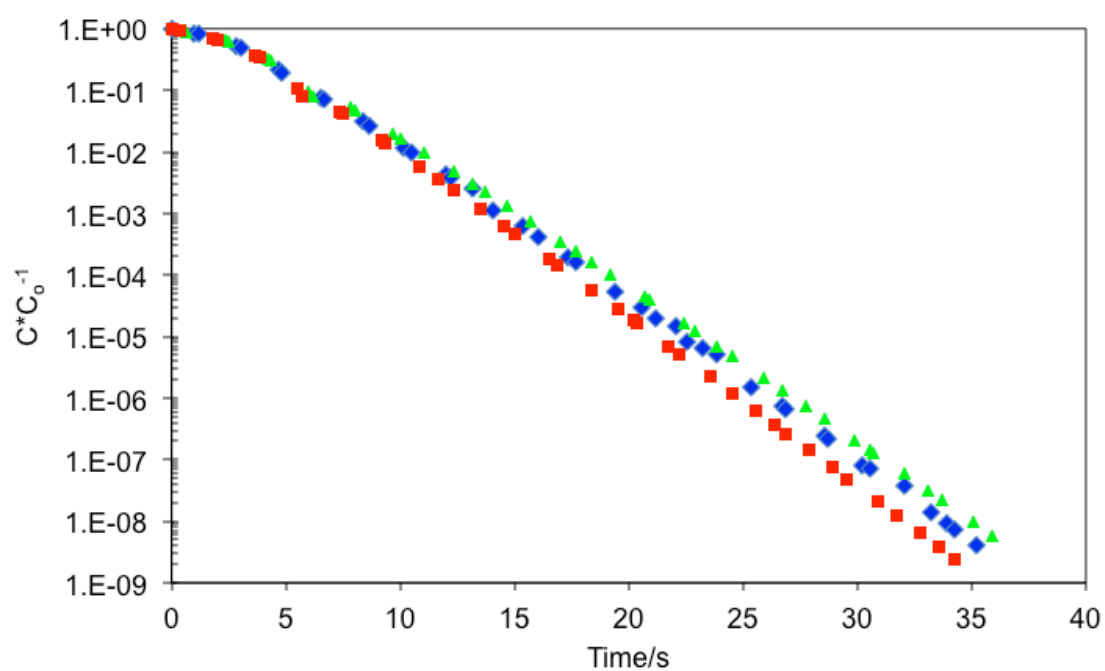
(e)



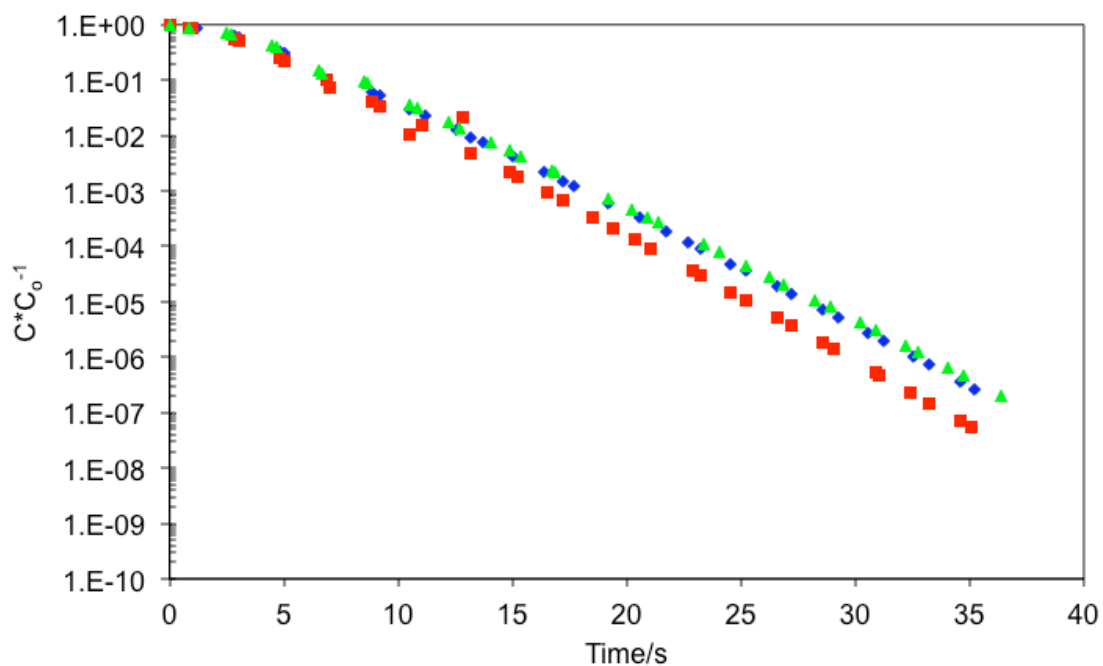
Experimental and fitted FRT-ZLC curves for ZSM 55 for all three cycles (1st - ▲, 2nd - ■, and 3rd - ◆) at 25 °C



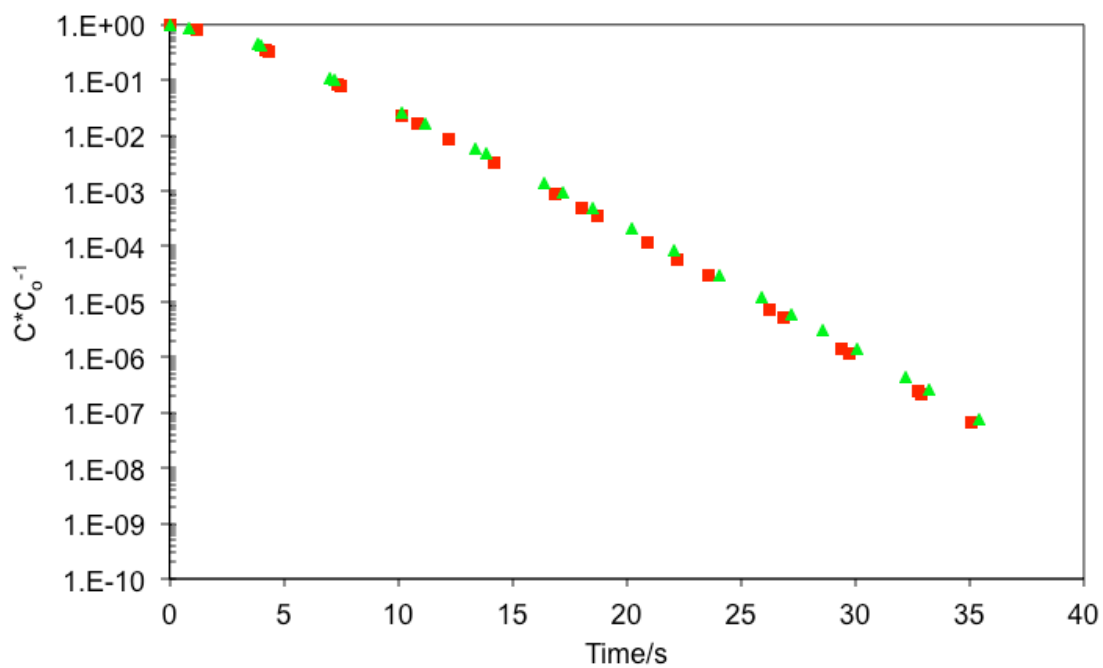
Experimental and fitted FRT-ZLC curves for F.CP914C for all three cycles (1st - ▲, 2nd - ■, and 3rd - ◆) at 25 °C



Experimental and fitted FRT-ZLC curves for F.CP914 for all three cycles (1st - ▲, 2nd - ■, and 3rd - ◆) at 25 °C



Experimental and fitted FRT-ZLC curves for ZSM 280 for all three cycles (1st - ▲ and 2nd - ■) at 25 °C



Appendix G:

Static volumetric N₂ isotherms of zeolite samples

The textural characteristics of the zeolite samples were examined to shed light on the FRT-ZLC diffusivity measurements carried out in the CO₂ studies. Presented in Appendix G are the isotherms and corresponding pore distributions in the following order: F.CP914C, ZSM 55, F.CP914, ZSM 280.

The negative C constant value for the data sets implies that the materials in question are unphysical. This may be due to the fact that the quantity of sample analysed may have been surplus to the procedure due to the presence of micropores or that the classical range (relative pressure 0.05-0.3) was not within the linear range of the zeolite isotherm. A procedure to test for the linear range has been suggested by Rouquerol *et al.*, based on two criteria (Moellmer *et al.*, 2010):

1. C must be positive (i.e. any negative intercept on the BET plot indicates being outside the valid range of the BET equation) and
2. Application of the BET equation must be limited to the range where the term $V(1-P/P_0)$ continuously increases with P/P_0 .

The isotherms were analysed using the Rouquerol test and the linear BET range was concluded as $P/P_0 = 0.024-0.184$ for the zeolite samples.

References

Moellmer, J., Celer, E. B., Luebke, R., Cairns, A. J., Staudt, R., Eddaoudi, M., & Thommes, M. (2010). Insights on Adsorption Characterization of Metal-Organic Frameworks: A Benchmark Study on the Novel soc-MOF. *Microporous and Mesoporous Materials*, 129(3), 345–353.

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

Page 1

Sample: F_CP914C

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:52PM

Warm Free Space: 7.3964 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.2535 g

Cold Free Space: 24.6958 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
			00:39	758.64758
0.010143193	7.69544	79.8318	02:04	
0.031551616	23.93769	82.6982	02:11	
0.057588783	43.69176	84.2789	02:16	
0.084809372	64.34376	85.3472	02:20	
0.101992010	77.38012	85.8839	02:23	
0.124180383	94.21432	86.4642	02:26	
0.142178282	107.86924	86.8746	02:28	
0.162131037	123.00739	87.2756	02:31	
0.181005512	137.32742	87.6164	02:33	
0.201019528	152.51213	87.9367	02:36	
0.247596533	187.84998	88.5782	02:38	
			02:39	758.69427
0.300168319	227.73726	89.2111	02:40	
0.350587915	265.99500	89.7745	02:43	
0.398062551	302.01791	90.2827	02:45	
0.447789080	339.75021	90.8172	02:47	
0.497575835	377.52905	91.3801	02:49	
0.547361475	415.30789	91.9916	02:51	
0.597081326	453.04019	92.6783	02:54	
0.646785550	490.75916	93.4649	02:56	
0.696134175	528.21210	94.4084	02:59	
0.745485313	565.66504	95.5870	03:01	
0.794392605	602.78540	97.1273	03:04	
0.817852712	620.59735	98.0988	03:07	
0.846036386	641.99426	99.5800	03:10	
0.870309942	660.42474	101.2946	03:13	
0.893972923	678.39630	103.6740	03:17	
0.922203249	699.84644	108.2865	03:24	
0.945859990	717.83130	116.2114	03:32	
0.968639559	735.16437	137.1217	03:43	
0.973796066	739.11517	149.0454	03:52	
0.991412886	752.57056	183.1955	04:12	
0.991673409	752.77673	186.5548	04:14	
0.981416377	744.99481	184.9855	04:15	
0.977027758	741.67584	182.9102	04:18	
0.974006196	739.39453	180.6120	04:21	
			04:40	759.20776
0.954567782	724.71527	145.1984	04:41	
0.929275593	705.51324	118.6220	04:58	
0.897772063	681.59552	108.4929	05:12	
0.880531013	668.50598	105.6786	05:17	
0.850534293	645.73224	102.4640	05:22	
0.814834398	618.62860	99.9471	05:28	
0.791259247	600.73016	98.7347	05:31	
0.755103764	573.28064	97.3049	05:34	
0.704326683	534.73029	95.8554	05:37	
0.654381832	496.81177	94.8005	05:40	
0.603753640	458.37445	93.9641	05:42	
0.553037819	419.87061	93.2717	05:44	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

Page 2

Sample: F_CP914C

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:52PM

Warm Free Space: 7.3964 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.2535 g

Cold Free Space: 24.6958 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
0.502558595	381.54639	92.6757	05:46	
0.448794062	340.72794	91.4107	05:50	
0.399383625	303.21515	90.7520	05:53	
0.354353534	269.02795	90.1973	05:55	
0.302016985	229.29364	89.5697	05:57	
0.251809310	191.17558	88.9430	06:00	
0.201522788	152.99767	88.2705	06:02	
0.142843506	108.44790	87.2596	06:05	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

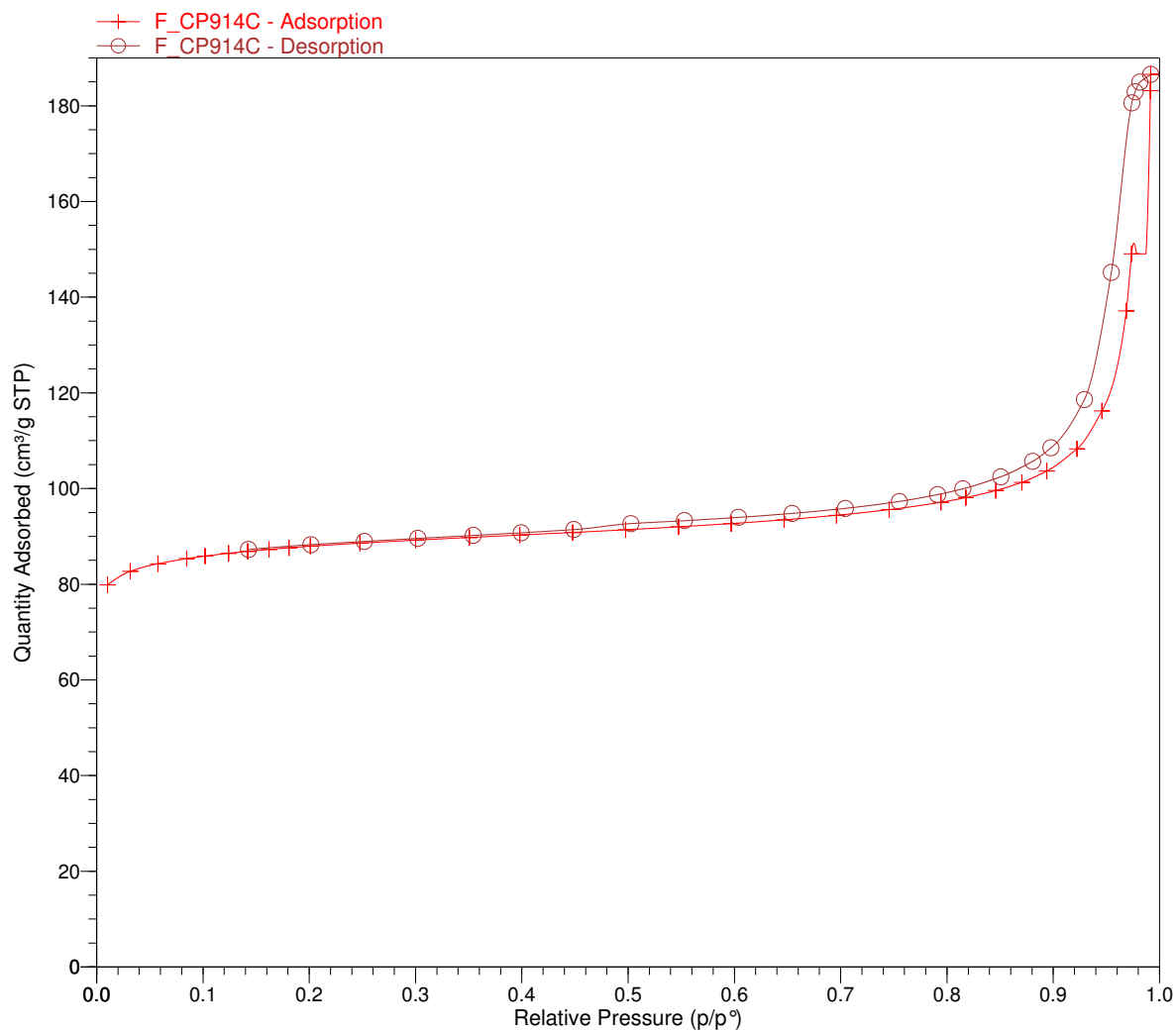
Page 3

Sample: F_CP914C
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM
Completed: 02/07/2010 15:49:45PM
Report Time: 02/07/2010 16:35:52PM
Warm Free Space: 7.3964 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2535 g
Cold Free Space: 24.6958 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

Page 4

Sample: F_CP914C

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:52PM

Warm Free Space: 7.3964 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.2535 g

Cold Free Space: 24.6958 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Surface Area Report

BET Surface Area: 296.0096 ± 5.2823 m²/gSlope: 0.014884 ± 0.000260 g/cm³ STPY-Intercept: -0.000177 ± 0.000036 g/cm³ STP

C: -82.900739

Qm: 67.9982 cm³/g STP

Correlation Coefficient: 0.9990864

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.057588783	84.2789	0.000725
0.084809372	85.3473	0.001086
0.101992010	85.8839	0.001322
0.124180383	86.4642	0.001640
0.142178282	86.8746	0.001908
0.162131037	87.2756	0.002217
0.181005512	87.6164	0.002522
0.201019528	87.9367	0.002861

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

Page 5

Sample: F_CP914C

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:52PM

Warm Free Space: 7.3964 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

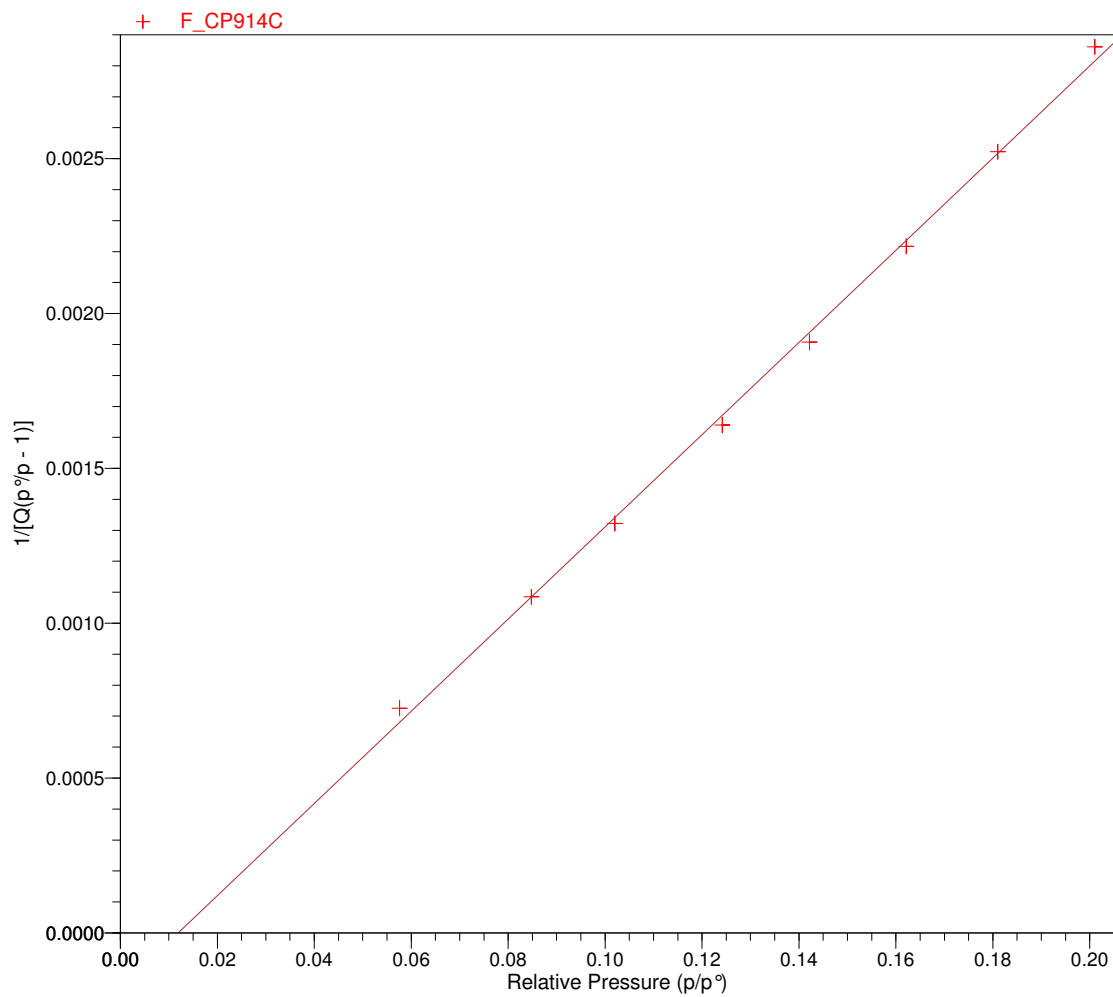
Sample Mass: 0.2535 g

Cold Free Space: 24.6958 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Surface Area Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

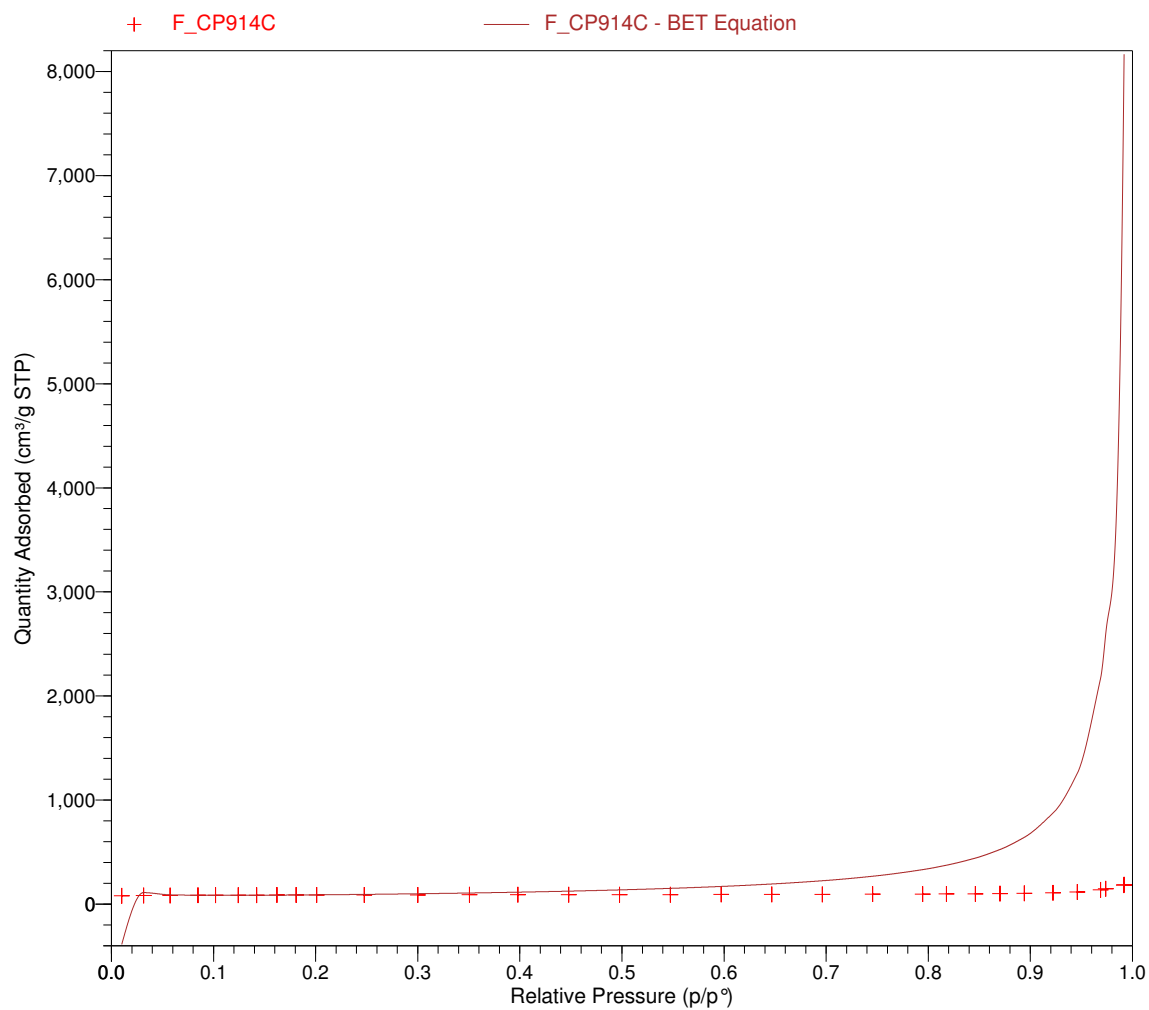
Page 6

Sample: F_CP914C
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM
Completed: 02/07/2010 15:49:45PM
Report Time: 02/07/2010 16:35:52PM
Warm Free Space: 7.3964 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2535 g
Cold Free Space: 24.6958 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Isotherm Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 3

Serial #: 2132

Page 22

Sample: F_CP914C

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\F_CP914C.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:52PM

Warm Free Space: 7.3964 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.2535 g

Cold Free Space: 24.6958 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Summary Report**Surface Area**Single point surface area at $p/p^\circ = 0.201019528$: 305.8545 m²/gBET Surface Area: 296.0096 m²/gLangmuir Surface Area: 389.9150 m²/gt-Plot Micropore Area: 251.0979 m²/g

BJH Adsorption cumulative surface area of pores

between 1.7000 nm and 300.0000 nm diameter: 33.4866 m²/g

BJH Desorption cumulative surface area of pores

between 1.7000 nm and 300.0000 nm diameter: 36.4113 m²/g**Pore Volume**

Single point adsorption total pore volume of pores

less than 63.6315 nm diameter at $p/p^\circ = 0.968639559$: 0.212100 cm³/g**Pore Size**

Adsorption average pore width (4V/A by BET): 2.86612 nm

BJH Adsorption average pore diameter (4V/A): 20.1421 nm

BJH Desorption average pore diameter (4V/A): 18.6363 nm

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

Page 1

Sample: ZSM_50
 Operator: Deji
 Submitter:
 File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM Analysis Adsorptive: N2
 Completed: 02/07/2010 15:49:45PM Analysis Bath Temp.: -195.800 °C
 Report Time: 02/07/2010 16:35:10PM Sample Mass: 0.1965 g
 Warm Free Space: 6.7929 cm³ Measured Cold Free Space: 22.2302 cm³ Measured
 Equilibration Interval: 5 s Low Pressure Dose: None
 Sample Density: 1.000 g/cm³ Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
0.010057997	7.63073	96.0562	00:39	758.64758
0.029321512	22.24550	100.2764	01:43	
0.063399765	48.10005	105.3262	01:50	
0.078027783	59.19817	107.0949	01:59	
0.099060562	75.15556	109.2928	02:04	
0.120361152	91.31619	111.1604	02:10	
0.142043242	107.76629	112.7520	02:15	
0.163887597	124.33956	114.1144	02:19	
0.184465499	139.95206	115.2108	02:23	
0.203923194	154.71465	116.1224	02:27	
0.246377934	186.92505	117.7902	02:30	758.69427
0.300294564	227.83165	119.4816	02:34	
			02:38	
			02:39	
0.352519139	267.45724	120.8572	02:41	
0.396923378	301.15192	121.8973	02:44	
0.446718455	338.93600	123.0052	02:46	
0.496956101	377.05884	124.0871	02:49	
0.546618793	414.74438	125.1800	02:51	
0.596544947	452.63321	126.3278	02:54	
0.646193397	490.31259	127.5798	02:57	759.20776
0.695596736	527.80725	129.0221	03:00	
0.744872636	565.20331	130.7779	03:02	
0.793769690	602.31610	133.0344	03:05	
0.818040297	620.74316	134.3796	03:08	
0.846213997	642.13263	136.1971	03:11	
0.871148403	661.06470	138.0609	03:14	
0.895262305	679.37476	140.2798	03:17	
0.918745325	697.21057	143.2609	03:21	
0.946112192	718.00262	149.0880	03:27	
0.969911905	736.09711	160.7453	03:35	759.20776
0.976495722	741.11035	167.4980	03:39	
0.984271485	747.05353	185.4097	03:49	
0.991727071	752.76276	206.7373	04:01	
0.986117446	748.51318	204.0327	04:03	
0.983209848	746.31451	200.6081	04:05	
0.980767380	744.47302	196.8472	04:08	
0.951171046	722.09204	156.6186	04:29	
			04:40	
0.918509976	697.33990	145.8753	04:40	
0.899568208	682.95917	143.2240	04:44	759.20776
0.873187575	662.93079	140.8706	04:48	
0.855040816	649.15363	139.7297	04:50	
0.829365955	629.66107	138.4638	04:53	
0.802952923	609.60809	137.4191	04:55	
0.754239697	572.62463	135.9101	04:58	
0.704269121	534.68658	134.6534	05:00	
0.654233628	496.69925	133.5065	05:02	
0.603257131	457.99750	132.4349	05:05	
0.553205398	419.99783	131.4271	05:07	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

Page 2

Sample: ZSM_50

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:10PM

Warm Free Space: 6.7929 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.1965 g

Cold Free Space: 22.2302 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
0.503064429	381.93042	130.4121	05:10	
0.456103413	346.27725	124.2642	05:18	
0.403147555	306.07275	122.2028	05:22	
0.341860589	259.54321	120.6596	05:25	
0.305956374	232.28445	119.7054	05:28	
0.253446678	192.41869	118.1230	05:32	
0.204198054	155.02875	116.2399	05:36	
0.138319599	105.01331	112.6344	05:44	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

Page 3

Sample: ZSM_50

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:10PM

Warm Free Space: 6.7929 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

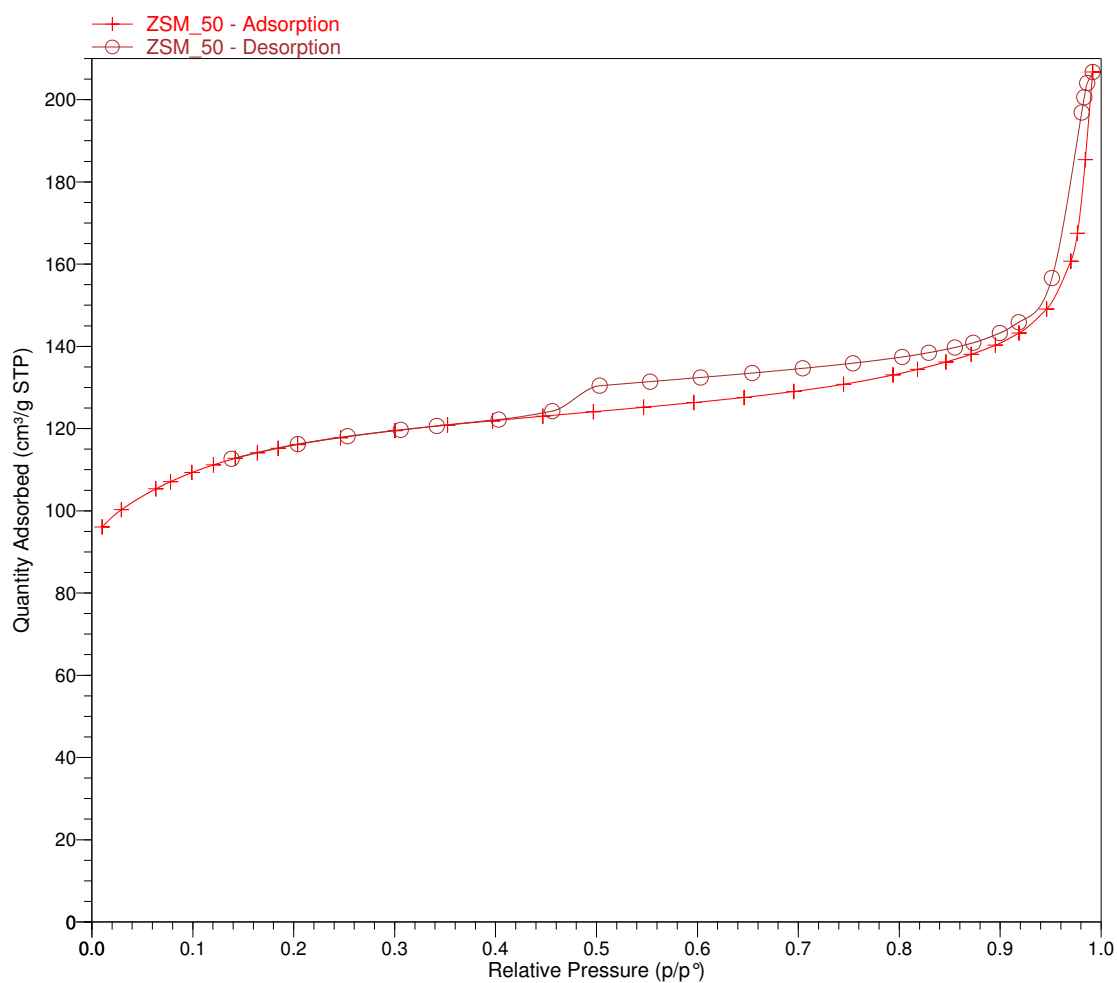
Sample Mass: 0.1965 g

Cold Free Space: 22.2302 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Linear Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

Page 4

Sample: ZSM_50
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM Analysis Adsorptive: N2
Completed: 02/07/2010 15:49:45PM Analysis Bath Temp.: -195.800 °C
Report Time: 02/07/2010 16:35:10PM Sample Mass: 0.1965 g
Warm Free Space: 6.7929 cm³ Measured Cold Free Space: 22.2302 cm³ Measured
Equilibration Interval: 5 s Low Pressure Dose: None
Sample Density: 1.000 g/cm³ Automatic Degas: No

BET Surface Area Report

BET Surface Area: 395.8911 ± 5.7518 m²/g
Slope: 0.011079 ± 0.000158 g/cm³ STP
Y-Intercept: -0.000083 ± 0.000022 g/cm³ STP
C: -132.246475
Qm: 90.9426 cm³/g STP
Correlation Coefficient: 0.9993888
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o /p - 1)]
0.063399765	105.3262	0.000643
0.078027783	107.0949	0.000790
0.099060562	109.2929	0.001006
0.120361152	111.1604	0.001231
0.142043242	112.7520	0.001468
0.163887597	114.1144	0.001718
0.184465499	115.2108	0.001963
0.203923194	116.1224	0.002206

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

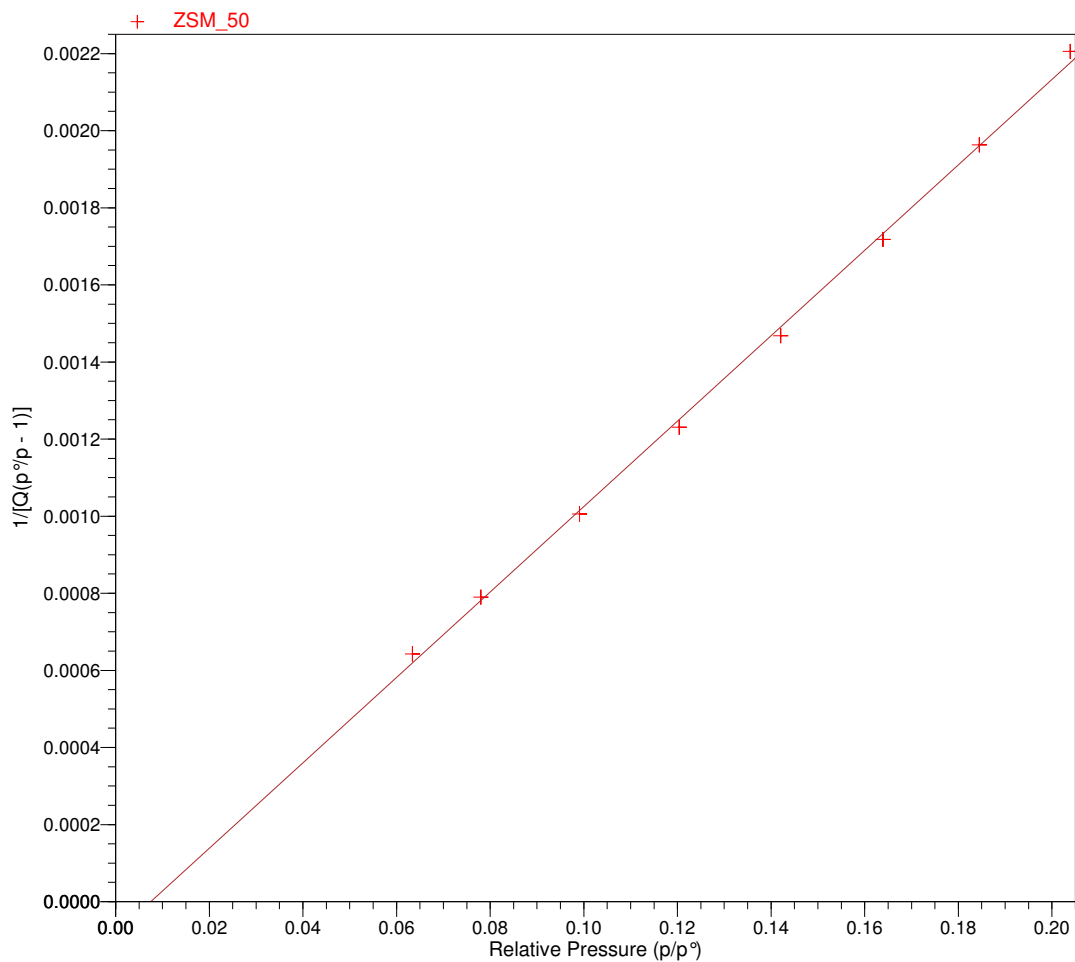
Page 5

Sample: ZSM_50
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM
Completed: 02/07/2010 15:49:45PM
Report Time: 02/07/2010 16:35:10PM
Warm Free Space: 6.7929 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.1965 g
Cold Free Space: 22.2302 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

Page 6

Sample: ZSM_50

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:10PM

Warm Free Space: 6.7929 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

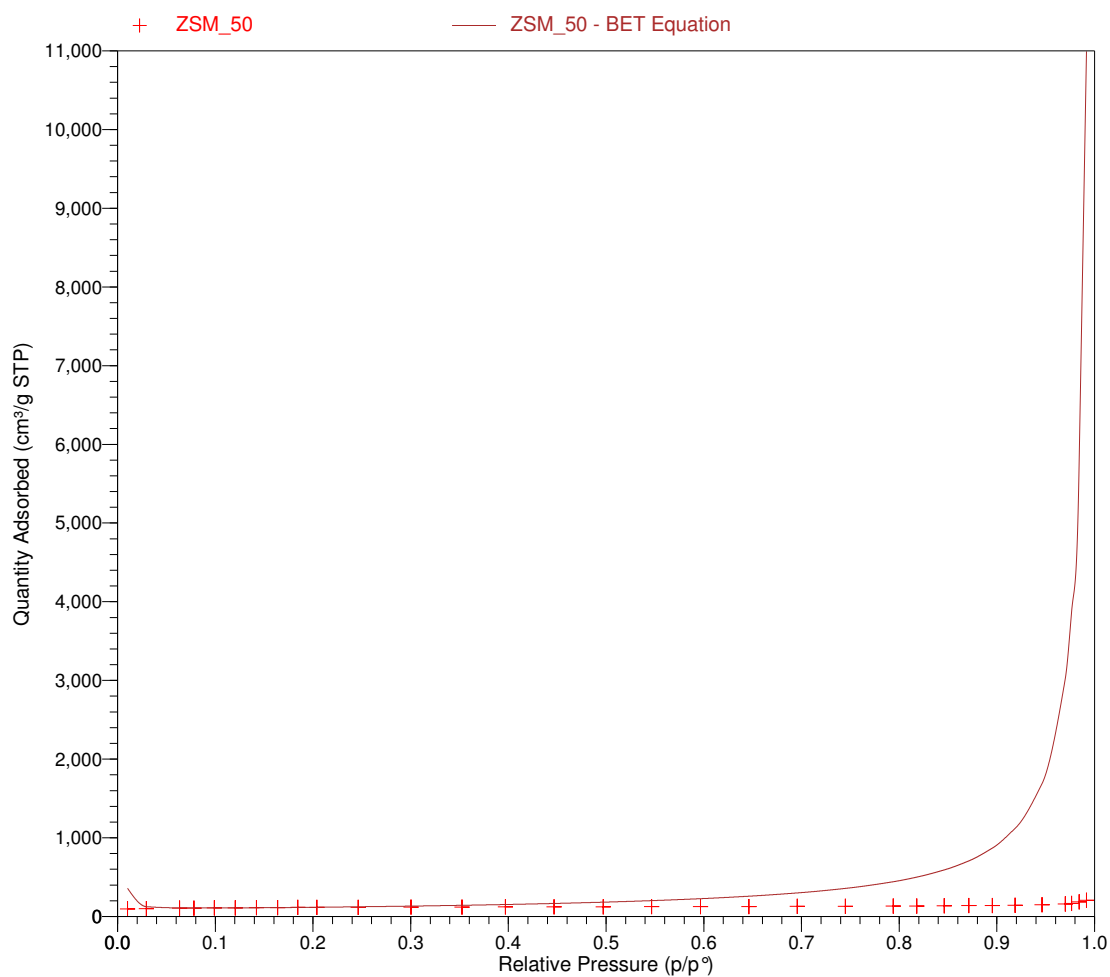
Sample Mass: 0.1965 g

Cold Free Space: 22.2302 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Isotherm Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 1

Serial #: 2132

Page 22

Sample: ZSM_50

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_50.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:35:10PM

Warm Free Space: 6.7929 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.1965 g

Cold Free Space: 22.2302 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Summary Report**Surface Area**Single point surface area at $p/p^\circ = 0.203923194$: 402.4200 m²/gBET Surface Area: 395.8911 m²/gLangmuir Surface Area: 530.8112 m²/gt-Plot Micropore Area: 253.4894 m²/g

BJH Adsorption cumulative surface area of pores

between 1.7000 nm and 300.0000 nm diameter: 81.3517 m²/g

BJH Desorption cumulative surface area of pores

between 1.7000 nm and 300.0000 nm diameter: 94.8341 m²/g**Pore Volume**

Single point adsorption total pore volume of pores

less than 66.2556 nm diameter at $p/p^\circ = 0.969911905$: 0.248641 cm³/g**Pore Size**

Adsorption average pore width (4V/A by BET): 2.51222 nm

BJH Adsorption average pore diameter (4V/A): 8.7707 nm

BJH Desorption average pore diameter (4V/A): 7.7731 nm

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 1

Sample: DEGI01

Operator: PC

Submitter:

File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM

Completed: 27/08/2010 22:27:21PM

Report Time: 31/08/2010 9:15:59PM

Warm Free Space: 6.8465 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.1241 g

Cold Free Space: 22.0984 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (P/Po)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
0.009506056	7.30562	75.6250	00:39	768.18756
0.031557929	24.25490	78.7290	01:01	
0.062111608	47.74079	80.5504	01:05	
0.081908558	62.95979	81.3265	01:08	
0.101026233	77.65785	81.9192	01:10	
0.121449351	93.36060	81.9192	01:12	
0.140951176	108.35634	82.4494	01:14	
0.160801514	123.61875	82.8773	01:16	
0.180453895	138.73233	83.2536	01:17	
0.200257967	153.96373	83.5833	01:19	
0.248345305	190.93835	83.8854	01:21	
0.299707700	230.43706	84.4981	01:22	
0.349782480	268.94351	85.0504	01:24	
0.398169687	306.15997	85.5370	01:25	
0.448005640	344.48657	85.9848	01:27	
0.497732968	382.73874	86.4431	01:28	
0.547547838	421.05292	86.9320	01:30	
0.597268271	459.30508	87.4594	01:31	
0.647021783	497.57587	88.0618	01:33	
0.696388544	535.56134	88.7670	01:34	
0.746009478	573.74530	89.6473	01:36	
0.794981385	611.43311	90.7813	01:38	
0.817583125	628.82892	92.3304	01:40	
0.846117769	650.80157	93.3023	01:41	
0.870514052	669.59277	94.8616	01:43	
0.894632742	688.18555	96.6646	01:45	
0.917571477	705.87280	99.1531	01:48	
0.943662441	726.01599	102.7921	01:51	
0.972990563	748.75763	110.3348	01:56	
0.977774410	752.52832	135.2460	02:08	770.02972
0.988653891	760.93164	145.6552	02:14	
0.989754281	761.79364	153.9736	02:16	
0.981972160	755.83380	160.6835	02:17	
0.976161369	751.40576	156.3967	02:19	
0.972571729	748.70184	152.5243	02:22	
0.952895579	733.69989	148.4243	02:26	
0.917914768	706.82166	125.9340	02:36	
0.900317109	693.27094	107.8938	02:40	
0.874206484	673.16498	103.8263	02:45	
0.855255721	658.57233	100.0021	02:49	
0.829330335	638.60901	98.0852	02:52	
0.802881493	618.24261	96.1419	02:57	
0.754534162	581.01373	94.6765	02:59	
0.703279372	541.54602	92.6470	03:01	
0.653305160	503.06439	91.1324	03:03	
0.602638305	464.04941	90.0386	03:05	
0.552245266	425.24527	89.1876	03:06	
0.502005284	386.55899	88.5063	03:07	
		87.9181	03:09	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 2

Sample: DEGI01

Operator: PC

Submitter:

File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM

Completed: 27/08/2010 22:27:21PM

Report Time: 31/08/2010 9:15:59PM

Warm Free Space: 6.8465 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.1241 g

Cold Free Space: 22.0984 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (P/Po)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
0.454052606	349.63400	86.8893	03:12	
0.400937385	308.73370	86.2446	03:13	
0.352541703	271.46759	85.7501	03:15	
0.301488281	232.15494	85.2400	03:16	
0.251256344	193.47485	84.6961	03:18	
0.201137160	154.88159	84.0657	03:20	
0.141731865	109.13775	83.0822	03:22	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

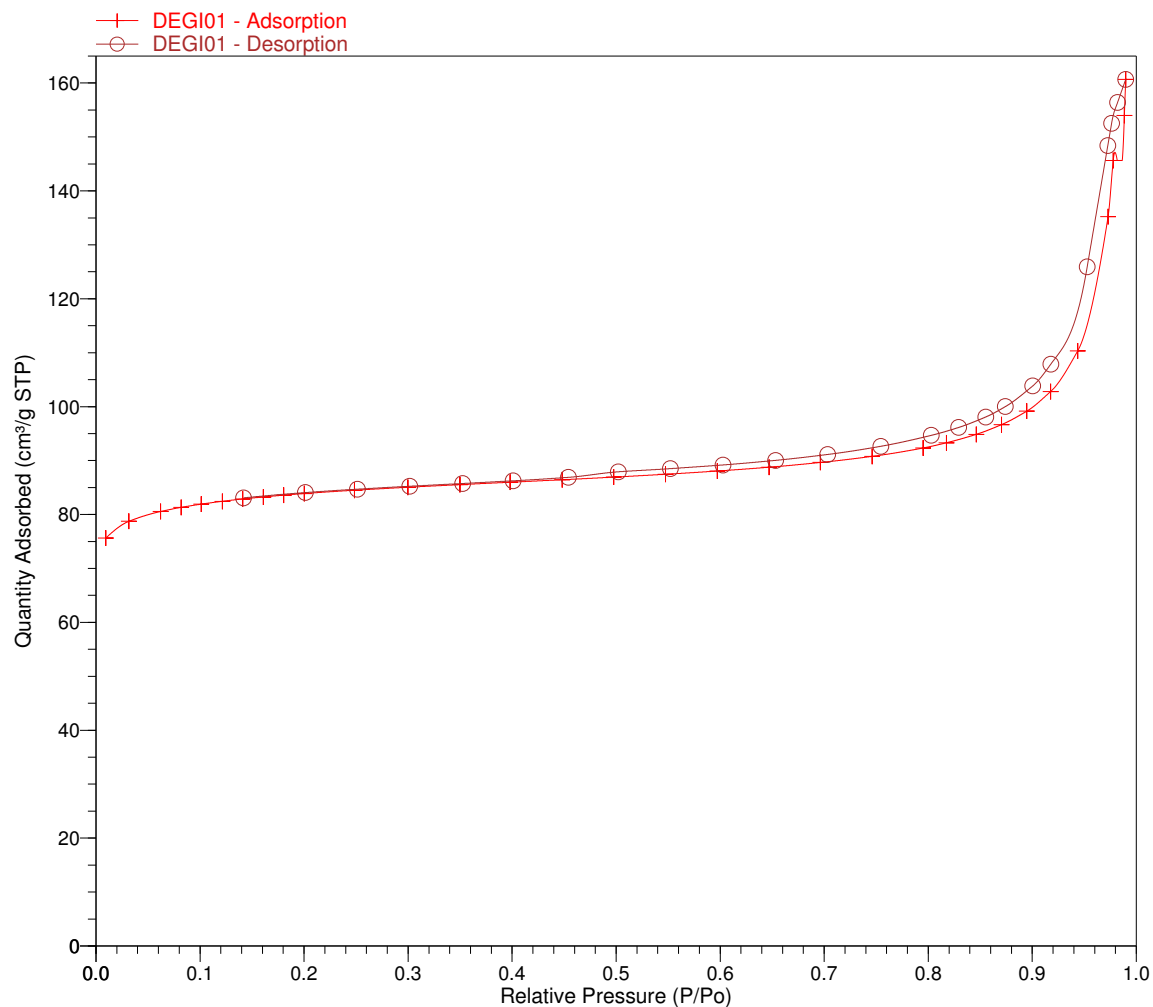
Page 3

Sample: DEGI01
Operator: PC
Submitter:
File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM
Completed: 27/08/2010 22:27:21PM
Report Time: 31/08/2010 9:15:59PM
Warm Free Space: 6.8465 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.1241 g
Cold Free Space: 22.0984 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 4

Sample: DEGI01

Operator: PC

Submitter:

File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM

Completed: 27/08/2010 22:27:21PM

Report Time: 31/08/2010 9:15:59PM

Warm Free Space: 6.8465 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.1241 g

Cold Free Space: 22.0984 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Surface Area Report

BET Surface Area: 281.9911 ± 4.8051 m²/gSlope: 0.015628 ± 0.000261 g/cm³ STPY-Intercept: -0.000191 ± 0.000036 g/cm³ STP

C: -80.998388

Qm: 64.7779 cm³/g STP

Correlation Coefficient: 0.9991671

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(Po/P - 1)]
0.062111608	80.5504	0.000822
0.081908558	81.3265	0.001097
0.101026233	81.9192	0.001372
0.121449351	82.4494	0.001677
0.140951176	82.8773	0.001980
0.160801514	83.2536	0.002302
0.180453895	83.5833	0.002634
0.200257967	83.8854	0.002985

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 5

Sample: DEGI01

Operator: PC

Submitter:

File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM

Completed: 27/08/2010 22:27:21PM

Report Time: 31/08/2010 9:15:59PM

Warm Free Space: 6.8465 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

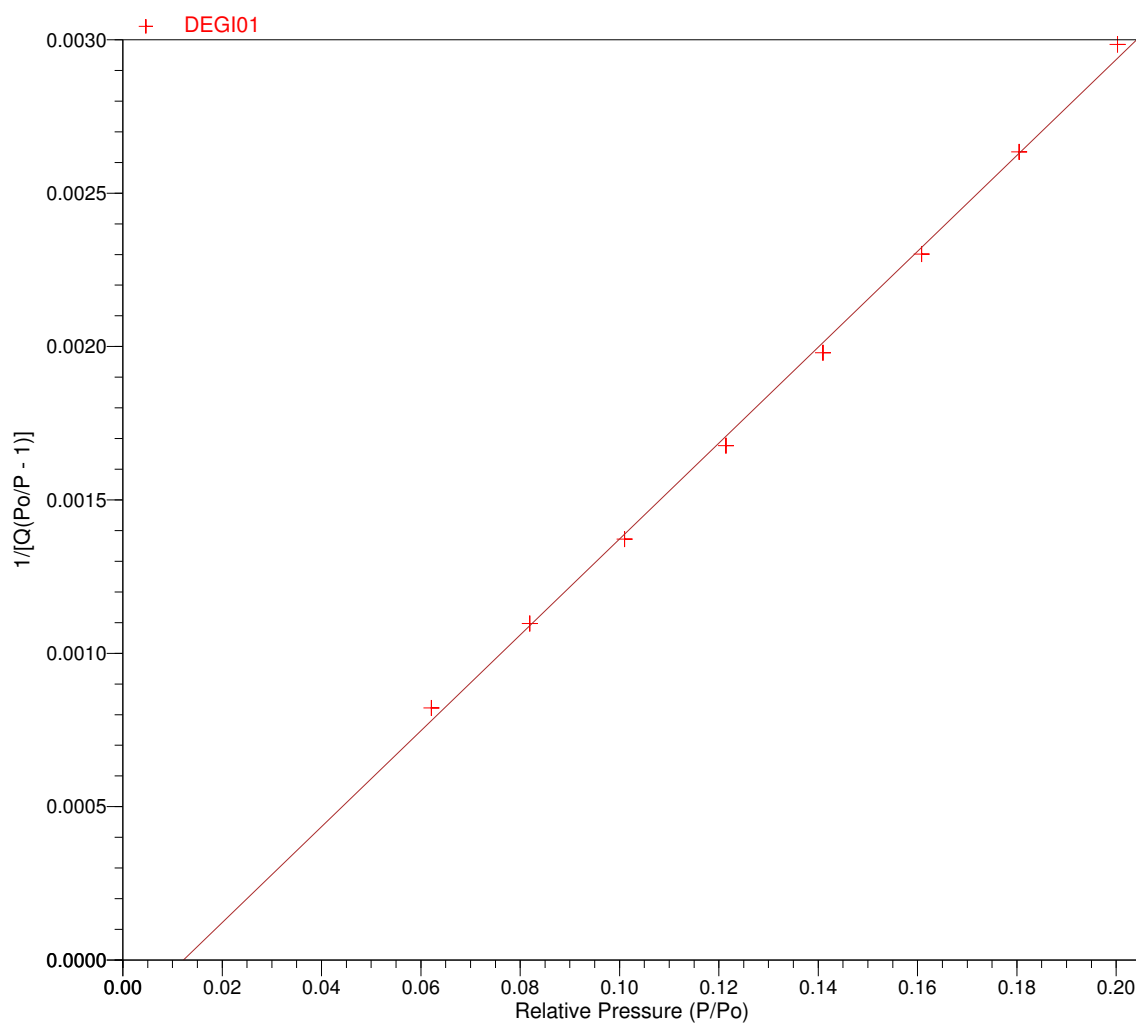
Sample Mass: 0.1241 g

Cold Free Space: 22.0984 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Surface Area Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 6

Sample: DEGI01

Operator: PC

Submitter:

File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM

Completed: 27/08/2010 22:27:21PM

Report Time: 31/08/2010 9:15:59PM

Warm Free Space: 6.8465 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

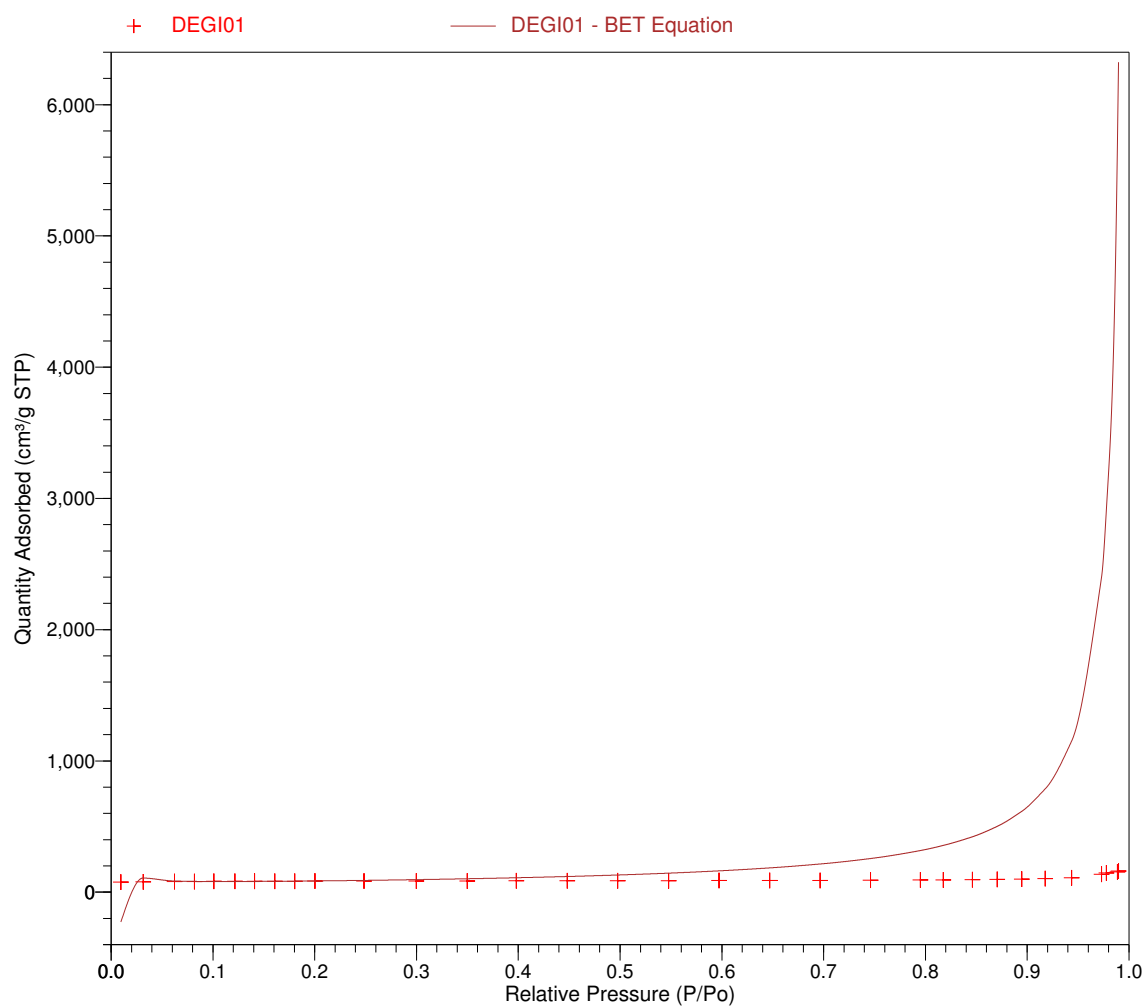
Sample Mass: 0.1241 g

Cold Free Space: 22.0984 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Isotherm Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 22

Sample: DEGI01

Operator: PC

Submitter:

File: C:\...\AS2010~1\DEGI01.SMP

Started: 27/08/2010 17:39:02PM

Completed: 27/08/2010 22:27:21PM

Report Time: 31/08/2010 9:15:59PM

Warm Free Space: 6.8465 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.1241 g

Cold Free Space: 22.0984 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/Po = 0.200257967: 292.0416 m²/g

BET Surface Area: 281.9911 m²/g

Langmuir Surface Area: 372.2709 m²/g

t-Plot Micropore Area: 239.1492 m²/g

BJH Adsorption cumulative surface area of pores

between 17.000 Å and 3000.000 Å diameter: 30.6838 m²/g

BJH Desorption cumulative surface area of pores

between 17.000 Å and 3000.000 Å diameter: 33.2581 m²/g

Pore Volume

Single point adsorption total pore volume of pores

less than 736.204 Å diameter at P/Po = 0.972990563: 0.209199 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 29.6745 Å

BJH Adsorption average pore diameter (4V/A): 174.064 Å

BJH Desorption average pore diameter (4V/A): 161.801 Å

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 1

Sample: ZSM_280

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:29:27PM

Warm Free Space: 7.4288 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2

Analysis Bath Temp.: -195.800 °C

Sample Mass: 0.2607 g

Cold Free Space: 24.9191 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
			00:39	758.64758
0.009862135	7.48216	91.7168	01:52	
0.030724577	23.31006	94.6672	01:57	
0.063229505	47.97098	97.0876	02:03	
0.082514494	62.60221	98.2075	02:06	
0.100945699	76.58578	99.1898	02:10	
0.121775259	92.38901	100.2877	02:14	
0.140116721	106.30472	101.5143	02:20	758.69427
0.155986410	118.34527	103.3226	02:27	
			02:39	
0.177470507	134.64812	108.3932	02:42	
0.198546495	150.64873	112.3868	02:54	
0.243717930	184.93222	117.2074	03:03	
0.316365019	240.06461	120.4647	03:09	
0.380868855	289.01636	122.0641	03:12	
0.413376591	313.68961	122.7284	03:15	
0.447248818	339.39914	123.3905	03:18	
0.497205736	377.31577	124.3057	03:21	
0.546684447	414.86844	125.2031	03:23	
0.596800882	452.90845	126.1077	03:26	
0.646967992	490.98544	126.9728	03:28	
0.696719470	528.74786	127.7932	03:30	
0.746217828	566.31903	128.6128	03:32	
0.795320581	603.59418	129.5768	03:35	
0.818227795	620.98267	130.1209	03:36	
0.847318460	643.07141	130.9203	03:39	
0.872650049	662.30420	131.6835	03:41	
0.897717894	681.33344	132.4557	03:42	
0.921759300	699.59167	133.3073	03:45	
0.945788864	717.83752	134.4504	03:47	
0.974190179	739.41431	137.4392	03:52	
0.980471981	744.19470	138.9551	03:55	
0.987568897	749.59814	142.1371	03:59	
0.992837466	753.60138	146.0343	04:00	
0.987503604	749.56116	143.4695	04:02	
0.980571550	744.31189	141.0139	04:05	
0.973493548	738.95166	138.8763	04:08	
0.953400721	723.71594	135.8418	04:12	
0.920247643	698.56152	134.1919	04:15	
0.887469552	673.69092	133.4436	04:18	
0.859585532	652.52740	133.0172	04:19	
0.834037348	633.14038	132.6443	04:21	
0.825346530	626.54645	132.5011	04:22	
0.800697445	607.83795	132.1322	04:23	
0.754556647	572.82043	131.3307	04:26	
0.701693681	532.69556	130.4829	04:28	
0.652081974	495.03802	129.8090	04:30	
0.602365736	457.30029	129.2243	04:32	
0.552414968	419.38367	128.6704	04:34	
0.501945323	381.07227	128.1430	04:36	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 2

Sample: ZSM_280
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM Analysis Adsorptive: N2
Completed: 02/07/2010 15:49:45PM Analysis Bath Temp.: -195.800 °C
Report Time: 02/07/2010 16:29:27PM Sample Mass: 0.2607 g
Warm Free Space: 7.4288 cm³ Measured Cold Free Space: 24.9191 cm³ Measured
Equilibration Interval: 5 s Low Pressure Dose: None
Sample Density: 1.000 g/cm³ Automatic Degas: No

Isotherm Tabular Report

Relative Pressure (p/p ^o)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm ³ /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
			04:40	759.20776
0.443290221	336.54938	124.8883	04:45	
0.395110927	299.97128	123.4336	04:48	
0.334590228	254.02350	122.1351	04:53	
0.303757097	230.61475	121.5619	04:56	
0.253489749	192.45139	120.5444	04:59	
0.203506772	154.50392	119.2567	05:03	
0.141442413	107.38418	116.0533	05:11	

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

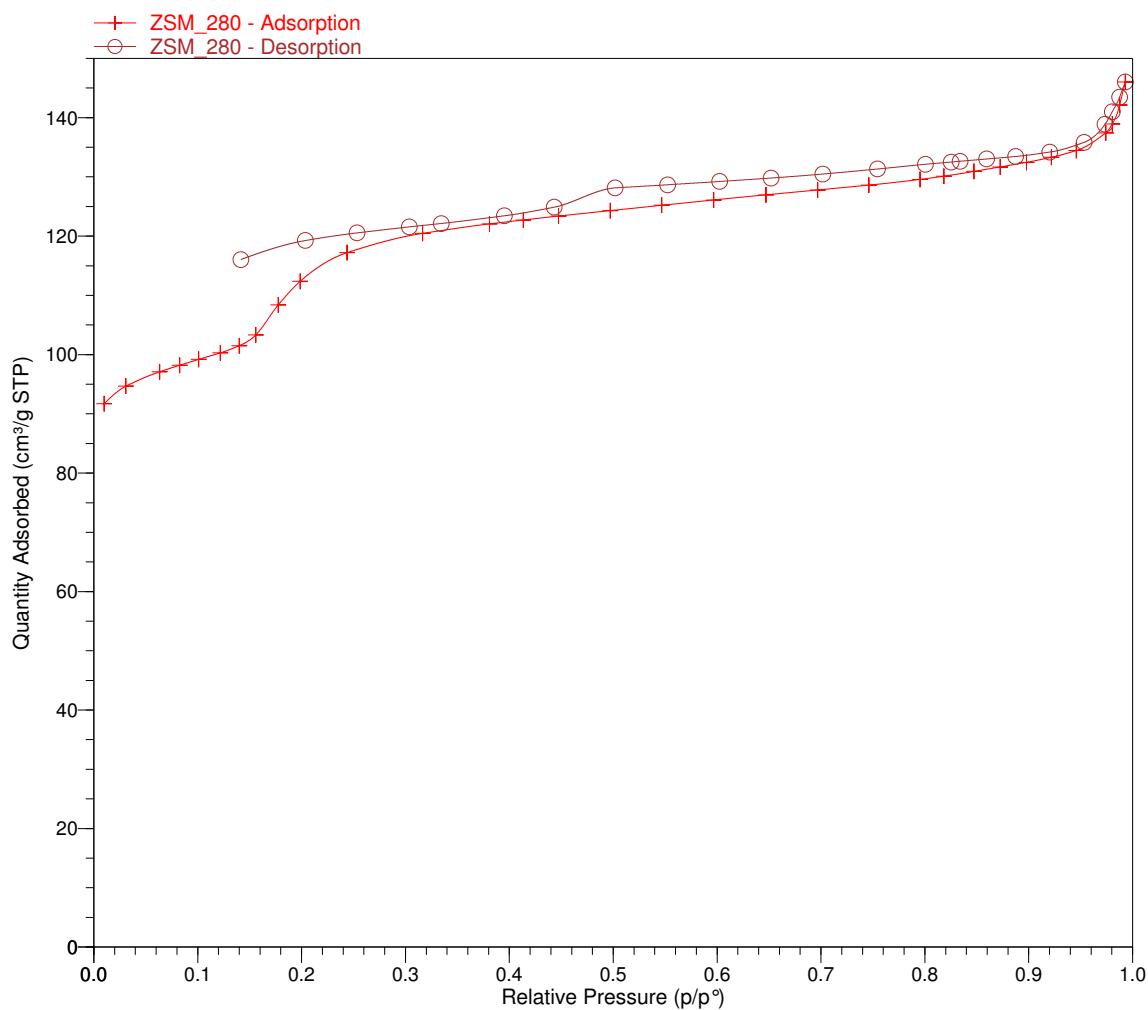
Page 3

Sample: ZSM_280
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM
Completed: 02/07/2010 15:49:45PM
Report Time: 02/07/2010 16:29:27PM
Warm Free Space: 7.4288 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N₂
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2607 g
Cold Free Space: 24.9191 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Isotherm Linear Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 4

Sample: ZSM_280
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM
Completed: 02/07/2010 15:49:45PM
Report Time: 02/07/2010 16:29:27PM
Warm Free Space: 7.4288 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2607 g
Cold Free Space: 24.9191 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

BET Surface Area Report

BET Surface Area: 385.8542 ± 6.6719 m²/g
Slope: 0.011286 ± 0.000193 g/cm³ STP
Y-Intercept: -0.000004 ± 0.000027 g/cm³ STP
C: -3074.777889
Qm: 88.6369 cm³/g STP
Correlation Coefficient: 0.9991214
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°p - 1)]
0.063229505	97.0876	0.000695
0.082514494	98.2075	0.000916
0.100945699	99.1898	0.001132
0.121775259	100.2877	0.001383
0.140116721	101.5143	0.001605
0.155986410	103.3226	0.001789
0.177470507	108.3932	0.001991
0.198546495	112.3868	0.002204

Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 5

Sample: ZSM_280

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:29:27PM

Warm Free Space: 7.4288 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

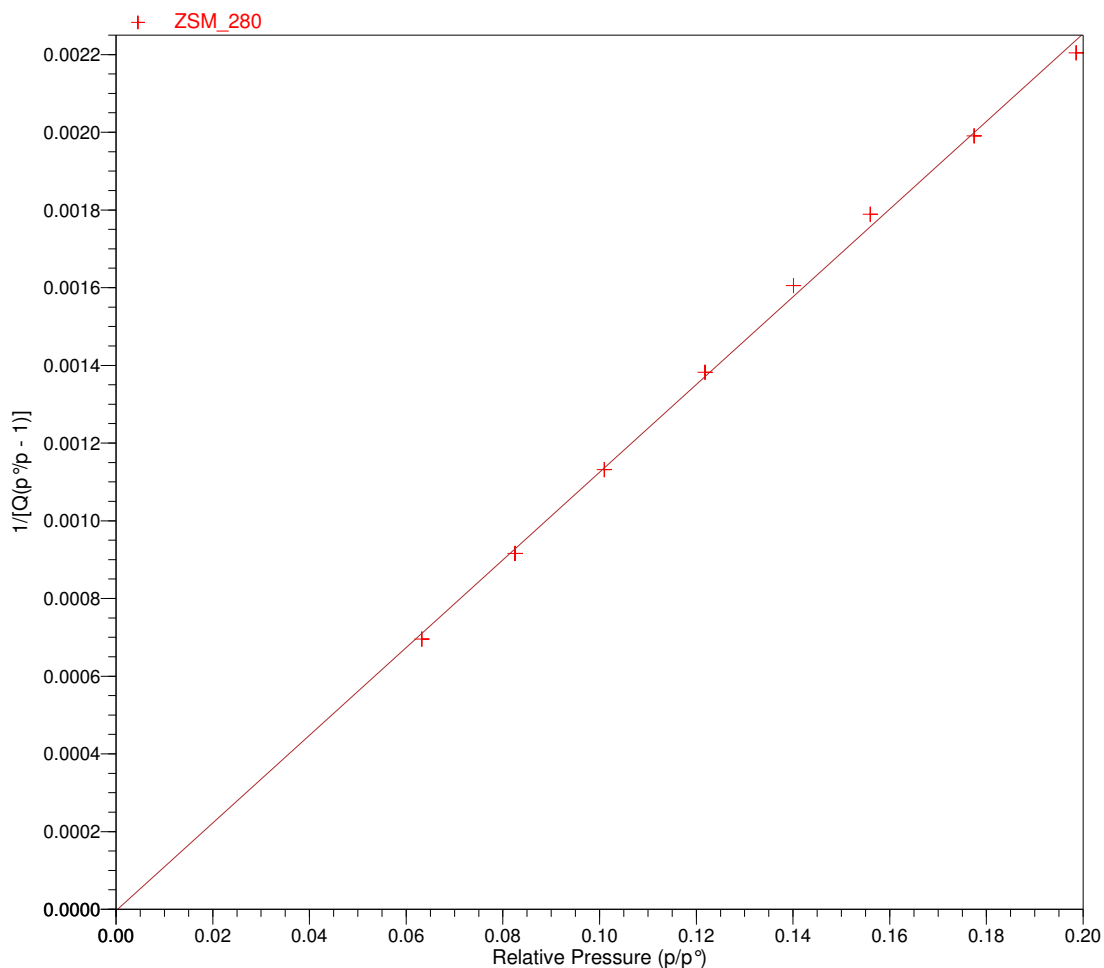
Sample Mass: 0.2607 g

Cold Free Space: 24.9191 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Surface Area Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 6

Sample: ZSM_280

Operator: Deji

Submitter:

File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM

Completed: 02/07/2010 15:49:45PM

Report Time: 02/07/2010 16:29:27PM

Warm Free Space: 7.4288 cm³ Measured

Equilibration Interval: 5 s

Sample Density: 1.000 g/cm³Analysis Adsorptive: N₂

Analysis Bath Temp.: -195.800 °C

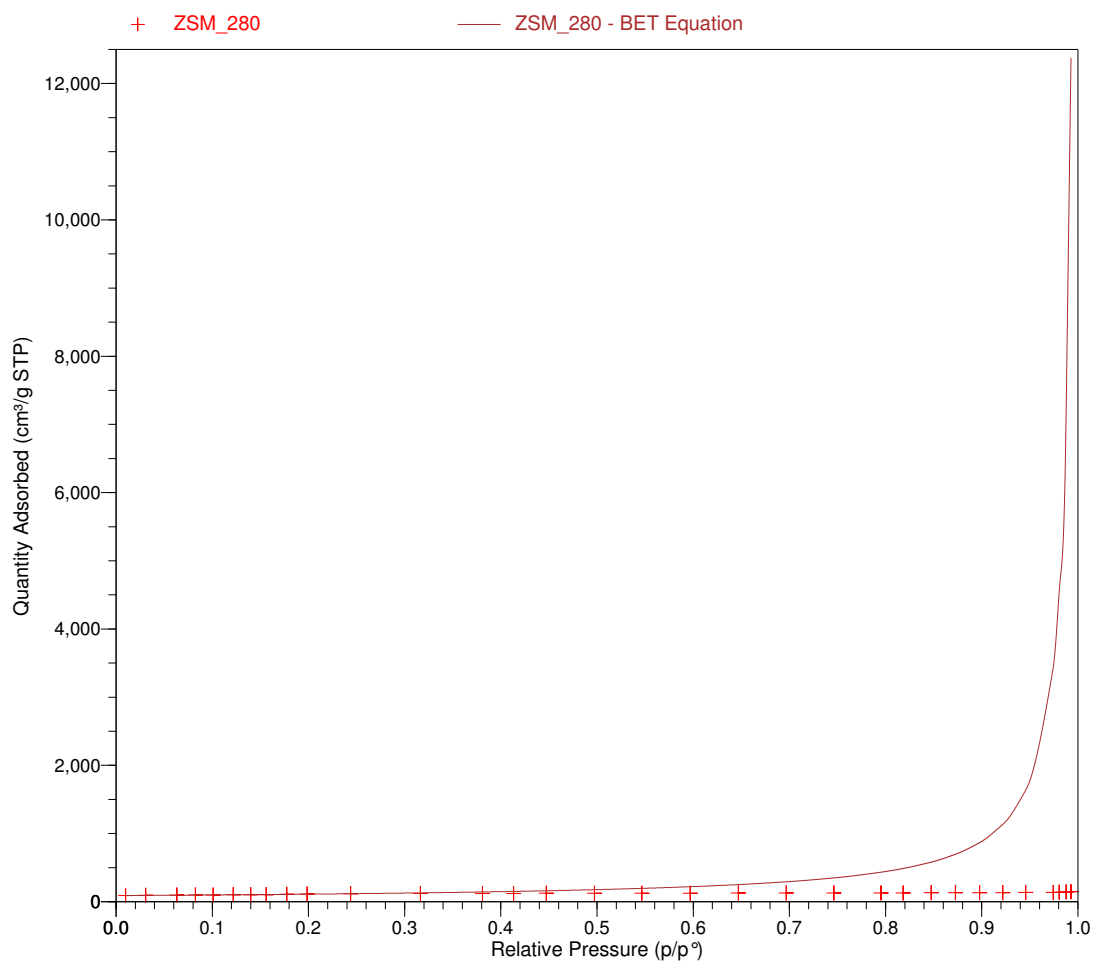
Sample Mass: 0.2607 g

Cold Free Space: 24.9191 cm³ Measured

Low Pressure Dose: None

Automatic Degas: No

BET Isotherm Plot



Full Report Set

TriStar 3000 V6.07 A

Unit 1 Port 2

Serial #: 2132

Page 22

Sample: ZSM_280
Operator: Deji
Submitter:
File: C:\...\DEJIS~1\ZSM_280.SMP

Started: 02/07/2010 9:42:48PM	Analysis Adsorptive: N2
Completed: 02/07/2010 15:49:45PM	Analysis Bath Temp.: -195.800 °C
Report Time: 02/07/2010 16:29:27PM	Sample Mass: 0.2607 g
Warm Free Space: 7.4288 cm ³ Measured	Cold Free Space: 24.9191 cm ³ Measured
Equilibration Interval: 5 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm ³	Automatic Degas: No

Summary Report**Surface Area**Single point surface area at $p/p^\circ = 0.198546495$: 392.1046 m²/gBET Surface Area: 385.8542 m²/gLangmuir Surface Area: 520.8019 m²/gt-Plot Micropore Area: 103.1211 m²/gBJH Adsorption cumulative surface area of pores
between 1.7000 nm and 300.0000 nm diameter: 184.8761 m²/gBJH Desorption cumulative surface area of pores
between 1.7000 nm and 300.0000 nm diameter: 70.3496 m²/g**Pore Volume**Single point adsorption total pore volume of pores
less than 76.9624 nm diameter at $p/p^\circ = 0.974190179$: 0.212591 cm³/g**Pore Size**

Adsorption average pore width (4V/A by BET): 2.20385 nm

BJH Adsorption average pore diameter (4V/A): 3.0239 nm

BJH Desorption average pore diameter (4V/A): 4.2282 nm