

CATALYSIS ON ION EXCHANGED ZSM5 TYPE ZEOLITES

By

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ABSTRACT

Catalytic data on ion exchanged ZSM5 are limited in extent. The aim of this work is to investigate the effect of sodium and caesium cations in ZSM5 on the selectivity and activity of the toluene disproportionation and xylene isomerisation reactions. It is predicted that the larger ionic radius of the caesium ion will increase the para-selectivity of ZSM5 relative to the sodium ion, due to increased intra-crystalline diffusion resistance.

Ion exchange isotherms were constructed for the Na/NH_4 and Cs/NH_4 equilibria, on ZSM5 samples with Si/Al ratios of 28 and 45. Thermodynamic analysis of the isotherms was performed. The isotherms were used to prepare ZSM5 samples of consistent cation loading for catalytic studies.

The para-selectivities for the ion exchanged samples for the toluene disproportionation reaction were related to the conversion and contact time. The conversion data were fitted to first order kinetics and the activity per unit site was found to vary with both cation type and loading. The effect was related to variations in the Arrhenius parameters with cation loading.

The xylene isomerisation reaction was kinetically modelled by a three-component reversible parallel reaction scheme. Para-selectivities paralleled those found for the toluene disproportionation reaction; this was attributed to increased diffusional control caused by electrostatic rather than steric effects.

By analogy of the ZSM5 lattice to a "diamond-like" network, simple calculations were performed in order to calculate the

minimum number of cations per unit cell required to observe a percolation effect. High-alumina ZSM5 samples were prepared by direct synthesis and alumination techniques. The para-selectivities of these samples were ascertained for the toluene disproportionation reaction and related to the physical characteristics of the samples.

TO MY PARENTS FOR THEIR LOVE AND SUPPORT

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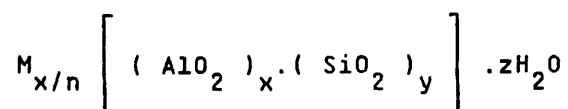
I would like to express my sincere thanks to Dr. D. Keir for his substantial contribution to the construction of the catalytic rig and to both Dr. D. Keir and Dr. P. Graham for their further help and encouragement throughout the duration of the project. Finally I would like to mention all the members of the coffee-club who have so greatly contributed to my happiness at Imperial College.

INTRODUCTION

1.1 ZEOLITE MOLECULAR SIEVES (1)

Zeolites are a class of crystalline aluminosilicates which exist in a wide number of meta-stable phases, all of which are characterised by a well-defined crystal structure. Hypothetically, each structure can be considered as being built from SiO_4 tetrahedra, which are linked via oxygen bridges, to form an "infinite" three-dimensional lattice. AlO_4 tetrahedra can be substituted into this lattice with the introduction of a net negative charge into the framework. This can be balanced either by an exchangeable cation such as sodium or calcium, by a proton which leads to a Bronsted acid site, or by a positively charged complex. Thus, the presence of aluminium atoms in the zeolite framework has the effect of introducing both ion exchange and catalytic properties, which were not present in the hypothetical pure silica analogues.

As there are no unshared oxygens in the framework, the atomic ratio of the anionic network is $(\text{Al} + \text{Si}) / \text{O} = 0.5$ and the general chemical formula of a zeolite is :



where z is dependent on the free volume and n is the valency of the cation, M . The proportion of aluminium present in the zeolite framework is characterised by the Si/Al ratio, which is found to

be greater than or equal to one for all zeolites so far characterised. The simplest interpretation of this is expressed in Lowenstein's rule, which states that two AlO_4 tetrahedra cannot be linked directly within the framework.

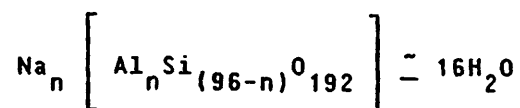
Each zeolite framework contains a one-, two- or three-dimensional channel network which is normally filled by water molecules, however after dehydration the voids can be filled by other molecules which can also pass through the pore openings. Molecules which are too large will be excluded and this molecular sieving action characterises the adsorptive and separative properties of zeolites.

Zeolites occur naturally, stilbite being the first to be discovered in 1756. Subsequent to such discoveries, some of these structures have also been produced synthetically, whilst recent research into the synthesis problem has led to the production of novel zeolite frameworks with no known natural counterparts e.g. ZSM5 (2) and zeolite A (3).

1.2 ZSM5 STRUCTURE CHARACTERISATION

The high silica zeolite ZSM5 was first patented by Mobil in 1972 (2). Typically it is synthesised by the reaction of a silica and alumina source in the presence of a templating agent e.g. tetrapropylammonium bromide. Reaction proceeds readily under alkaline conditions at temperatures between 100-200°C, and at autogeneous pressure for a period of 2-14 days. The ZSM5 crystals produced contain occluded alkylammonium ions which can be removed by calcination in air at temperatures in excess of 500°C. The

unit-cell formula of the sodium form of ZSM5 is (4):



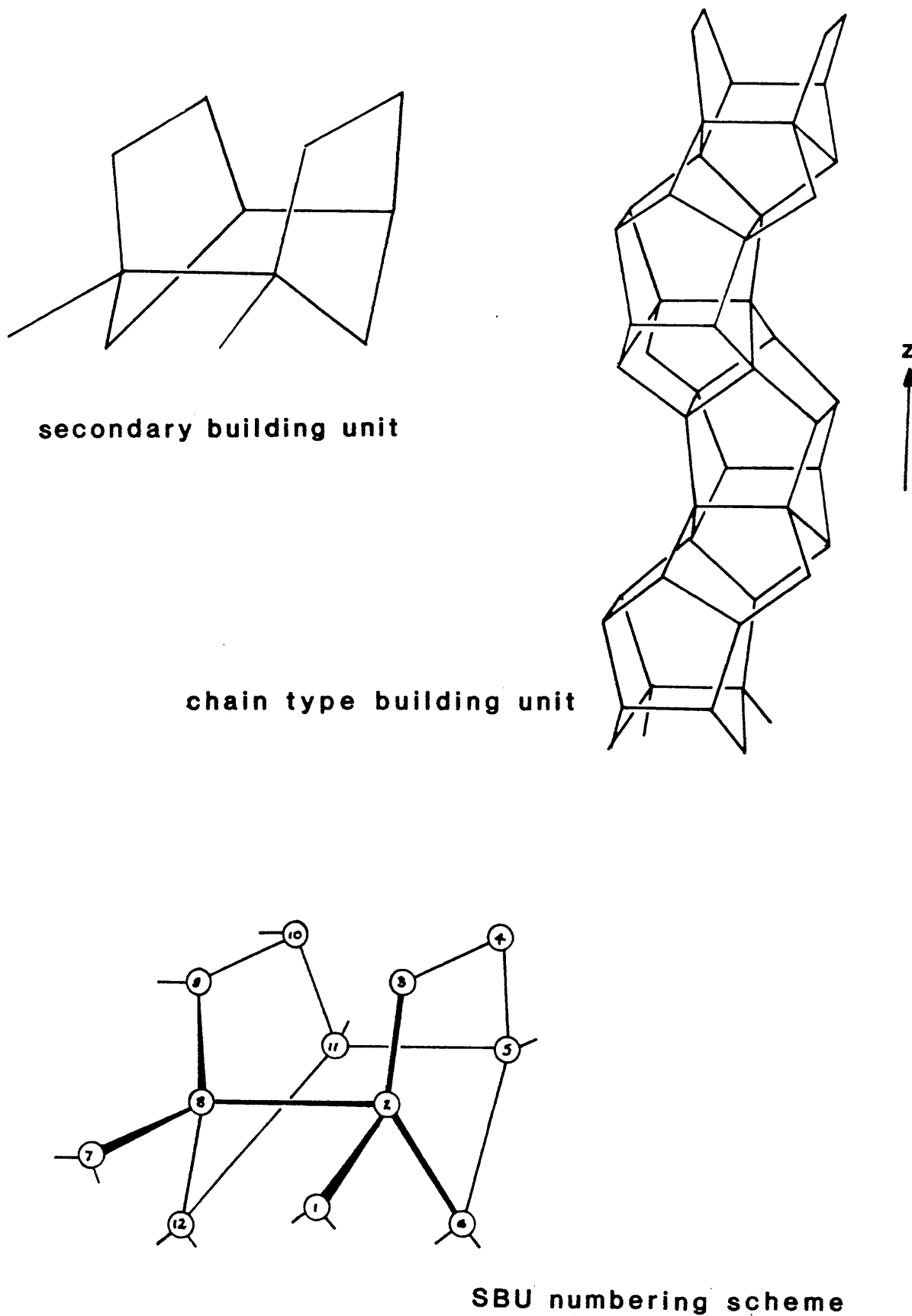
The value of n can range from 0 to 27, however the siliceous end-member of the ZSM5 series, known as silicalite-I (5), exhibits none of the properties such as cation exchange or catalysis which are typical of ZSM5, and which are normally associated with the presence of aluminium in the framework.

Crystal structure

The crystal structures of ZSM5 and silicalite-I have been determined by both powder and single crystal X-ray diffraction techniques. At room temperature the calcined crystals are orthorhombic, whilst at higher temperatures (above about 50°C) (6), or when the zeolite is loaded with sorbate (e.g. para-xylene, benzene or acetylacetone) (8), a reversible phase change occurs to monoclinic symmetry. This can be monitored by ^{29}Si MASNMR; deconvolution of the Si(0Al) peak suggests that in both forms the unit cell comprises 24 non-equivalent Si atom sites, which yields the low-symmetry space groups $P2_1/n$ and $Pn2_1a$ for the monoclinic and orthorhombic forms respectively (6,7). Lattice constants for the unit-cell have been refined to give $a=20.076$, $b=19.926$ and $c=13.401$ Å (9).

The secondary building unit (SBU) of the framework is most adequately based on the arrangement of twelve T atoms shown in figure 1.1 (10), where T represents both Al and Si framework atoms. The SBU is easily recognisable as a pair of 5-1 units, and

FIGURE 1.1 : Secondary Building Unit and its Linkage within Chains



so ZSM5 is a member of the pentasil class of zeolites: high silica zeolites containing five-membered rings (10). To generate the ZSM5 structure, these SBU's can be linked through edges to form chains and then sheets as shown in figures 1.1 and 1.2 (11). Pairs of such sheets can be joined in two ways so that neighbouring sheets are related either by the symmetry operation of a mirror plane or by an inversion. The latter applies to ZSM5 (11), whereas the former occurs in the related structure, ZSM11 (12). Any number of possible structures can be postulated by the linking of such sheets using combinations of the mirror and inversion operations, so that ZSM5 and ZSM11 can be considered as the structural end-members of an essentially continuous series of intermediate structures in the pentasil series (10,11).

The ZSM5 and ZSM11 frameworks form three-dimensional channel systems based on ten-membered rings as shown in figure 1.3. In ZSM5, two types of channel exist; straight channels running parallel to the [010] plane and with openings of size 5.4 x 5.6 Å and sinusoidal channels parallel to the [100] plane, of size 5.1 x 5.5 Å (13). In ZSM11, both channels are elliptical and straight, with a cross-sectional diameter of 5.1 x 5.5 Å (13). Diffusion in the [001] direction can readily occur between the overlapping channels parallel to [100] and [010].

Aluminium distribution

The chemical and physical properties of ZSM5 are influenced both by the framework topology which has been described above, and as stated in Section 1.1 by the presence of aluminium in the framework. The question of the location of aluminium atoms within

FIGURE 1.2 : Linking of ZSM5 Chains within Sheets

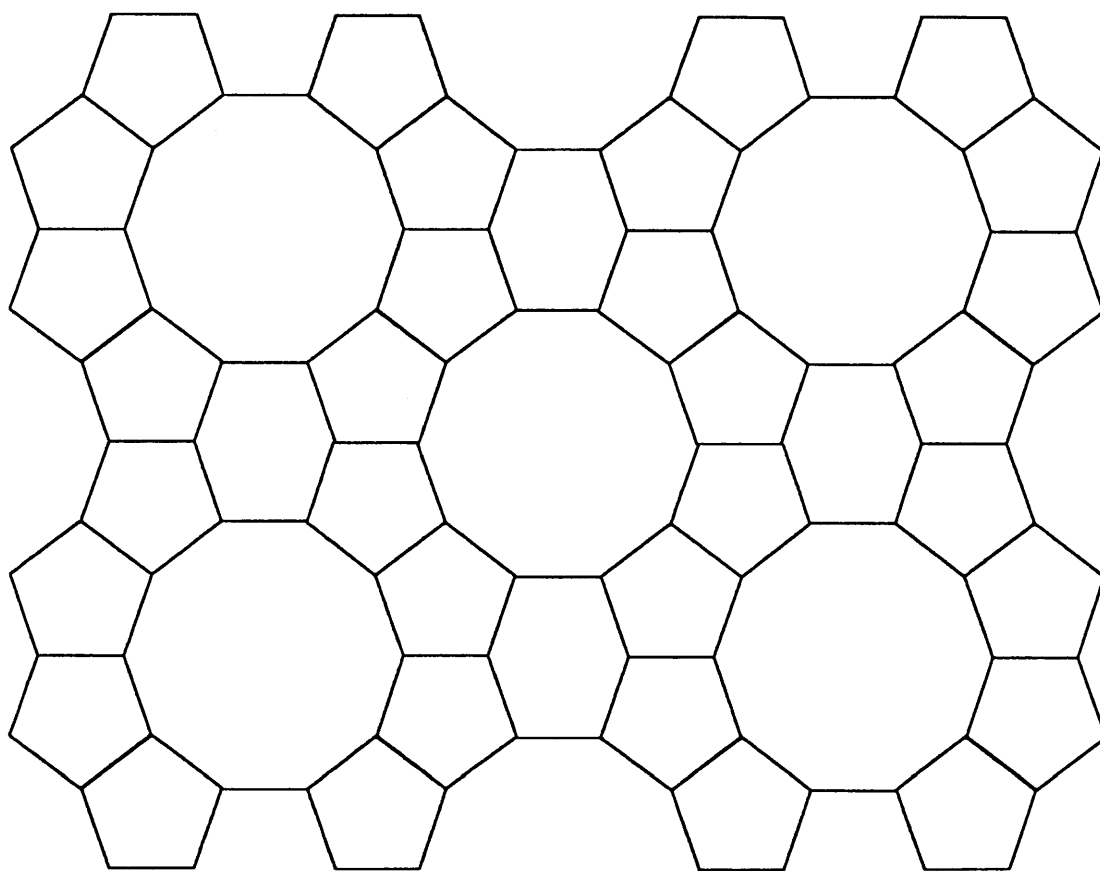
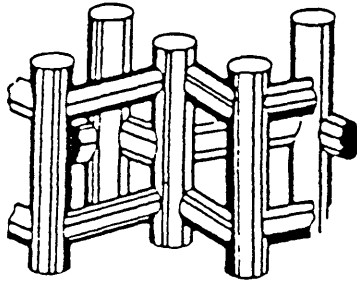
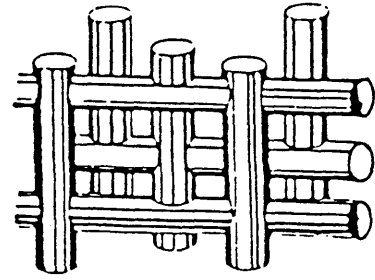


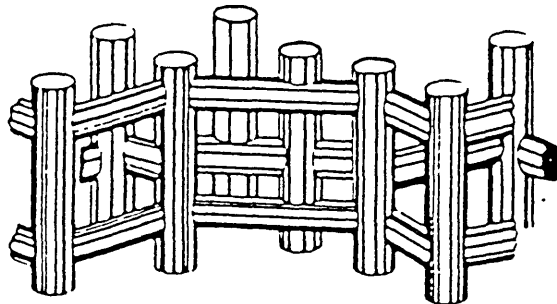
FIGURE 1.3 : Pentasil Channel Systems



ZSM5



ZSM11



ZSM5/ZSM11 intergrowth

the zeolite crystal can be approached in two ways, either by considering the distribution of aluminium throughout the zeolite crystal or by investigating the preferred aluminium positions in the ZSM5 unit cell.

Several studies have been made on ZSM5 crystals to compare the bulk Si/Al ratio of a particular sample as measured by wet chemical analysis, with the Si/Al ratio determined for the surface of the crystal by the use of some surface sensitive technique. Studies have produced contradictory results; concluding that the aluminium distribution in ZSM5 could be essentially homogeneous (14), whilst other samples exhibited a inhomogeneous distribution, the nature of the zoning being dependent on the synthetic conditions (15). Attempts to correlate these results with crystal size have revealed that small single crystals ($<0.3\mu\text{m}$) possess a silica-rich surface, whilst larger crystals ($>3\mu\text{m}$) show a distinct preference for a silica-rich core (16).

Within a single crystal entire aluminium profiles can be obtained using electron-microprobe analysis (17); however only large crystals may be studied because of the resolution limit of the technique. The aluminium distribution through a single ZSM5 crystal has been determined for crystals ranging from 60 to 100 microns in diameter, and with a bulk Si/Al ratio of 50 to 100. This revealed the presence of considerable aluminium zoning; the surface being aluminium rich and the core of the crystal being virtually pure silicalite. Overall the aluminium concentration through the crystal varied by a factor of more than ten. The authors are however cautious in generalising their results,

realising that most ZSM5 samples used as catalysts are composed of crystals of about 1 micron diameter, and hence may not exhibit the same zoning found in these larger crystals.

The elucidation of preferred aluminium sites within the ZSM5 unit-cell can be approached using the techniques of neutron diffraction or by quantum mechanical studies. Recent *ab initio* molecular orbital calculations performed on pentameric model clusters (18,19), with a geometry derived from the known structure of zeolite ZSM5, have suggested that aluminium atoms are preferentially located at the T12 and T2 sites in the ZSM5 framework. These sites are illustrated in figure 1.1, which show that the preferred sites belong to the five-membered rings. The direct observation of aluminium positions by neutron diffraction is not yet experimentally feasible. However, as each aluminium is electrically balanced by a cation, the location of cations by this technique will give some clue to the location of the aluminium atoms within the unit cell. Studies on nickel exchanged ZSM5 (20), have indicated two preferred positions for the location of the nickel ions within the ZSM5 unit cell. The first is at site S1 which is at the centre of the six-membered rings at the intersection of the two channels, but which is outside the channel itself, whilst the second is at site S2 in the sinusoidal channel, approximately 1.6 Å from the centre of the ten-membered rings.

Internal silanol groups

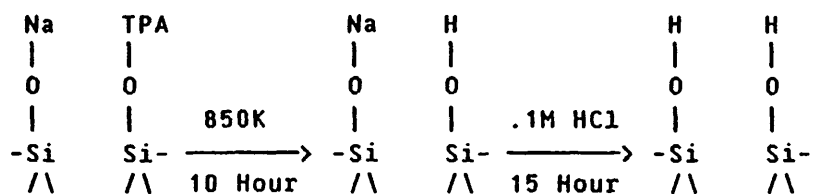
Recently, investigations of the ZSM5 structure have focused on the presence of internal silanol groups and their effect on the properties of ZSM5. Evidence for their existence in large numbers was originally proposed to explain the anomalous ion exchange properties of zeolites ZSM5 and ZSM11 (21). More direct evidence was subsequently obtained by using ^1H MASNMR (22) and IR spectroscopy (23), which directly observed the physical environment of the protons.

Ion exchange studies (21) on a series of ZSM5 samples of differing Si/Al ratio, show that under conditions of alkaline exchange, all samples with a Si/Al ratio greater than 35 exhibit a cation exchange capacity well in excess of that required to balance the framework aluminium charge. The presence of this effect is strongly pH-influenced and is not dependent on the nature of the cation. FTIR studies of ZSM5 zeolites of varying Si/Al ratio, show two bands in the O-H stretching region at 3620 and 3740 cm^{-1} . These have been assigned to Bronsted acid sites and to terminal Si-OH groups respectively. As the Si/Al ratio increases the 3620 cm^{-1} band intensity diminishes however concomitant with the loss of this band, a significant increase in the 3740 cm^{-1} band is seen to occur along with the appearance of a new, broad band at 3500 cm^{-1} (24,25).

The use of ^1H MASNMR (22) has led to the suggestion that these internal silanol groups occur as a direct result of the ZSM5 synthesis, and in particular the calcination of the ZSM5 to remove the TPA templating agent. The decomposition of TPA can be followed by IR spectroscopy (23), both by the observation of the band at

3720 cm^{-1} corresponding to the stretching frequency of the Si-OH group, and the CH_3 and CH_2 bands at 1475 cm^{-1} . The intensity of the OH band is seen to increase as the TPA template decomposes, which is itself observed by a concurrent decline in intensity of the C-H bands.

The defects are thought to result from Si-O-Si "bonds" which were never formed and up to 8% of the lattice silicon has been found to be present as Si-OH (22). The following reaction scheme has been suggested to account for their formation:



ZSM5 samples synthesised from organic-free gels show highly intact lattices without the high concentration of internal silanol groups observed in the samples synthesised in the presence of TPA (22,26).

The adsorption of pyridine onto ZSM5 zeolites which contain internal silanol groups, causes no change in the intensity of the 3720 cm^{-1} O-H band, indicating that these groups are not strongly acidic (23). Their acidic weakness is confirmed by the temperature programmed desorption studies of bases; the peak for desorption of ammonia from silanol groups is over 150 $^{\circ}\text{C}$ lower than for the desorption from Lewis and Bronsted acid groups. Hence the contribution of internal silanol groups to the acidic properties of ZSM5, is not significant in comparison with the Bronsted and Lewis acid sites discussed in the next section.

Acid sites

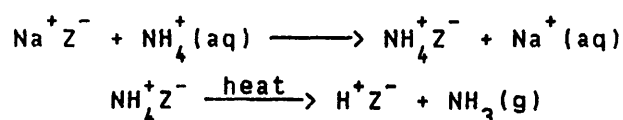
Zeolites are often used as a porous crystalline framework in which physical and chemical processes are performed. However the framework does not act as an inert surface but contains active sites, upon which both adsorption and chemical reactions can occur. The nature of these active sites varies, ranging from exchangeable cations to metals, oxides, complexes and other occluded species. Most commercially important reactions involve the exploitation of hydrocarbon transformations, which utilise a further type of active site: the Bronsted acid site.

Bronsted acidity is provided by O-H groups, which can be introduced into the structure in three main ways:

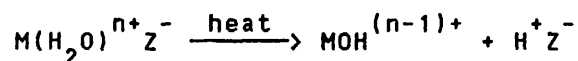
1. Direct proton exchange with mineral acids:



2. Ammonium exchange followed by calcination to expel ammonia:



3. Calcination of hydrated polyvalent cations (e.g. La^{3+}):



Superficially it would appear that the direct substitution method would be the simplest way of introducing Bronsted acidity into the zeolite framework. However the instability of high alumina zeolites such as zeolites A and Y in acid solutions is well known; the direct substitution method has the potential to

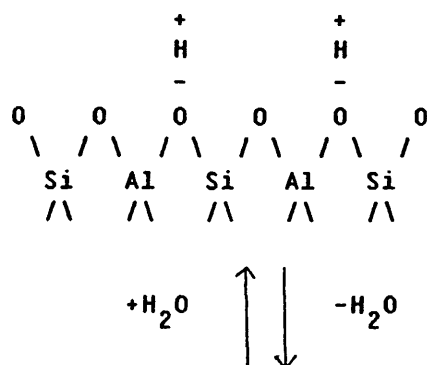
cause a large amount of structural degradation in these zeolites. There is now evidence from MASNMR that even high silica zeolites which were previously considered to be acid-stable, undergo surface dealumination when treated with mineral acids (27,28). Hence when zeolite structural integrity is required, the direct ion-exchange method is generally avoided.

Infra-red spectroscopy provides evidence for the physical structure of the active sites. Studies performed on evacuated samples show two main absorption bands in the O-H stretching region of the spectrum; at 3720 cm^{-1} and 3600 cm^{-1} which have been assigned to silanol and Bronsted acid groups respectively (29). A direct proportionality is found to exist with ZSM5 samples of differing Si/Al ratios, between the number of aluminium atoms per unit cell and the infrared absorbance of the 3600 cm^{-1} band per unit zeolite thickness. It is also found that upon adsorption of pyridine, the 3600 cm^{-1} band disappears, and a new band appears at 1540 cm^{-1} , identified as the C-C stretching frequency of the pyridinium ion, characteristic of adsorption on a Bronsted acid site. This suggests that the catalytically active acid sites can be regarded as protons associated with the framework oxygen atom of AlO_4 tetrahedra (29).

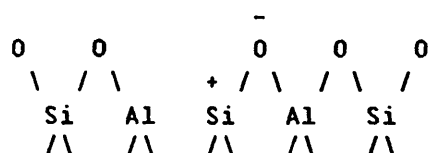
Bronsted acid sites are mobile at elevated temperatures. Above about 400°C a reversible reaction occurs, involving the formation of Lewis acid sites which is accompanied by a simultaneous decline in the number of Bronsted acid sites. The course of this reaction can be followed by infrared spectroscopy, showing that the band at 3600 cm^{-1} lowers in intensity at high temperatures. On subsequent pyridine adsorption, a band at 1450 cm^{-1} appears

which is characteristic of the C-C stretching frequency of pyridine coordinated to a Lewis acid site (30). The reaction is believed to follow the approximate scheme detailed below:

Bronsted sites

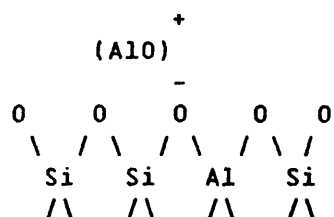


Lewis sites



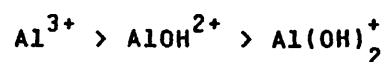
The existence of tri-coordinated aluminium has not been proven. It is now thought that such structures are not stable and at high temperatures in the presence of water vapour, the structure is "healed" to produce "true" Lewis acid sites (31):

"True" Lewis sites



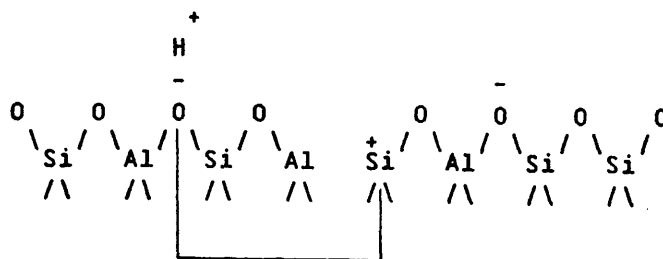
The exact nature of the dislodged aluminium species is not known. Quantum mechanical calculations used to investigate the stability of various extra-lattice aluminium compounds suggest, that such species can act as Lewis acid sites, and that for the three

simplest, the following acidity order exists (32):



X-ray diffraction (XRD) studies on ZSM5 samples which have undergone extensive dehydroxylation, have indicated the presence of octahedral aluminium species which have a structure similar to boehmite (33). This was formed under severe conditions and it is unlikely that such a bulky aluminium species will be formed on mild hydrothermal treatment.

There is evidence from catalytic studies that a small number of very strong acid sites exist which are in the super-acid category. Reaction data show that the temperature leading to maximum activity is greater than the temperature corresponding to the maximum number of Bronsted acid sites (34). It is postulated that a Lewis acid group acts inductively through the lattice on the Bronsted acid site, reducing the electron density at the O-H bond and causing the proton to be more acidic. The representation shown below is not structurally true as the Lewis acid sites are not lattice groups but Al-O species leached from the framework at high temperatures, however the idea of synergism between Bronsted hydroxyl groups and Lewis sites is still valid (35).



As well as their structure, a knowledge of the acid sites' performance as adsorption and catalytic centres is also required. This involves an appreciation of both the acid strength distribution and the sites' accessibility within the zeolite. A large number of physical techniques have been developed to investigate this problem. Of particular relevance to the acid strength distribution, are temperature programmed desorption of bases, base titration by Hammett indicators, and microcalorimetry. Application of these techniques to the study of ZSM5 zeolites carries the additional problem of the low density of acid sites in comparison to that found in the high-alumina zeolite Y, which has been more commonly studied.

Investigation of the heats of desorption of appropriate bases such as ammonia from ZSM5 samples, gives information on their acid site distribution or acidity spectrum. These studies have shown that the acidity spectrum is dependent on the Si/Al ratio, the method of preparation, and the cation content of the sample.

Considering the low aluminium contents that are characteristic of ZSM5 zeolites, it is expected that their acid strength distribution, and the ease of formation of Lewis acid sites will be heavily dependent on the Si/Al ratio of the sample: both Lewis site formation and acid heterogeneity occur at low Si/Al ratios where acid sites are close enough to interact. This effect is observed experimentally. Samples which contain less than two aluminium atoms per unit cell mainly possess strong adsorption sites, characterised by a heat of interaction with ammonia of 150 kJ/mol, whereas samples with a higher aluminium content exhibit a heterogeneous energy distribution (36). For example, a ZSM5 sample

containing four aluminium atoms per unit cell, had about 80% of its sites characterised by a heat of interaction of 150 kJ/mol (i.e. strong acid sites), whilst the remainder were much weaker, characterised by a heat of ammonia adsorption of less than 80 kJ/mol (37). Obviously, samples of intermediate Si/Al ratio will possess intermediate energy distributions, so that as the Si/Al ratio increases the relative number of strong acid sites will also increase (36).

On heating, ZSM5 appears to be relatively resistant to dehydroxylation with no significant decrease occurring in the intensity of the O-H stretching frequency at 3600 cm^{-1} up to 450°C (38). This can also be attributed to the low acid site density in most ZSM5 samples, as the ease of dehydroxylation does appear to increase with the number of aluminium atoms per unit cell. Controlled pyridine adsorption monitored by IR spectroscopy, suggests that Lewis sites are stronger than Bronsted acid sites, which are in turn stronger than sodium cations as adsorption centres for bases (37).

The introduction of exchangeable cations into ZSM5 has the effect of reducing the total number of Bronsted acid sites available for catalysis, but it also affects the acidity distribution of the remaining acid sites. IR studies suggest that at high levels of sodium exchange the Bronsted acid sites are much weaker than in the pure HZSM5, but below approximately 60-70% exchange the strength of the acid sites in the two samples is essentially identical (38). These findings are confirmed by the TPD of pyridine from sodium exchanged samples of ZSM5, which show that the number of strong acid sites declines very rapidly with

the introduction of sodium into the sample. It appears that sodium preferentially occupies the high energy ion exchange sites (39).

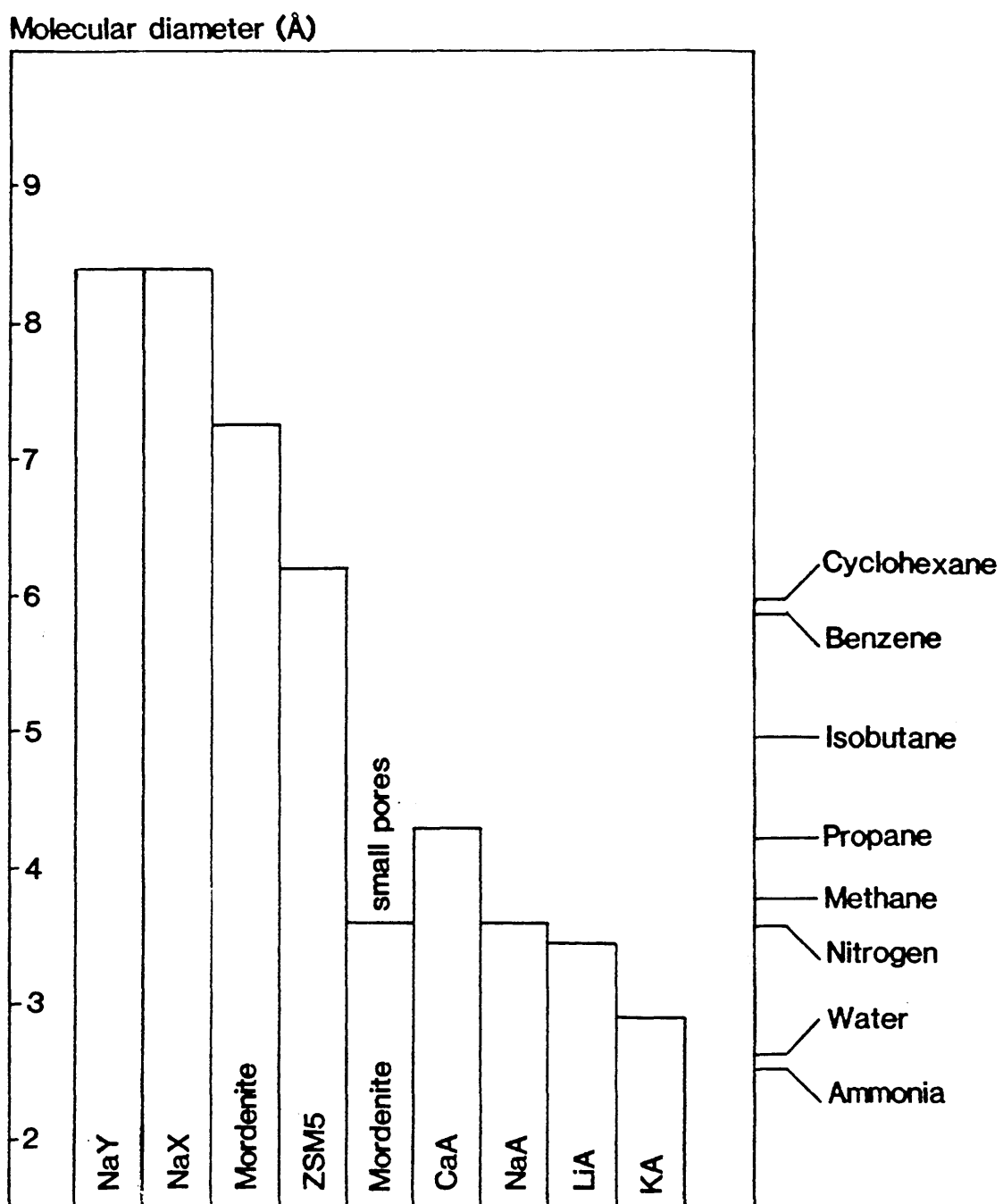
1.3 ADSORPTION AND DIFFUSION IN ZSM5

The different channel structures of zeolites, can drastically modify the adsorption and diffusion characteristics of sorbates within them. As the catalytically active sites are situated within the channel system, an understanding of diffusion and adsorption in zeolites is required, in order to fully appreciate the influence of topology upon catalysis.

Access to the interior of zeolite crystals is controlled by windows of peripheral oxygen atoms which normally contain 8, 10 or 12-membered rings (1). In order for sorption to take place the sorbate must be of a size sufficient to allow free passage through the smallest dimension of these windows. Figure 1.4 (40) shows the relationship between window size and the kinetic diameter for a number of common zeolites and sorbates. Such data provide the physical basis for molecular sieving (1), because molecules which are larger than the window size can be excluded from the zeolite pore system.

As well as its effect on sorption, structure also has a significant effect on the diffusion of molecules through the pore system (1). Classically, diffusion is described in terms of the mean free path of the diffusing species, which results in the recognition of two distinct diffusion regimes. The molecular diffusion regime, describes diffusion in the absence of any molecule-wall collisions, and can be considered as occurring in a

FIGURE 1.4 : The Origin of Molecular Sieving in Zeolites

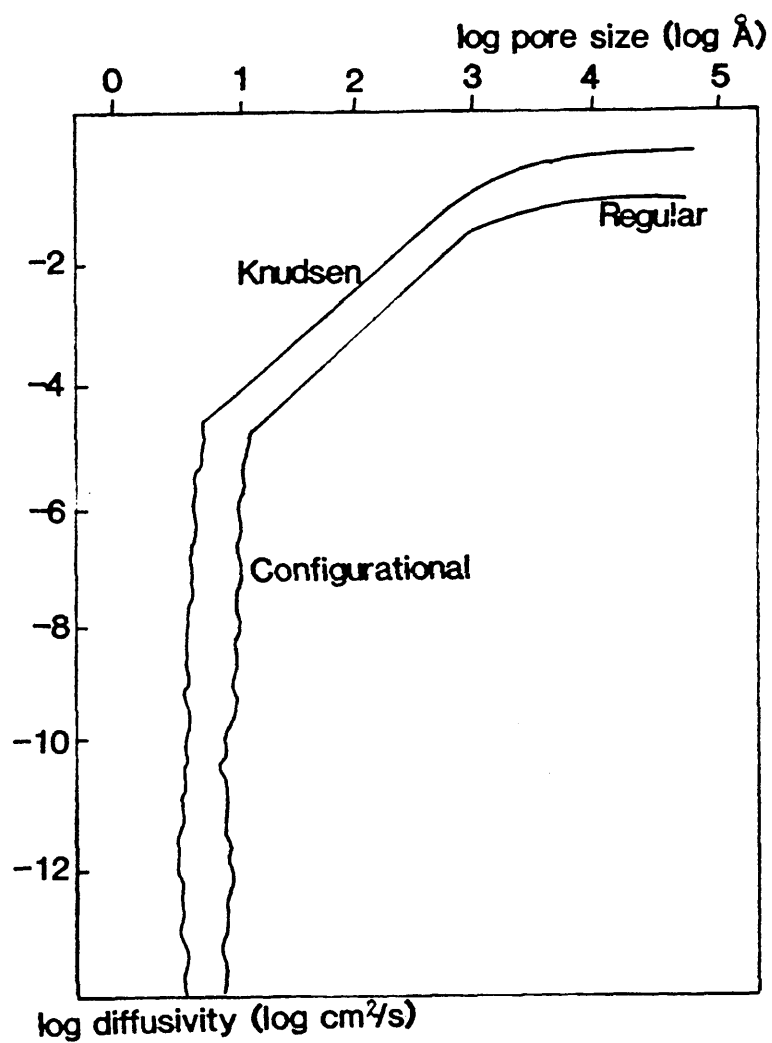


porous material with a pore radius greatly in excess of the molecular mean free path. The second regime, termed Knudsen diffusion, occurs when molecule-wall collisions become significant. In a porous material, Knudsen diffusion describes the situation when the pore radius is less than the molecular mean free path. The diffusivity is inversely proportional to the pore radius, due to the increase in the flow resistance with the increased frequency of molecule-wall collisions (41).

In the case of zeolite molecular sieves, a third diffusion regime can be recognised. The radius of the pores are so reduced that they approach the critical dimensions of many simple diffusants. This close matching of the two dimensions means that the cross-sectional diameter of the diffusing species is critical in determining the ease of passage through the zeolitic pore network. Furthermore, the diffusing species will constantly be under the influence of the zeolite surface, leading to greatly enhanced diffusional resistance. This third regime is termed configurational diffusion; the diffusing species exhibit a greatly reduced diffusivity requiring a close matching of the size, shape and configuration of the diffusing species within the channel network (42). A schematic representation of the range of the three diffusion regimes is given in figure 1.5 (43).

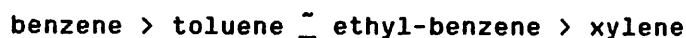
Diffusion studies on ZSM5 are limited in their extent, even with the development of new techniques which provide data at a much faster rate than the older sorption-uptake and gas chromatography based methods. The accumulation of data is restricted both by the time that it takes to collect, and the limitations of these techniques in the range of diffusion

FIGURE 1.5 : Diffusion Regimes in Porous Solids



coefficients they can measure (43).

Diffusion measurements of simple aromatic species adsorbed on ZSM5 reveal a diffusivity order of (44):



Among the xylene isomers, para-xylene diffuses approximately one thousand times faster than the other two isomers (39). This order of diffusivities is attributed to the greater cross-sectional diameters of ortho- and meta-xylenes (7.4 Å and 7.1 Å respectively), compared with that of para-xylene (6.7 Å) (46).

The ZSM5 framework can be modified in a number of ways to alter the diffusion coefficients of sorbed species within the channels. The major variables in the system are the nature and number of the cations balancing the framework aluminium, coke deposition, and various chemical modifications to the framework e.g. deposition of silica and treatment with acids and salts (45). Unfortunately, only a limited amount of work has so far been attempted, in order to determine the effect of such treatments on the diffusion coefficients of adsorbed species in these modified samples. Their effect is usually deduced from secondary evidence involving changes in the catalytic properties of such samples.

Adsorption data have been obtained for a ZSM5 sample (Si/Al=24) exchanged with various Group I cations, to elucidate the effect of cation size on the adsorptive and diffusive properties of simple molecules in ZSM5. It is found that for all the adsorbates studied including alkyl-substituted aromatics, the sorption capacity decreases as the radius of the cation increases (47). Diffusion coefficients can be calculated from the rates of

adsorption. The diffusion coefficients decrease as cation size increases, however the change is small and considered to be within the experimental error. An explanation is sought in which diffusion is considered to occur through the straight channels, as they offer less diffusional resistance than their sinusoidal counterparts in ZSM5. This would be particularly true for molecules with a diameter close to that of the channel size i.e. benzene and the xylene isomers. Assuming that the cations are located at the channel intersections and in the vicinity of the sinusoidal channels, then the cation may not affect the diffusion in any significant manner, whilst adsorption which involves complete pore-filling will be influenced by the cations wherever they are located (47).

1.4 SHAPE SELECTIVE CATALYSIS

Considering zeolites in their role as heterogeneous catalysts, allows an appreciation of their novel properties which make them so commercially important. Any catalytic reaction inside a porous crystal can be considered to involve the following five sequential processes:

1. Adsorption
2. Diffusion to the active site
3. Reaction or reactions at the active site
4. Diffusion out of the crystal
5. Desorption

It is the influence of the zeolite on these five processes which gives zeolite catalysts their distinctive properties compared to conventional non-porous catalysts.

Zeolites can be modified to contain a wide variety of different active sites, but commercially these tend to be limited to either Bronsted acid sites or to supported metals such as platinum, which are introduced by ion-exchange, followed by reduction. It is not the chemical nature of these active sites which makes zeolites so interesting but their physical environment. Each site is located inside a zeolitic pore which commonly has a cross-sectional diameter of less than $10\text{\AA}$. Thus for catalysis to occur, reactants and products must be able to diffuse freely into and out of the crystal and the transition state must be sized, so that it is readily contained within the confines of the zeolitic cavity or pore. These restrictions result in the effect known as shape-selective catalysis (48).

Reactant selectivity

When access to the active site is restricted for one or more of the reactant molecules, preferential reaction can occur. This type of exclusion can be on the basis of size (i.e. a molecular sieving effect) or due to unfavourable electrostatic interactions. For example the dipole moments of butenes are such, that the isomerisation of cis-2-butene is hindered in zeolite-A, relative to that of trans-2-butene and 1-butene (49).

Product selectivity

Product selectivity can take two very closely related forms. The first form occurs, when certain product molecules are too bulky to

diffuse out of the crystal, (i.e. they have a diffusion coefficient of zero), and they are retained at the active site to undergo further reaction. This results in the formation of either less-bulky secondary products, which are able to diffuse out of the crystal, or in the formation of "coke" which remains trapped at the active site. A second form of product selectivity occurs, when one of the product molecules is small enough to diffuse out of the crystal, but does so at a much slower rate than a second product. The product with the lower diffusion coefficient is retained for a longer period of time within the crystal, and as a consequence is much more likely to undergo further reaction and be modified in a similar manner to that occurring in the first form of product selectivity (50).

Restricted transition state selectivity

If the spatial configuration around an active site is too restricted for the transition state to form, then no reaction will occur even though all the reactants and products are small enough to allow easy diffusion both in and out of the crystal. Thus, in the isomerisation of ortho-xylene, the reaction proceeds via consecutive methyl shifts which involve a unimolecular transition state. Xylene disproportionation proceeds via a relatively large diaryl intermediate which is too large to be satisfactorially accommodated within the zeolite pore. When the rates of these two reactions are measured on different zeolites, the ratio of the rate of isomerisation to disproportionation increases as the size of the cavity decreases (40).

Molecular traffic control

Molecular traffic control may occur in zeolites with more than one type of intersecting pore system, and is thus relevant to catalysis on ZSM5 (51). It is believed that reactant molecules may diffuse to the active site preferentially through one set of pores, whilst the products leave the crystal through the other. This has the effect of minimising counterdiffusion, and hence enhancing the reaction rate. The concept of molecular traffic control has not been proven by analysing the kinetics of reactions in ZSM5 (51,52); furthermore, sequential adsorption measurements do not support this theory (53). It is however questionable whether kinetic phenomena can be tested by adsorption measurements, and so the role of molecular traffic control in understanding shape-selective reactions in zeolites is still open to debate (54).

1.5 AROMATIC REACTIONS ON ZSM5

Combining the concept of configurational diffusion, with the experimentally determined acidity spectra, leads to an understanding of the acid-catalysed aromatic reactions that occur on ZSM5. Particular reactions of interest are xylene isomerisation, toluene disproportionation, methanol conversion and toluene methylation. Although these reactions are already known to occur on other acid catalysts, they have received much attention in the literature and patent reports, due to the possibility of enhancing the proportion of para-xylene in the final product mixture, using the shape-selective properties of ZSM5.

Para-xylene is a very commercially desirable product; its oxidised form terephthalic acid, is a key component in the synthesis of polyesters. It is an expensive process to obtain para-xylene in the desired high purity, involving the use of energy-intensive crystallisers to separate the para-xylene, and a recycling mechanism to further isomerise the remaining isomers. Any process which will increase the primary yield of para-xylene will thus be commercially important (55).

ZSM5 is considered to be an interesting catalyst to achieve this end, due to the relative magnitudes of the xylene diffusion coefficients, detailed in Section 1.3. If the diffusion paths within the ZSM5 crystals are sufficiently long then the difference in the diffusivities will be reflected in the product distribution; the product with the highest diffusivity (i.e. para-xylene), should be found in excess due to its comparatively short residence time within the crystal. A more detailed account of this phenomenon on the toluene disproportionation reaction is given in Chapter 3.

For any reaction that yields xylene as a product, it is experimentally found that the small crystals of unmodified ZSM5 produce the xylene isomers in the equilibrium composition given in table 3.2 (56,58). The wide differences in the diffusion coefficients of the three xylene isomers, is being overwhelmed by a second factor. Kinetic measurements suggest that xylene isomerisation is a relatively facile reaction (45): the approximate values of the first order rate constants are (56):

$$\text{isomerisation} = 10 \times \text{alkylation} = 100 \times \text{disproportionation}$$

Thus, the tendency of the diffusivity differences to increase the proportion of para-xylene in the final product, can be cancelled out by the ease with which the xylene isomerisation reaction occurs, resulting in the production of an equilibrium mixture of xylene isomers. To achieve para-selectivity at practical conversions requires either enhancing the effect of the diffusion parameters or decreasing the effect of the difference in rates of the relevant reactions.

Chemically unmodified ZSM5 samples exhibit para-selectivity caused by the influence of "coke" and by the use of large crystals. Both of these effects are interpreted as being due to lengthening of the diffusion paths. In the case of crystal size this is a physical effect, whilst in the case of coke formation the introduction of pore blockages increases the xylene residence time within each crystal.

Small ZSM5 crystals ($<0.5 \text{ \AA}$) produce a product with a xylene composition comparable to the equilibrium distribution when performing the reactions of toluene disproportionation, toluene methylation and xylene isomerisation (58,59). Whereas larger crystals ($3\text{\AA}$) show an increase in para-selectivity, which in the case of xylene isomerisation further increases with crystal size (59).

During hydrocarbon transformations over ZSM5 various side-reactions occur one of which is the formation of coke. The ease of coke formation in different zeolites is dependent on the nature of the pore system (60,61); ZSM5 has a high resistance to coke formation which is believed to be due to transition state selectivity, restricting the formation of the bulky intermediates

prior to the formation of coke (44). Although the rate of coke formation on ZSM5 is relatively slow, its effect is still quite appreciable. Studies on the alkylation of toluene with methanol shown that over a period of 3-4 days the activity of the catalyst declines drastically. Concurrent with this decline there is a large increase in the para-selectivity, with the para-xylene component rising from the equilibrium value of 24% to 64% of the total xylene product. During this time there is a considerable build-up of coke. The increased para-selectivity was attributed to this coking since removal of the coke by controlled calcination produced a catalyst, which on further reaction gave an equilibrium distribution of xylene isomers (62).

Apart from the use of unmodified ZSM5 samples as detailed above, the para-selectivity of ZSM5 can also be enhanced by the use of chemical treatments. Of particular interest are the reactions with phosphorus (58,62), boron (57), magnesium (58) and silicon (63) compounds. These species are believed to interact with the Bronsted acid sites and although they decrease the total number of acid sites available for catalysis, they also have the effect of decreasing the pore size and hence increasing the diffusional resistance within the channel network. These treatments can increase the yield of para-xylene to over 90% of the total xylene product.

1.6 CATALYSIS ON ION-EXCHANGED ZSM5

The above discussion of the methods used to enhance the para-selectivity of ZSM5 in aromatic reactions is not exhaustive. A

further possibility involves the introduction by ion exchange of different sized cations into the ZSM5 pore network. These would be expected to increase the diffusional resistance within the channels, and hence increase para-selectivity in a similar manner to the modification with coke or by the various chemical treatments outlined above.

It is expected that the diffusional resistance caused by cations located in the channels, will be dependent on the ionic radius of the exchanged cation. Thus the Group I cations sodium and caesium, with ionic radii of 0.97 and 1.67 Å respectively (64), will be expected to increase the para-selectivity of H-ZSM5, with the caesium form being more selective than the sodium form. Whether the cations would have such an effect is not certain; diffusion coefficients measured in ZSM5 show little variation on the introduction of cations (47). This suggests that the cations are located in the sinusoidal channels. If molecular traffic control causes the aromatics to diffuse preferentially through the straight channels, then the cations may have no effect on the course of the catalytic reaction.

A limited amount of catalytic work has already been performed on cation-exchanged ZSM5 samples, to investigate the effect of the cations on the activity and para-selectivity. For facile reactions such as ortho-xylene isomerisation, and the dimethylether-to-hydrocarbon transformation, it has been shown that the catalytic activity is directly proportional to the extent of proton exchange (65). In these works the extent of sodium exchange ranged between 20 and 80%.

The variation in both activity and selectivity in the

conversion of methanol and ethanol to an aromatic hydrocarbon mixture was monitored as a function of sodium content. The conversion is found not to be strictly related to the total number of acid sites per unit cell, but shows a strong correlation to the number of strong acid sites as measured by irreversible pyridine adsorption at 673K. Differences in selectivity were also found; the ratio of para- to ortho-xylene in the product was found to increase concurrent with the degree of sodium exchange. This was attributed to an increase in diffusional resistance as the sodium content of the zeolite increased (66).

These results suggest that a linear relationship between the number of active sites and the activity of the catalyst exists only when the reaction is so facile that all the acid sites are considered to be strong by the reactant. When a reaction is kinetically demanding, such as toluene disproportionation (67), then catalysis only occurs on the strong acid sites. In such reactions no correlation will exist between the extent of ion-exchange and the activity of the samples. It is the acid strength distribution, not the total number of acid sites, which determines the activity of each sample.

Catalytic data concerning reactions on ZSM5 are limited in extent, with data being presented in terms of conversion and no kinetic manipulation being attempted. The aim of this work is to investigate the effect of sodium and caesium cations on the para-selectivity of ZSM5, and to correlate the activity of the samples with this data by a kinetic analysis of both the toluene disproportionation and xylene isomerisation reactions.

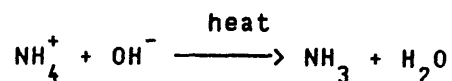
ION EXCHANGE ON ZEOLITE ZSM5

2.1 CHARACTERISATION OF ZSM5 CATALYST

Preparation

The zeolite sample initially used in the ion exchange and catalysis studies was supplied by ICI; details of the synthetic and calcination conditions employed in its preparation were not given, however the Si/Al ratio of the reactant gel was reported to be 45. Although the methods outlined below describe the preparation and analysis of this original sample, they are identical to the methods used to characterise the ZSM5 samples prepared in Chapter 5.

In order to prepare samples in the appropriate homoionic forms, batches were repeatedly exchanged with concentrated solutions of the relevant chloride salts (i.e. NaCl, CsCl or NH_4Cl). For the high-alumina ZSM5 samples prepared in Chapter 5, the pH of the exchanging solution was adjusted to 7, by adding the appropriate hydroxide salt. The exchanges were continued until the pH of the exchanged solution was also equal to 7, indicating that the hydronium ions had been completely removed from the zeolite phase. When each sample was considered to be homoionic, the zeolite was washed with distilled water, until no trace of cation could be detected in the washings. In the case of the sodium and caesium forms, this was tested by atomic absorption spectroscopy. For the ammonium forms, the following reaction with concentrated sodium hydroxide solution was utilised (68):



The liberated ammonia was detected by its neutralisation of a weak solution of hydrochloric acid. Once the sample was considered to be thoroughly washed, it was dried overnight at 85°C, and immediately transferred to a desiccator containing a saturated sodium chloride solution, over which it was stored at room temperature, to ensure a constant water content.

Chemical Analysis

The water contents of the samples were determined after they had stood over the saturated sodium chloride solution for at least ten days. Preweighed samples were heated at 500°C in a furnace for two hours. The dehydrated zeolites were then rapidly transferred to a desiccator containing silica gel, and cooled to room temperature prior to reweighing. This technique yielded water capacities comparable to those obtained by the use of a thermo-gravimetric balance. In the case of the NH_4 -ZSM5 samples, heating to 500°C causes the decomposition of the ammonium ion with the release of ammonia. Thus for these samples, the weight loss measured by thermo-gravimetric analysis (TGA), will be the combined mass of water and ammonia liberated by calcination.

Exchangable sodium and caesium contents (meq/g) were determined radiochemically, using solutions labelled with either the ^{22}Na or ^{134}Cs isotope. The zeolite was rotated for 24 hours with a known volume of the labelled chloride solution in sealed polypropylene tubes. After equilibrium had been established, the solid and solution phases were separated by centrifugation,

followed by washing with Analar-grade ethanol. Washing of the solid phase was continued until the count rate of the washings approached that of the background. The activity of the solution phase both before and after exchange was measured by the gamma-counter supplied by Compugamma. The activities of the solution and zeolite phases can be directly related to the cation exchange capacity (CEC) by the following formula:

$$\text{CEC (meq/g)} = \frac{V \times M \times C_z}{m \times 1000 \times C_s} \quad \{2.1\}$$

where:

V is the volume of the solution (dm^3)

M is the molarity of the solution (mol dm^{-3})

m is the mass of zeolite (g)

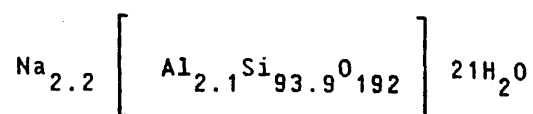
C_s is the activity of the solution after exchange

C_z is the activity of the zeolite after exchange (i.e.

initial solution activity - final solution activity)

Total aluminium contents were determined by the dissolution of approximately 0.1g of zeolite, in a mixture of 40% HF and 1:1 H_2SO_4 . The resulting solution was analysed by back titration of excess EDTA with ZnCl_2 solution, in the presence of buffered xylenol orange indicator (68). The silicon content was calculated by subtraction, using the values for the aluminium, sodium and water contents previously determined.

The ZSM5 sample supplied by ICI, has a Si/Al ratio of 45, and a unit cell composition of:

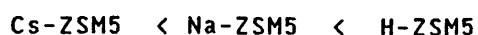


Chemical analyses of the three cation exchanged forms are given in table 2.1.

Structural Characterisation

The powder X-ray diffraction (XRD) pattern for the ICI sample shows the pattern characteristic of ZSM5 (2); indicated by the presence of two separate peaks between 2θ values of 49 and 50 degrees. Scanning electron micrographs (SEM) were recorded by ICI, and are shown in figure 2.1. The crystals are approximately two microns in diameter, and no amorphous impurities can be seen on the external surfaces of the crystals. Particle size analysis was performed on each of the ion-exchanged forms using a Master particle sizer supplied by Malvern Instruments. The particle-size distributions are given in table 2.2, which shows that ion exchange does not significantly affect the particle size-distribution.

Para-xylene sorption capacities were used to screen for amorphous impurities within the zeolite channels. Each sample was heated at 500°C for one day to expel zeolitic water, and then rapidly transferred to a dessicator containing para-xylene, over which it was left to equilibrate for at least ten days. Sorption capacities were determined by TGA and are summarised in table 2.1. The sorption capacities increase in the order:



which is in the order of decreasing "bare" ionic radius.

Table 2.1 : Chemical analysis of the I.C.I ZSM5 sample

	Cs-ZSM5	Na-ZSM5	NH ₄ -ZSM5
C.E.C (meq/g)	0.35	0.35	---
H ₂ O (mol./U.C.)	20	25	21
M ⁺ (ions/U.C.)	2.18	2.18	
Al (atoms/U.C.)		2.09	
Si (atoms/U.C.)		93.91	
Si/Al		44.9	
Para-xylene sorption capacity (mol./U.C.)	8.7	10.1	10.3 [*]

* H-ZSM5

FIGURE 2.1 : Scanning Electron Micrographs of ICI produced Na-ZSM5

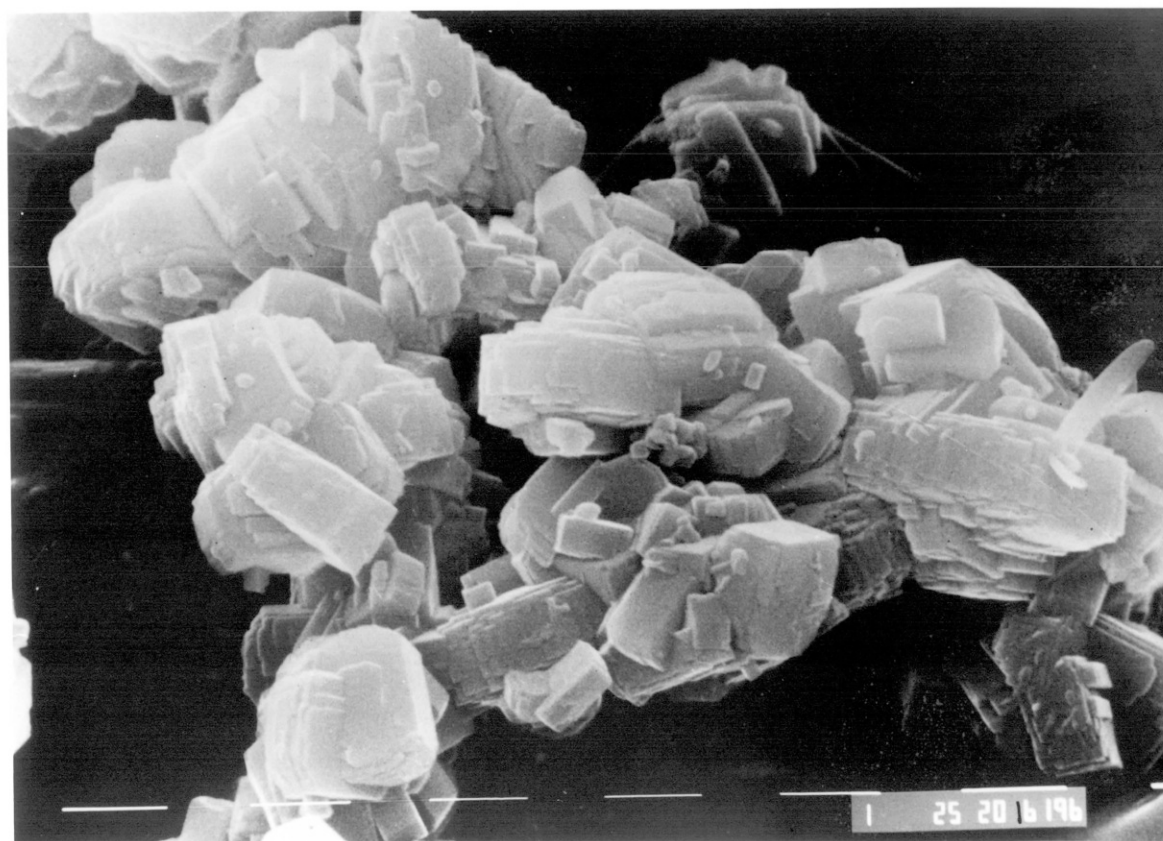
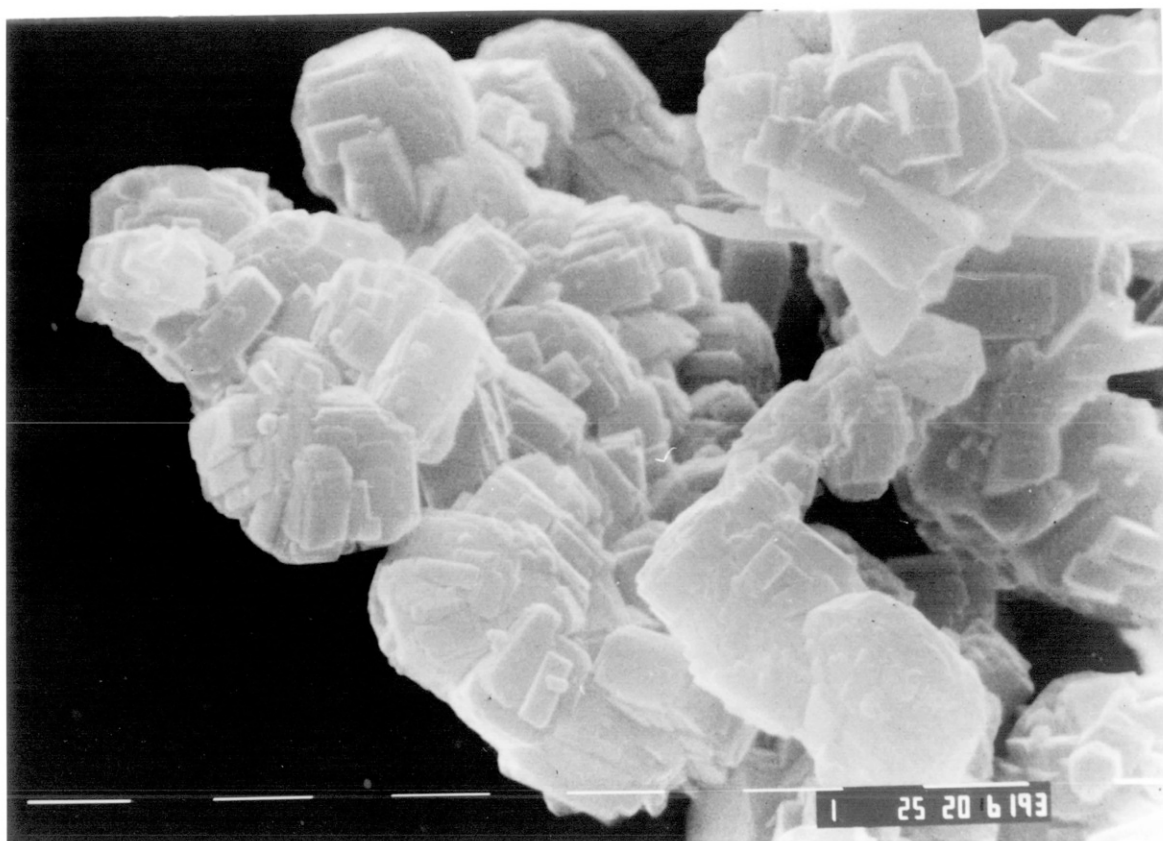


Table 2.2 : Particle size distributions

	Cs-ZSM5	Na-ZSM5	NH ₄ -ZSM5
Size band (microns)	<i>z</i>	<i>z</i>	<i>z</i>
188.0 - 87.2	0.0	0.0	0.0
87.2 - 53.5	0.0	0.0	0.0
53.5 - 37.6	0.0	0.0	0.0
37.6 - 28.1	0.0	0.0	0.0
28.1 - 21.5	0.1	0.0	0.0
21.5 - 16.7	1.4	0.2	0.1
16.7 - 13.0	6.3	1.9	1.4
13.0 - 10.1	12.0	5.8	4.9
10.1 - 7.9	18.3	13.5	11.9
7.9 - 6.2	18.9	19.9	20.9
6.2 - 4.8	12.0	18.1	19.8
4.8 - 3.8	11.7	31.6	16.4
3.8 - 3.0	12.0		13.0
3.0 - 2.4	4.8	6.4	6.3
2.4 - 1.9	1.4	2.6	2.8
median (microns)	7.3	6.0	5.8

MASNMR has been used to determine the state of the aluminium and silicon within the zeolite framework (69). The ^{27}Al and ^{29}Si MASNMR spectra are shown in figures 2.2 and 2.3 respectively. The ^{27}Al spectrum consists of a single peak at 53.8 ppm. This has previously been assigned to tetrahedrally-coordinated framework aluminium. The absence of any peak at 0 ppm, the characteristic shift of non-framework octahedral aluminium, indicates that all the aluminium detected by wet chemical analysis is located in framework positions. The ^{29}Si spectrum is less informative, even though two peaks are observed; the main peak at 113 ppm is attributed to framework silicon atoms with no aluminium atoms in the first coordination sphere, whilst the smaller peak at 106 ppm is indicative of silicon with one aluminium in the second coordination sphere. The relative intensities of these two peaks is that expected, considering the high Si/Al ratio of the sample.

2.2 THERMODYNAMICS OF ION EXCHANGE (70)

Zeolites exhibit ion exchange properties associated with the cations balancing the net negative charge on the framework. When a zeolite is contacted with a solution containing a metal salt, exchange between the cations in the zeolite and the solution phase will occur, until equilibrium is reached. The equilibrium distribution of the two ions between the zeolite and solution phases is determined by the nature of the ions and their relative proportions in each system. Consider the univalent exchange between ion A^+ in solution and ion B^+ in the zeolite phase:

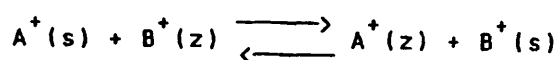


FIGURE 2.2 : ^{27}Al MASNMR Spectrum of ICI produced Na-ZSM5

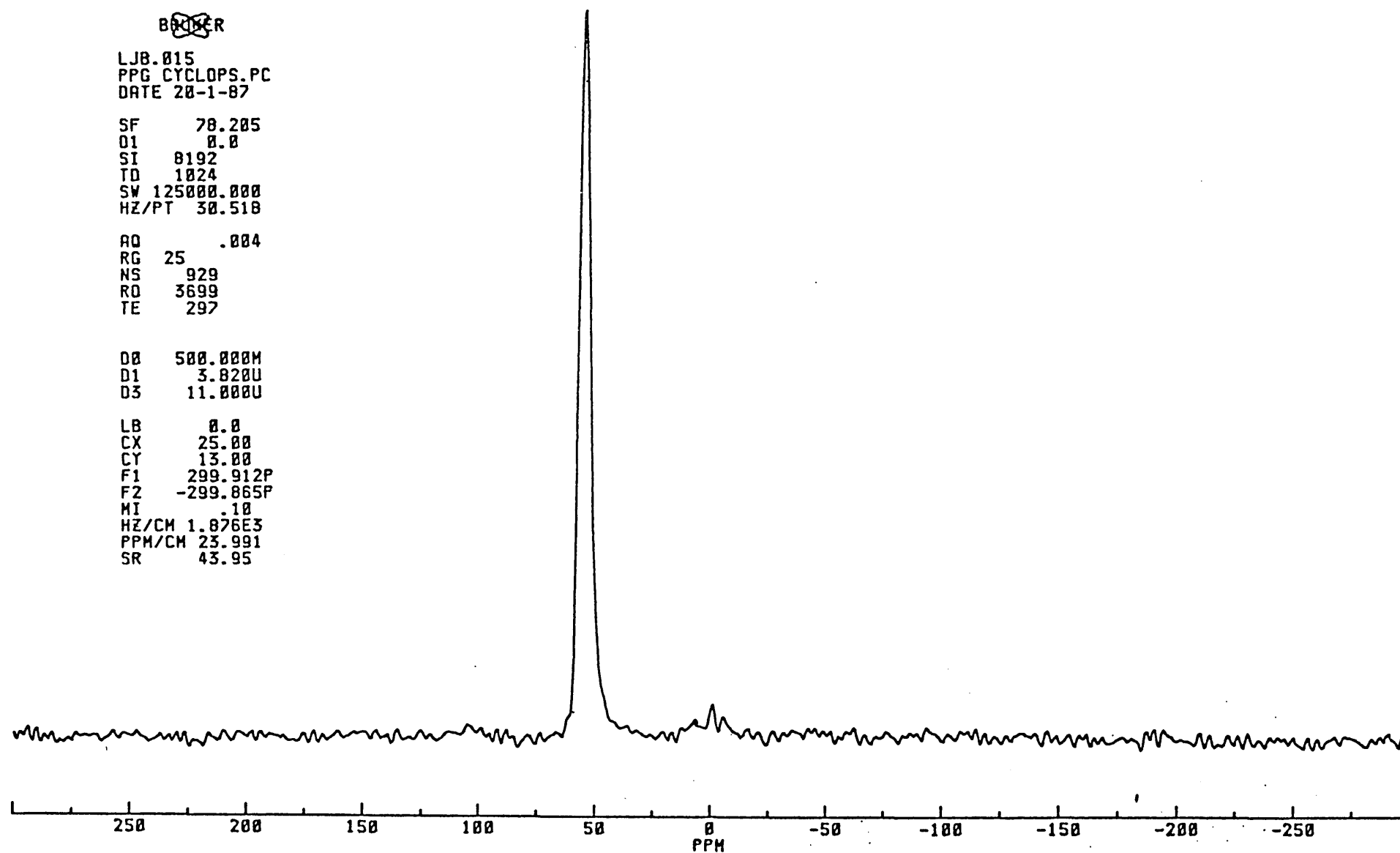
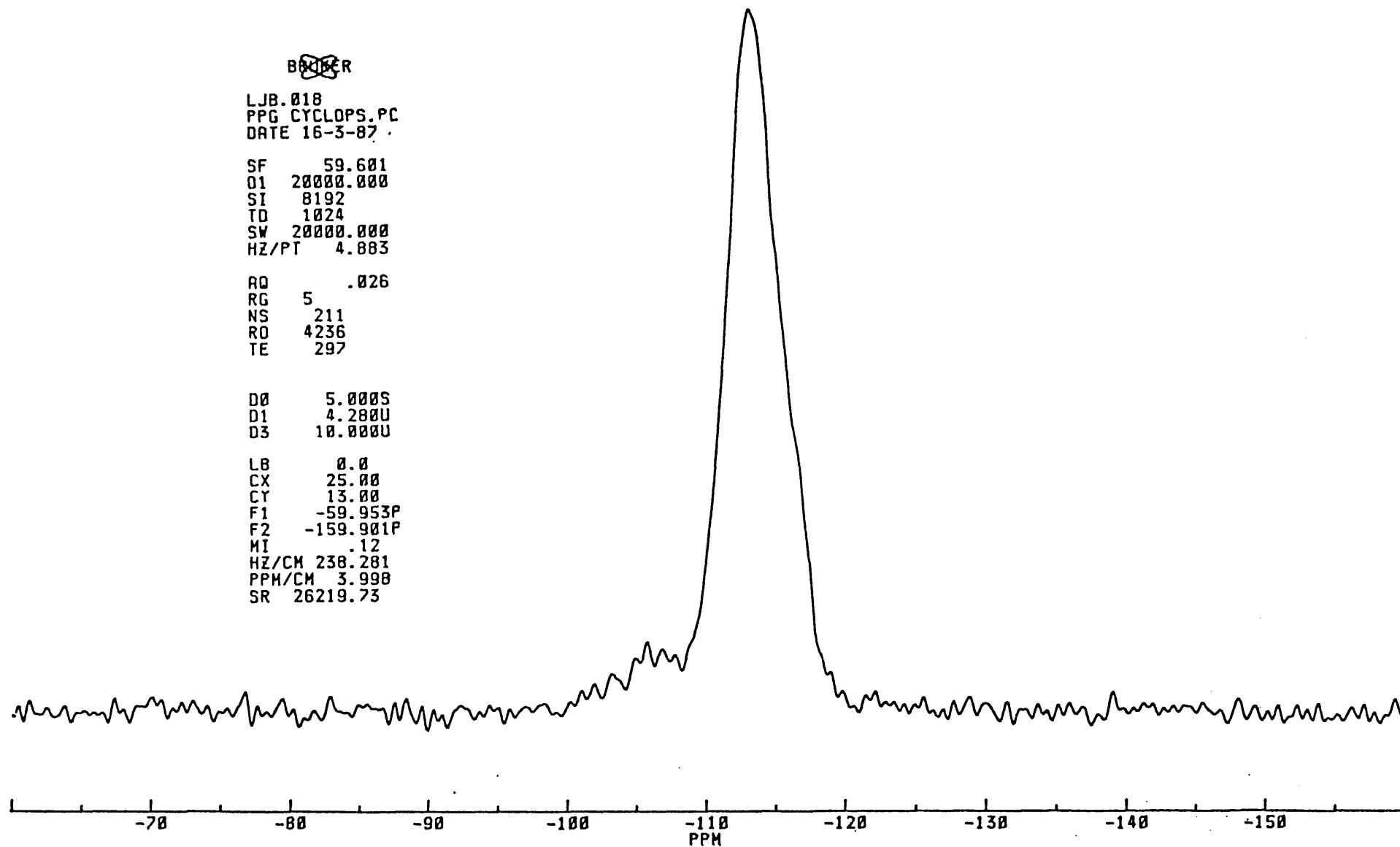


FIGURE 2.3 : ^{29}Si MASNMR Spectrum of ICI produced Na-ZSM5



The exchange equilibria for these ions can be characterised by an ion exchange isotherm; an equilibrium plot of the concentration of the exchanging ion in solution, against the concentration of the same ion in the zeolite, under conditions of both constant temperature and solution normality. It is conventional for the isotherm to be plotted in terms of the equivalent fraction of the entering ion, in both the solution (A_s) and the zeolite (A_z) phase. For univalent exchange these are defined as:

$$A_s = \frac{m_A}{(m_A + m_B)} \quad \{2.2\}$$

where $m_{A,B}$ is the concentration (mol/dm^3) of the respective ions in solution.

$$A_z = \frac{M_A}{(M_A + M_B)} = \frac{M_A}{Q} \quad \{2.3\}$$

where Q is the cation exchange capacity of the zeolite (meq/g), and $M_{A,B}$ is the concentration (mol/kg) of the respective ions in the zeolite.

Theory and interpretation

The ion exchange isotherm produced by plotting A_z versus A_s gives an indication of the selectivity of the zeolite phase for the two competing ions. If one ion is preferentially exchanged into the zeolite above the ratio imposed by the relative concentrations of the two ions, then it is apparent that this will be reflected in the thermodynamics of the system. Thus an understanding of the thermodynamics of ion exchange may yield information on site

heterogeneity, particularly if the selectivity changes with degree of exchange. The mass action quotient (K_m), describes the selectivity for the ion exchange reaction at each equilibrium point or value of A_z :

$$K_m = \frac{A_z \times m_B}{B_z \times m_A} \quad \{2.4\}$$

The variation of K_m with A_z is a measure of the deviation of the system from ideality. The thermodynamic equilibrium constant K_a , is invariant with A_z as it contains correction terms for the non-ideality of both the zeolite and solution phases:

$$K_a = \frac{a_A(z) \times a_B(s)}{a_B(z) \times a_A(s)} \quad \{2.5\}$$

where $a_{A,B}(z)$ and $a_{A,B}(s)$ are the activity of the two ions in the zeolite and solution phase respectively.

In order to express the thermodynamic equilibrium constant in terms of activity coefficients and molarities, the ideal states of both phases must be defined. The ideal solution is defined in terms of Henry's Law, so that the reference state for each salt is the hypothetical ideal molar solution of that salt. This allows the ideal exchanger to be defined in relation to the ideal solution; namely the ideal exchanger is the homoionic form of the exchanger, immersed in an infinitely dilute solution of the same ion. Hence K_a can be written as:

$$K_a = \frac{A_z \times f_A \times m_B \times \gamma_A}{B_z \times f_B \times m_A \times \gamma_B} \quad \{2.6\}$$

$$\text{or} \quad K_a = K_m \Gamma \left\{ \frac{f_A}{f_B} \right\} \quad \{2.7\}$$

$$\text{where} \quad \Gamma = \left\{ \frac{\gamma_B}{\gamma_A} \right\}$$

$\gamma_{A,B}$ is the single ion activity coefficient in the solution phase

$f_{A,B}$ is the single ion activity coefficient in the zeolite phase.

Equations 2.6 and 2.7, define K_a in terms of the mass action quotient, with both a solution and a zeolite activity correction.

Solution Activity Correction

Obviously, γ_A and γ_B cannot be evaluated experimentally since each positive ion is always found in solution with a charge-balancing counter ion. The ratio Γ can however be evaluated in terms of the mean molar salt activity coefficient $\gamma_{\pm}(MX)$. For a salt M_pX_q this is defined as:

$$\gamma_{\pm}(M_pX_q) = \left[\gamma_M^{Z_X} \times \gamma_X^{Z_A} \right]^{\frac{1}{(Z_M + Z_X)}} \quad \{2.8\}$$

Substituting and simplifying for the case of univalent exchange gives:

$$\Gamma = \left\{ \frac{\gamma_B}{\gamma_A} \right\} = \left\{ \frac{(\gamma_{\pm}(BX))^2}{(\gamma_{\pm}(AX))^2} \right\} \quad \{2.9\}$$

Equation 2.9 gives Γ in terms of the pure, separate solutions of the two salts. In reality the activity coefficients for salts in

mixed solutions, are modified by the effect of one salt on the activity of the other. For a mixture of two salts, Gluckauf's semi-empirical expressions can be used to yield the required activity coefficients of the salts in mixed solutions (71):

$$\log \gamma_{\pm}(AX) = \log \gamma_{\pm}(AX) - \frac{m_B}{4I} \left\{ k_1 \log \gamma_{\pm}(AX) - k_2 \log \gamma_{\pm}(BX) - \frac{k_3}{(1 + I^{-0.5})} \right\} \quad \{2.10\}$$

$$\log \gamma_{\pm}(BX) = \log \gamma_{\pm}(BX) - \frac{m_A}{4I} \left\{ k_4 \log \gamma_{\pm}(BX) - k_5 \log \gamma_{\pm}(AX) - \frac{k_6}{(1 + I^{-0.5})} \right\} \quad \{2.11\}$$

I is the ionic strength, and k_1 to k_6 are given below along with the numerical values of these parameters in the case of univalent exchange:

$$k_1 = Z_B(2Z_B - Z_A + Z_X) = 2 \quad \{2.12\}$$

$$k_2 = Z_A(Z_B + Z_X)^2(Z_A + Z_X)^{-1} = 2 \quad \{2.13\}$$

$$k_3 = 0.5 [Z_A Z_B Z (Z_A - Z_B)^2 (Z_A + Z_X)^{-1}] = 0 \quad \{2.14\}$$

$$k_4 = Z_A(2Z_A - Z_B + Z_X) = 2 \quad \{2.15\}$$

$$k_5 = Z_B(Z_A + Z_X)^2(Z_A + Z_X)^{-1} = 2 \quad \{2.16\}$$

$$k_6 = 0.5 [Z_A Z_B Z_X (Z_A - Z_B)^2 (Z_A + Z_X)^{-1}] = 0 \quad \{2.17\}$$

Zeolite activity correction

Considering that the useful information about the zeolite is contained in the activity coefficients for that phase, it is convenient to define a new function, the Kielland quotient (K_c) which contains all the terms in the thermodynamic equilibrium constant K_a , that do not contribute to defining the zeolite phase:

$$K_c = K_m \Gamma \quad \{2.18\}$$

Substituting equation 2.18 into equation 2.7, yields a new expression for K_a :

$$K_a = K_c \left\{ \frac{f_A}{f_B} \right\} \quad \{2.19\}$$

It is apparent that for a given isotherm there exists a unique value of K_c for each value of A_z . A plot of K_c versus A_z will describe the deviation of the zeolite phase from the behaviour of an ideal exchanger.

The thermodynamic equilibrium constant, K_a is invariant with A_z , thus the evaluation of K_a involves the second i.e. the exchanger or zeolite correction to the mass action equilibrium constant, K_m . A simplified thermodynamic approach to the evaluation of the activity coefficients of the zeolite phase has been developed by Gaines and Thomas (72) and is based on the Gibbs-Duhem equation:

$$\sum n_i d\mu_i = 0 \quad \{2.20\}$$

The summation should include chemical potentials for all the

components within the system, but in practice it is found that salt imbibition can be ignored provided that the total concentration is less than 1 mol/dm^3 . Furthermore, Barrer and Klinowski have proved that the water activity terms are usually insignificant (73). Hence applying the Gibbs-Duhem equation to the zeolite phase, and substituting for the chemical potentials gives:

$$n_A RT d\ln f_A A_Z + n_B RT d\ln f_B B_Z = 0 \quad \{2.21\}$$

where $n_{A,B}$ are the number of moles of each ion in the zeolite phase. Describing these equations in terms of equivalent fractions, and using the definition of K_a , given in equation 2.19 leads to:

$$d\ln f_A^{Z_B} = (Z_B - Z_A)B_Z - B_Z d\ln K_C \quad \{2.22\}$$

$$d\ln f_B^{Z_A} = -(Z_B - Z_A) + A_Z d\ln K_C \quad \{2.23\}$$

Integration of equations 2.22 and 2.23 gives:

$$\ln f_A^{Z_B} = (Z_B - Z_A)B_Z - \ln K_C + A_Z \ln K_C + \int_{A_Z}^1 \ln K_C dA_Z \quad \{2.24\}$$

$$\ln f_B^{Z_A} = (Z_B - Z_A)A_Z - A_Z \ln K_C - \int_0^{A_Z} \ln K_C dA_Z \quad \{2.25\}$$

and hence: $\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_C dA_Z \quad \{2.26\}$

Equation 2.26 enables the calculation of K_a from isotherm

data, to which the solution activity corrections have been applied. K_a may be determined from a plot of $\log K_c$ against A_z which is referred to as a Kielland plot. The second term of equation 2.26 can be determined by graphical integration of the area under the Kielland plot, or by integrating directly the fitted polynomial expressions describing these plots. The standard free energy per equivalent of exchange (ΔG^0) is directly related to the thermodynamic equilibrium constant, K_a :

$$\Delta G^0 = -(RT \ln K_a) \quad \{2.27\}$$

For univalent exchange, it is generally found that the $\log K_c$ versus A_z plots are linear. Kielland used the following empirical equations to express the solid phase activity coefficients as a function of cation loading:

$$\log f_A = C B_z^2 ; \quad \log f_B = C A_z^2 \quad \{2.28\}$$

where C is an empirical constant

Substituting into equation 2.7 gives:

$$\log K_c = 2C A_z + \log K_m \quad \{2.29\}$$

Thus a plot of $\log K_c$ versus A_z should by this theory, produce a straight line of gradient $2C$, known as the Kielland coefficient. Kielland plots which are non-linear have been related to the presence of heterogeneous exchange sites.

2.3 EXPERIMENTAL

Prior to the determination of any isotherm points both the cation exchange capacities (CEC) and the maximum exchange capacities of the caesium and sodium exchanged forms of the ZSM5 sample were measured. The method used to determine the CEC is detailed in Section 2.1, and the values obtained are given in table 2.1. Maximum exchange capacities were measured by the rotation of 0.5g of radioactively labelled sample, with a large volume (20ml) of 0.05M ammonium chloride solution for one day. The two phases were separated by centrifugation and washed with Analar-grade ethanol. The activity of the solid phase was monitored after washing. The rotation and separation procedures were repeated until the activity of the solid phase attained a constant value. For both the sodium and caesium forms, the activities approached that of the background, indicating that the exchange reactions essentially went to completion.

Initial kinetic runs suggested that both the Na/NH_4 and Cs/NH_4 exchanges reached equilibrium within a period of three hours; this determined the lower time limit for the exchange reactions studied. Isotherm points for both the sodium and caesium exchanges with the ammonium ion were determined, by rotating approximately 0.1g of the homoionic forms of each sample, with mixed solutions of ammonium chloride and the relevant metal chloride, at a total solution molarity of 0.05M. The exchange was monitored radiochemically using labelled zeolite, with the activity of the cation in both phases being measured before and after the exchange, and the ammonium contents being calculated by difference. The activity of the solution and zeolite phases could

be directly related to the isotherm points using the following formulae:

$$B_s = \frac{C_s}{(C_s + C_z)} \left\{ \frac{m_z \cdot Q + M \cdot V_{BCl}}{M \cdot (V_{BCl} + V_{ACl})} \right\} \quad \{2.30\}$$

$$B_z = \frac{C_z}{(C_s + C_z)} \left\{ \frac{m_z \cdot Q + M \cdot V_{BCl}}{m_z \cdot Q} \right\} \quad \{3.31\}$$

where m_z is the mass of zeolite (g)

M is the molarity of the exchange solution (mol dm^{-3})

$V_{BCl,ACl}$ are the volumes of the respective ions used in the exchange (ml)

Q is the cation exchange capacity (meq/g)

C_s is the activity of the solution phase after exchange

C_z is the activity of the zeolite phase after exchange
(i.e. initial solution activity - final solution activity)

Ion exchange isotherms are conventionally plotted in terms of the equivalent fractions of the ingoing ion. These are easily calculated from those of the outgoing ion, by the relationships:

$$A_s + B_s = 1 \quad \{2.32\}$$

$$\text{and} \quad A_z + B_z = 1 \quad \{2.33\}$$

2.4 RESULTS AND DISCUSSION

Ion exchange isotherms were determined for the Cs/NH₄ and Na/NH₄ exchanges, at room temperature and at a total concentration of 0.05M. Two ZSM5 samples were studied, the sample supplied by ICI (Si/Al=45), and a sample which is characterised in Section 5.3 (Si/Al=28). The isotherms are represented in figures 2.4 and 2.5. Both samples show the same selectivity order for the three cations; ZSM5 is highly selective towards caesium and exhibits its lowest selectivity towards sodium. This is in accordance with the selectivity order found by Dyer (74), and is thought to be related to the charge-density or size of the cation.

The corrected selectivity coefficients, K_c were calculated from equation 2.18, and used to generate the Kielland plots illustrated in figures 2.6 to 2.9. The plots were analysed by a least squares method, to fit three types of polynomial: linear, quadratic and cubic. The error of each fit was reflected in an R factor calculated as (75):

$$R = \sqrt{\frac{\sum \{Y(\text{calc}) - Y(\text{exp})\}^2}{N - M - 1}} \quad \{2.34\}$$

where N is the number of pairs of log K_c , A_z values, and M is the order of the polynomial. Only the polynomial corresponding to the lowest value of R is shown on the Kielland plots. Full details of the fitting parameters and the calculated thermodynamic constants are given in tables 2.3 and 2.4.

The Kielland plots for the Na/NH₄ and Cs/NH₄ exchanges differ substantially, whilst those for the different ZSM5 samples are remarkable in their similarity. For the Cs/NH₄ system, both first

FIGURE 2.4 : Ion-Exchange Isotherms at Room Temperature of ZSM5 (Si/Al 45)

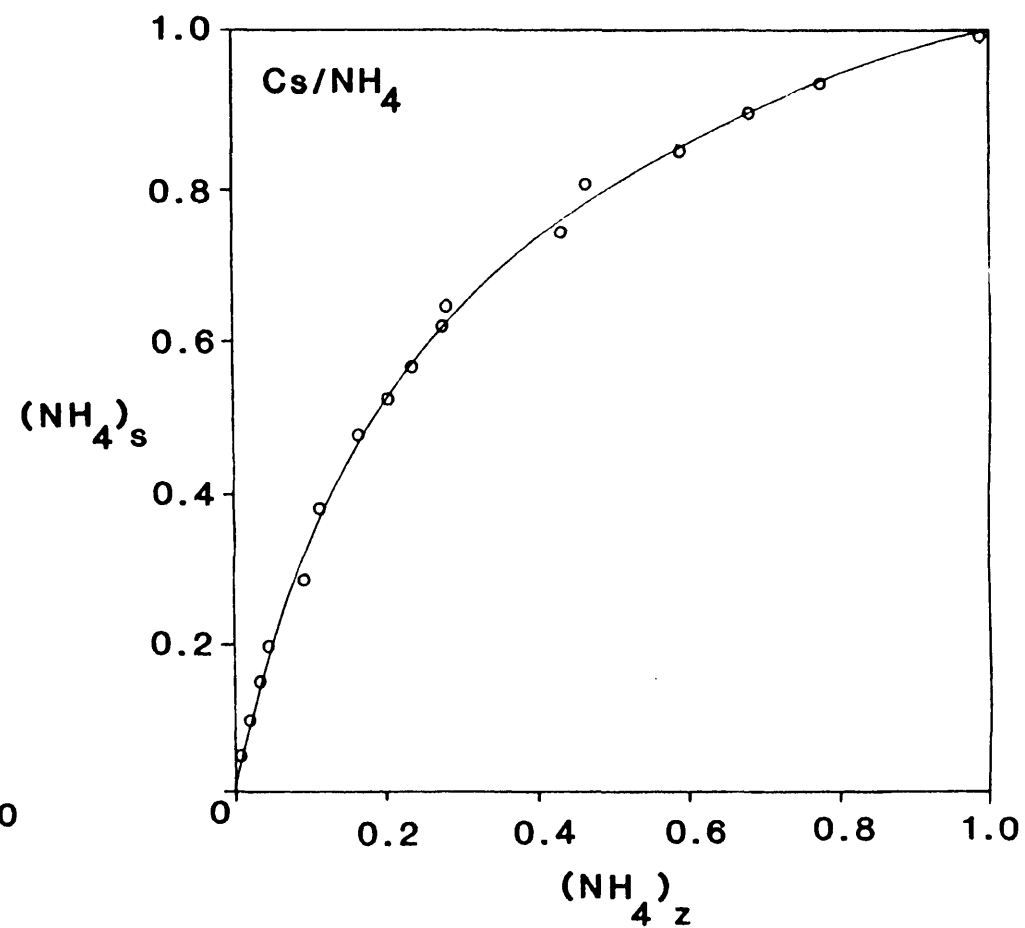
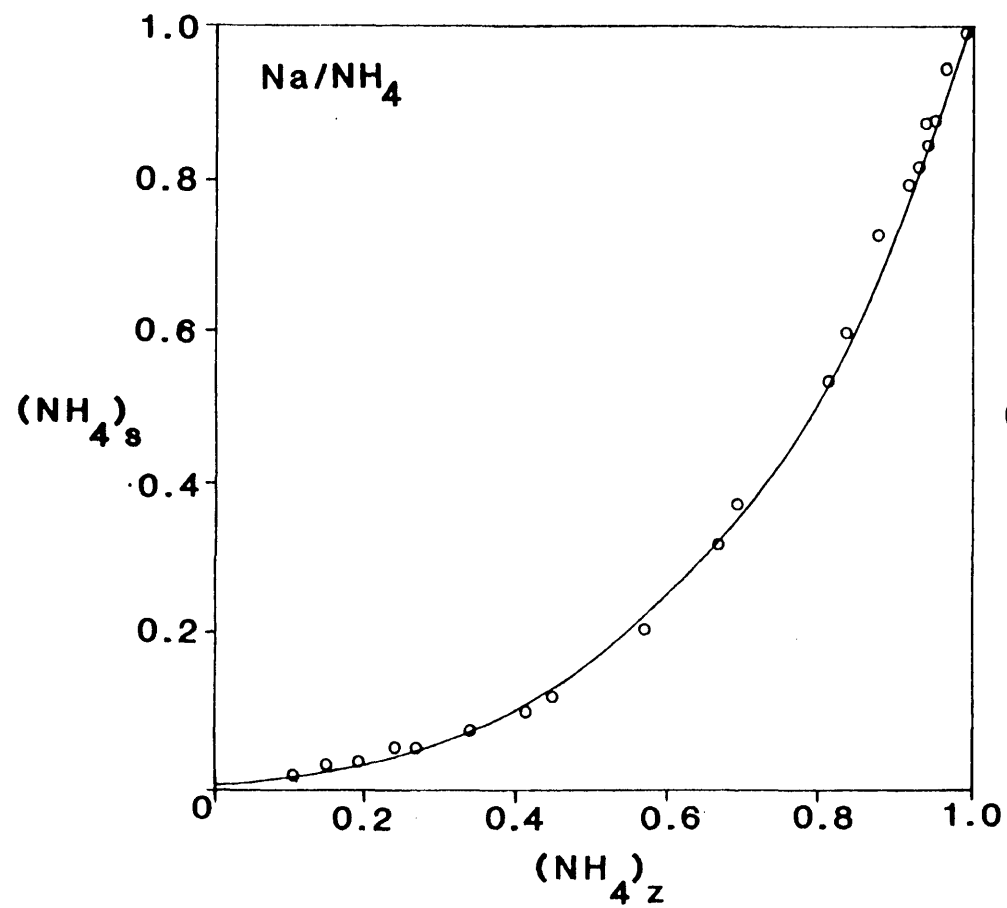


FIGURE 2.5 : Ion-Exchange Isotherms at Room Temperature of ZSM5 (Si/Al 28)

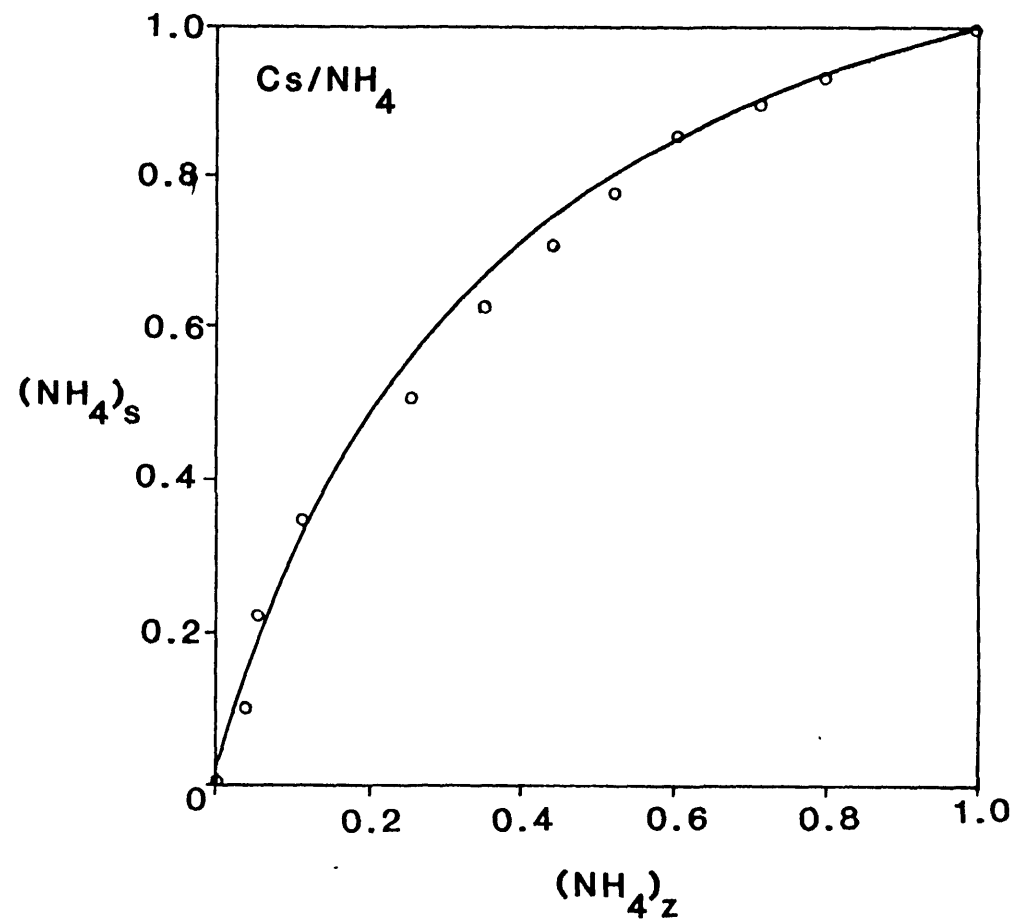
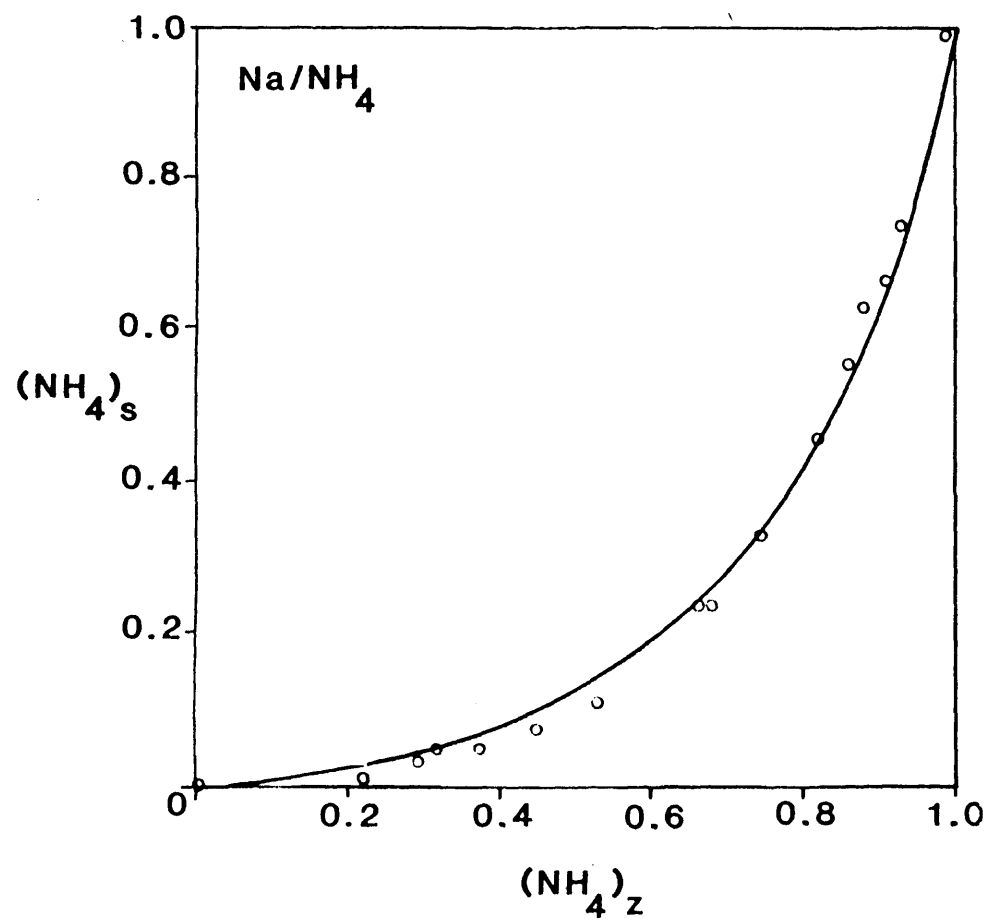


FIGURE 2.6 : Kielland Plot of the Na/ NH_4 Exchange on ZSM5 (Si/Al 45)

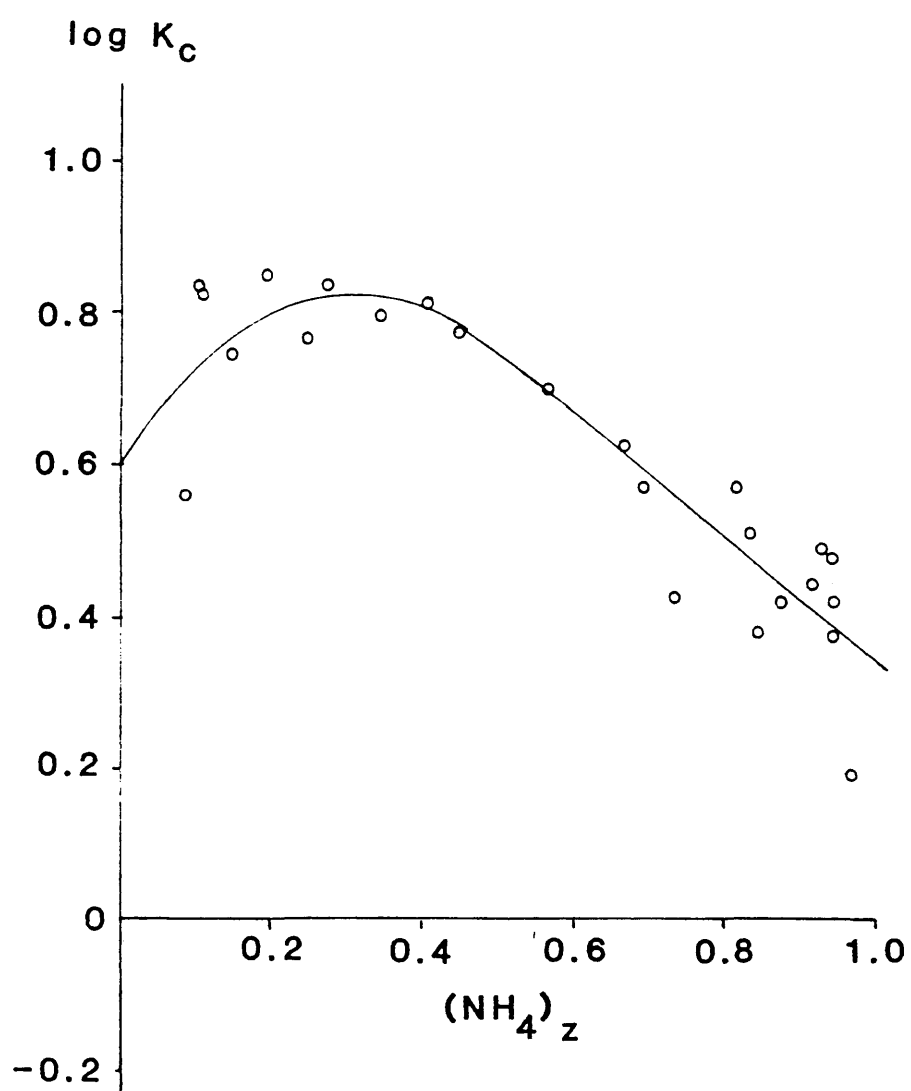


FIGURE 2.7 : Kielland Plot of the Na/NH₄ Exchange on ZSM5 (Si/Al 28)

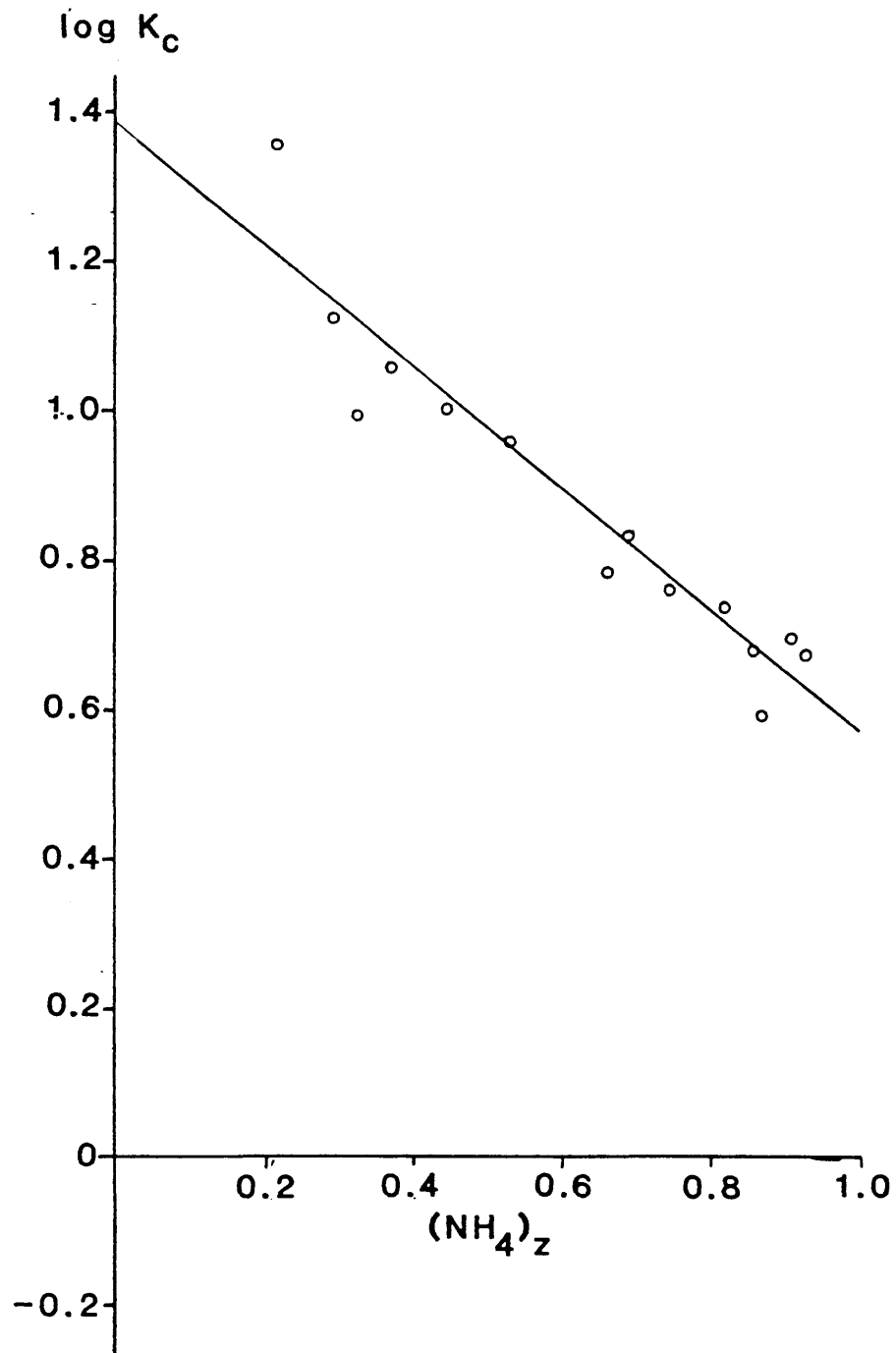


FIGURE 2.8 : Kielland Plot of the Cs/NH₄ Exchange on ZSM5 (Si/Al 45)

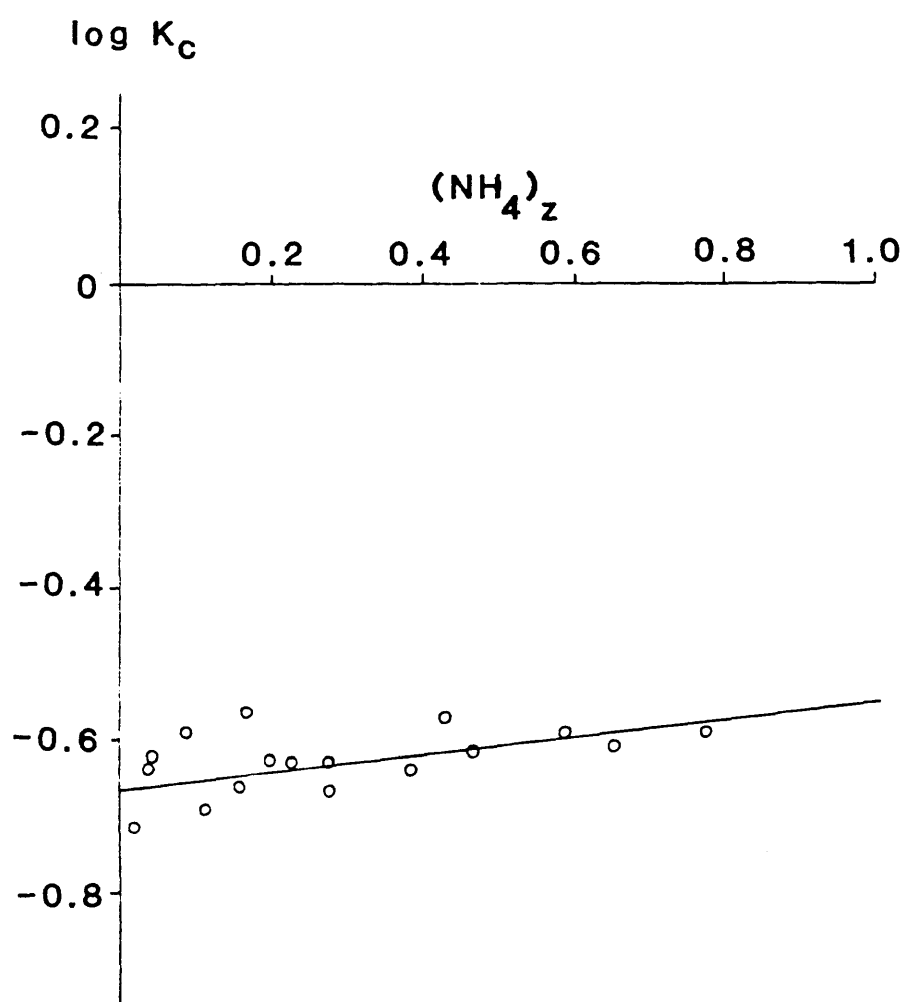


FIGURE 2.9 : Kielland Plot of the Cs/NH₄ Exchange on ZSM5 (Si/Al 28)

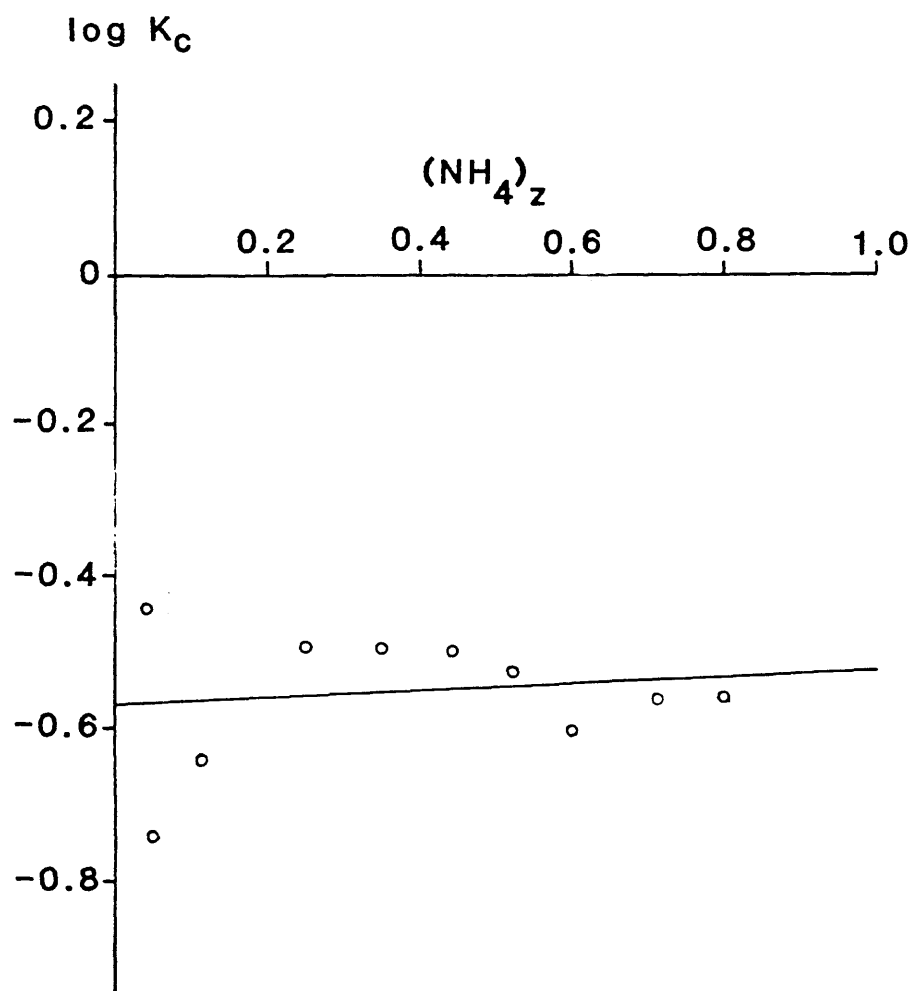


TABLE 2.3: Thermodynamic Parameters for Exchange on ZSM-5 (Si:Al=45) at Room Temperature

Polynomial Equation for log Kc versus Az	R	Ka	ΔG (kJ)/equiv.)
$\text{Na}^+(z) + \text{NH}_4^+(s) \rightleftharpoons \text{Na}^+(s) + \text{NH}_4^+(z)$ $\log Kc = 0.89 - 0.49A_z$ $\log Kc = 0.60 + 1.71A_z - 3.73A_z^2 + 1.80A_z^3$	0.1019 0.0830	4.39 4.51	-3.67 -3.73
$\text{Cs}^+(z) + \text{NH}_4^+(s) \rightleftharpoons \text{Cs}^+(s) + \text{NH}_4^+(z)$ $\log Kc = -0.66 + 1.22A_z$ $\log Kc = -0.69 + 0.32A_z - 0.26A_z^2$	0.0427 0.422	0.25 0.24	3.45 3.51

TABLE 2.4: Thermodynamic Parameters for Exchange on ZSM-5 (Si:Al=28) at Room Temperature

Polynomial Equation for log Kc versus Az	R	Ka	ΔG (kJ)/equiv.)
$\text{Na}^+(z) + \text{NH}_4^+(s) \rightleftharpoons \text{Na}^+(s) + \text{NH}_4^+(z)$ $\log Kc = 1.38 - 0.82A_z$	0.069	9.44	-5.56
$\text{Cs}^+(z) + \text{NH}_4^+(s) \rightleftharpoons \text{Cs}^+(s) + \text{NH}_4^+(z)$ $\log Kc = -0.57 + 0.04A_z$	0.0919	0.28	3.13

and second order polynomials adequately describe the data. Differences between the two polynomials occur only at high ammonium loadings of the zeolite phase, where experimental data are limited. The first order polynomial was chosen to describe the Kielland plots in figures 2.7 and 2.9, however both polynomials produce similar values for the thermodynamic constants as shown in tables 2.3 and 2.4.

The Na/NH_4 system for the ICI ZSM5 sample ($\text{Si}/\text{Al}=45$) shows considerable deviation from linearity, and is best described by a cubic polynomial. The region of deviation from linearity is also a region of high error in the radiochemical technique, and so a downward inflection in the K_c values must be treated with considerable care. The comparable isotherm for the sample with a higher aluminium content ($\text{Si}/\text{Al}=28$), has few data points in this region and has thus been fitted to a linear polynomial.

An initial increase in the selectivity for the ammonium ion with ammonium loading is startling, and thus this phenomena must be doubted. Irrespective of the presence of such a maxima in the Na/NH_4 isotherm for the $\text{Si}/\text{Al}=45$ sample, the isotherms for both ZSM5 samples, both exhibit a decline in the selectivity towards the ammonium ion as the ammonium loading increases. No such effect on the selectivity of the exchanger is observed for the Cs/NH_4 exchange. This suggests that the sodium ion may be able to differentiate between sites of varying strength, whilst the caesium ion, being less electropositive, is not able to differentiate between these sites.

It can be seen from tables 2.3 and 2.4, that ΔG^0 for the

Na/NH₄ exchange is negative, indicating that the exchanger shows an overall selectivity towards the ammonium ion. Conversely, for the Cs/NH₄ exchange ΔG^0 is positive, and the zeolites are exhibiting an overall selectivity towards caesium. Comparison of the thermodynamic data for both the ZSM5 samples, shows that ΔG^0 is more negative for both the Na/NH₄ and the Cs/NH₄ exchanges on the Si/Al=28 sample. This indicates that the Si/Al=28 sample is more selective to the ammonium ion.

TOLUENE DISPROPORTIONATION ON ION EXCHANGED ZSM5 ZEOLITES

3.1 THE EFFECT OF PORE STRUCTURE AND TRANSPORT PHENOMENA ON REACTION KINETICS. (76,77,78,79)

It is found that for many catalytic processes occurring in porous crystals such as zeolites, the observed (or global) rate of reaction is dependent on the transport properties of the reactant to the active site. When the rate at which the reactant is transported to the active site is lower than the rate at which it is converted, a concentration gradient with respect to the reactant results. For any system the rate of chemical reaction will always be proportional to some function of the concentration of the reactant. Hence, if mass-transport is the limiting process in a system, although all the sites are of identical activity, the sites at the centre of the porous crystal will be less efficiently utilised than the sites nearer to the surface, which will be experiencing the external reactant concentration.

The concentration profile within the catalyst crystal causes the global rate of reaction to be lower than the intrinsic rate of reaction. This is a theoretical rate, obtained by multiplying the rate of reaction per unit site by the total number of sites, assuming that each site is in contact with the external concentration of reactant. Alternatively, the intrinsic rate can be thought of as the rate associated with the same number of identical active sites as in the crystal spread over a planar surface.

The degree of mass-transport inhibition occurring in any process is given by the effectiveness factor (η); defined as the

observed global rate divided by the intrinsic rate:

$$\eta = \frac{\text{global rate}}{\text{intrinsic rate}} \quad \{3.1\}$$

When $\eta = 1$ mass-transport effects are unimportant, however as $\eta \longrightarrow 0$ the effect of mass-transport inhibition on the rate of reaction becomes predominant.

Expressing the effectiveness factor in a mathematical context allows an appreciation of the quantitative relationship between the relevant parameters contributing to this effect; namely reaction rate, diffusion rate and crystal size. Simple manipulation of the differential equation describing the mass-balance at steady-state, yields an expression for the concentration of the reactant at any point within the particle:

$$C = \frac{C_s R \sinh(\varphi r/R)}{r \sinh(\varphi)} \quad \{3.2\}$$

where C_s is the reactant concentration at the surface

R is the radius of the catalyst particle

r is the distance from the centre of the particle to the point of interest

φ is the Thiele's diffusion modulus:

$$\varphi = R \left\{ \frac{k_v C_s^{n-1}}{D_{eff}} \right\}^{1/2} \quad \{3.3\}$$

where k_v is the intrinsic rate constant per unit volume

n is the order of the reaction

D_{eff} is the effective diffusion coefficient

Calculating the global rate by differentiating with respect to r , allows the evaluation of η by substitution into equation 3.1:

$$\eta = \frac{3}{\varphi} \left\{ \frac{1}{\tanh(\varphi)} - \frac{1}{\varphi} \right\} \quad \{3.4\}$$

The relationship between η and φ implies that the extent of the mass transfer effect on the kinetics of the reaction is dependent on the ratio of $R^2 k/D$; thus it is the relative rather than the absolute values of the rates of diffusion and reaction that are of importance. In relation to this work, any investigation into the para-selective properties of ion exchanged zeolites, must take into account the effect of the cation, on both the diffusion coefficients and the rates of isomerisation of the three xylene isomers.

3.2 REACTOR CHARACTERISTICS AND THEIR RELATION TO KINETICS

(76,77,78,79)

In order to quantify the results of the catalytic experiments, so that meaningful comparisons between samples can be made, a way of accounting for the effects of different experimental variables on both conversion and selectivity is required. Initial runs suggested that the conversion of the reactant is dependent on the

following controllable variables:

1. Temperature
2. Mass of zeolite
3. Flow-rate of reactant

The dependence on temperature is described by the well-known Arrhenius equation;

$$k = A \exp(-E_A/RT) \quad \{3.5\}$$

whilst the second and third variables affect the mean time that reactant molecules spend in the catalyst bed. The relationship between the two variables is known as the contact (or residence) time, defined as the mean time for the reactant to traverse the length of the catalyst bed:

$$\text{contact time (min)} = \frac{\text{volume of bed (ml)}}{\text{volumetric flow-rate (ml/min)}} \quad \{3.6\}$$

As neither of the quantities on the right hand side of equation 3.6 are easy to measure experimentally, two approximations are made: the volume of the bed is substituted by the mass of zeolite, and the volumetric flow-rate by the liquid flow-rate at room temperature. A combination of these two approximations yields the weight-hourly-space-velocity (WHSV), which is inversely proportional to the contact time:

$$\text{WHSV (hr}^{-1}\text{)} = \frac{\text{liquid flow-rate (g/hr)}}{\text{mass of bed (g)}} \quad \{3.7\}$$

Although WHSV is experimentally easy to measure, it does vary with both temperature and pressure.

Design-equation for plug-flow

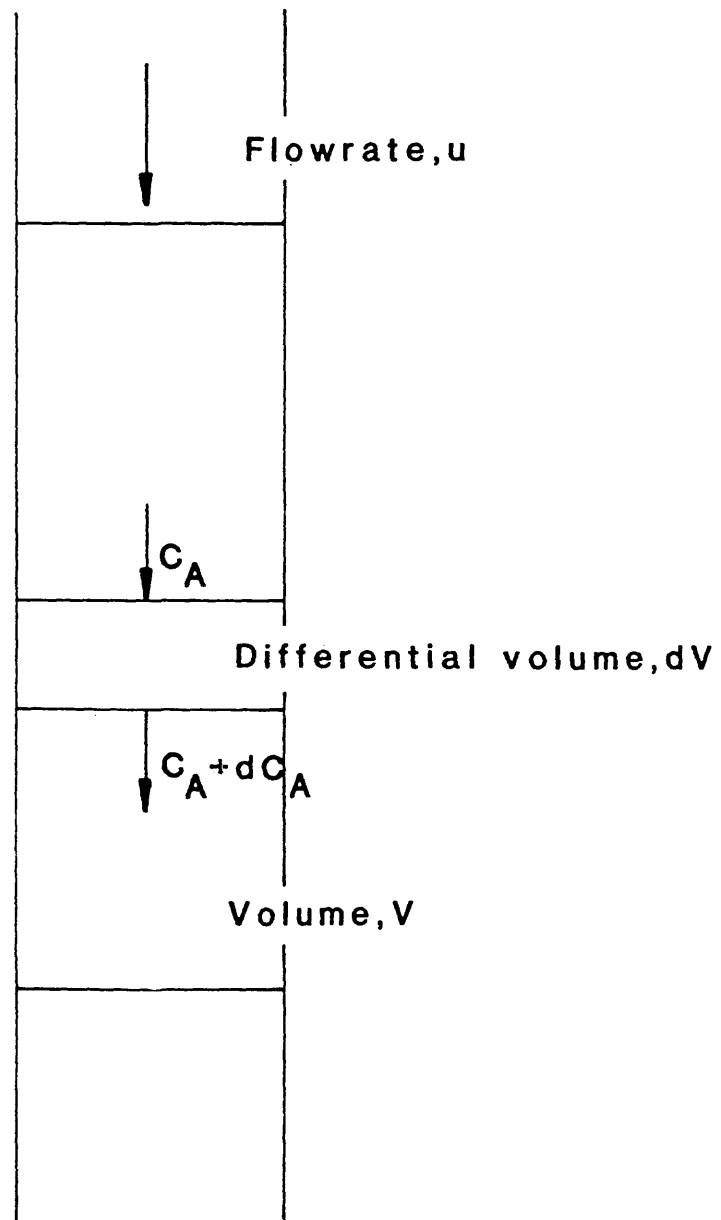
Experimentally determined conversions can be related to reaction rates by use of the design equation for the particular catalytic reactor used. The reactor used in these experiments is of the fixed-bed type, consisting of solid catalyst particles that are contained in a (usually) cylindrical vessel; furthermore the bed remains fixed until it is discarded. The flow of the reactant through the catalyst bed is modelled by that of plug-flow; an idealised model of the motion of a fluid (in this case a gas), in which all the molecules move with uniform velocity in a direction parallel to the walls of a tubular reactor.

The design-equation for plug-flow is developed, by considering a fixed-bed of volume V , contained within a tubular reactor. The reaction mixture flows through the bed at a flow-rate u ($\text{dm}^3 \text{ sec}^{-1}$) and passes through an infinite number of differential volume elements of volume δV , as shown in figure 3.1. Considering the key reactant, component A, which enters the differential volume δV , at concentration C_A , and leaves at concentration $(C_A + \delta C_A)$, mass-balance considerations imply that:

$$\begin{array}{ccccccc} \text{moles} & = & \text{moles} & - & \text{moles} & - & \text{moles} \\ \text{accumulating} & & \text{incoming} & & \text{outgoing} & & \text{reacting} \end{array}$$

At steady-state no material accumulates within the reactor, and thus the net flow through each element exactly balances the reaction within it:

FIGURE 3.1 : Development of the Design–Equation for Plug–Flow



$$r_v \delta V = -u \delta C_A \quad \{3.8\}$$

where r_v is the reaction rate per unit volume of the catalyst bed. Equation 3.8 is known as the design-equation for plug-flow, and it allows calculation of the rate of chemical reaction within the bed from experimentally measureable variables.

Pressure drop across fixed-bed gas reactors

The design-equation for plug-flow requires both a knowledge of the volumetric flow-rate through the bed, and the concentrations of reactant before and after the bed in order to determine reaction rates. These quantities are dependent on the pressure of the reactor, and hence the pressure drop across the bed as defined by the Ergun equation.

A pressure transducer was used to measure the pressure both before and after the bed, caused by the flow of nitrogen gas at room temperature. The pressure drop was found to be negligible, however the reactor was found to be at a pressure slightly above one atmosphere, which was thought to be caused by the use of capillary tubing beyond the reactor. The measured pressure was found to be proportional to the the flow-rate, which allowed the calibration of the apparatus. By measuring volumetric nitrogen flows and the associated reactor pressures, an iterative pressure and flow-rate calculation could be applied under catalytic conditions to the gaseous reactant, yielding estimates for both the pressure and volumetric flow-rate of the reactant.

Differential and integral rate analysis

The design-equation for plug-flow can be used to determine both reaction orders and rate constants for any reaction. The most straightforward method of determining reaction orders and rate constants for complex rate expressions utilises a differential reactor; a series of experiments are carried out on a small quantity of catalyst under isothermal conditions, whilst attempting to keep the conversion low enough for it to be considered as differential. A plot of conversion versus contact time yields a curve whose derivative is the reaction rate at the corresponding conditions of temperature and pressure. By varying the inlet concentration (with the use of a diluent gas), and plotting the measured rate versus the logarithm of the inlet concentration, then both the rate constant k , and the reaction order n , can be determined. Mathematically this is illustrated by consideration of the general rate equation:

$$r_A = k C_A^n \quad \{3.9\}$$

hence: $\ln r_A = \ln k + n \ln C_A \quad \{3.10\}$

Such a plot of $\ln r_A$ versus $\ln C_A$ will have intercept $\ln k$ and gradient n .

Differential analysis is an excellent procedure used in the elucidation of the rate equation for a process. Its use is however limited in the solution of the kinetics of toluene disproportionation and xylene isomerisation, as it requires very good analysis of the inlet and outlet streams of the reactor. The gas chromatograph and integrator used in the catalysis

experiments can detect all products formed above 1% conversion. Problems are however encountered because of the requirement that a series of runs need to be performed on each sample at varying inlet concentrations, C_A . This involves using a nitrogen gas diluent, which causes pulsing in the reactant stream and thus poor estimates of the inlet concentration.

Integral rate analysis, allows partial elucidation of the kinetics of a chemical reaction without the use of diluent nitrogen gas. Furthermore, the integral flow-reactor can be used at much higher conversions than the differential flow-reactor. Under isothermal conditions a specific rate equation is integrated in the design-equation for plug-flow:

$$\frac{V}{u} = - \int \frac{dC_A}{r_A} \quad \{3.11\}$$

For each set of flow conditions the left and right hand side of equation 3.11 are evaluated numerically, and the results tested for linearity. This provides an easy method of testing simple rate expressions, however integration becomes more complex for rate expressions of non-simple reaction mechanisms.

Integrated rate equations for first and second order reactions

Both the toluene disproportionation and xylene isomerisation reactions are considered to be kinetically simple, and it was decided to restrict the use of integral rate analysis to the discrimination of first and second order processes only. Substituting these rate equations into equation 3.11:

First order:

$$\frac{V}{u} = \int \frac{dC_A}{k_1 C_A}$$

Second order:

$$\frac{V}{u} = \int \frac{dC_A}{k_2 C_A^2}$$

and solving for the entire catalyst bed between the concentration limits of C_0 at the inlet and C at the outlet, yields:

$$\text{First order} \quad k_1 V/u = \log (C/C_0) \quad \{3.12\}$$

$$\text{Second order} \quad k_2 V/u = 1/C_0 - 1/C \quad \{3.13\}$$

These equations allow the evaluation of the first and second order rate constants for the relevant reactions, from a knowledge of the flow-rate through the bed, the mass of the bed and the concentrations of reactant at the inlet and outlet of the bed.

Activation energy and mass transfer

The dependence of the reaction rate on temperature is also influenced by the extent of diffusion-control occurring within the pores of the crystal. Empirically the temperature dependence of the rate constant k , for a reaction is found to be exponential in nature as described by the Arrhenius equation:

$$k = A \exp(-E_A/RT) \quad \{3.5\}$$

where k is the first order rate constant (s^{-1})
 A is the pre-exponential factor (s^{-1})
 E_A is the activation energy ($J \text{ mol}^{-1}$)
 R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
 T is the temperature (K)

Hence a plot of $\ln(k)$ versus $1/T$ will yield a straight line of slope $-E_A/R$, which allows calculation of the apparent activation energy for a process.

For reactions in porous crystals, the observed rate of disappearance of the reactant can be expressed in terms of the intrinsic rate multiplied by the effectiveness factor, η :

$$-\frac{dn}{dt} = k_v V C_s^n \eta \quad \{3.14\}$$

Diffusion effects become significant when η is less than 0.5, and equation 3.4 defining the Thiele modulus, approaches the limiting situation where:

$$\eta \longrightarrow \frac{1}{\phi} \quad \{3.15\}$$

Substituting equation 3.15 into equation 3.14 and simplifying, yields the rate equation:

$$-\frac{1}{V} \frac{dn}{dt} = \frac{C^{(n-1)/2}}{R} \left\{ D_{\text{eff}} k_v \right\}^{1/2} \quad \{3.16\}$$

Expressing the rates for diffusion and the intrinsic reaction in terms of the Arrhenius equation, gives:

$$k_v = A \exp(-E_A/RT) \quad D_{\text{eff}} = B \exp(-E_{\text{diff}}/RT)$$

Thus the temperature sensitive term in equation 3.16 becomes proportional to:

$$(k_v D_{\text{eff}})^{0.5} \propto \exp \frac{-(E_A + E_{\text{Diff}})}{2RT} \quad \{3.17\}$$

In a porous crystal at low temperatures, the effect of diffusion is negligible and the Arrhenius plot is described by equation 3.5; the measured activation energy is equal to the activation energy for the intrinsic reaction. As the temperature increases, the effect of diffusion becomes significant and η is no longer equal to unity. In this case the measured activation energy is equal to the mean of the activation energies for diffusion and reaction. For most gaseous reactions, the activation energy for diffusion is of the order of 1 to 10 kJ/mol, whilst that for a chemical reaction is typically 100 kJ/mol. Hence, when diffusion effects become important the observed activation energy will be approximately half of that for the intrinsic reaction. This gives a means of distinguishing between chemical and diffusion controlled processes within a porous crystal, assuming that a typical value for the activation energy for a chemical reaction is 100kJ/mol. Any process exhibiting activation energies considerably lower than 50 kJ/mol, will be under the influence of some degree of mass-transport control.

3.3 MODEL FOR SELECTIVE TOLUENE DISPROPORTIONATION (45)

At elevated temperatures, ZSM5 is a very efficient catalyst for the disproportionation of toluene. For any catalyst, thermodynamics predicts the equilibrium aromatic product distribution shown in table 3.1 (57) whilst the xylenes are produced in an equilibrium mixture of temperature-variable composition, as shown in table 3.2 (62).

The proposed mechanism which is represented in figure 3.2

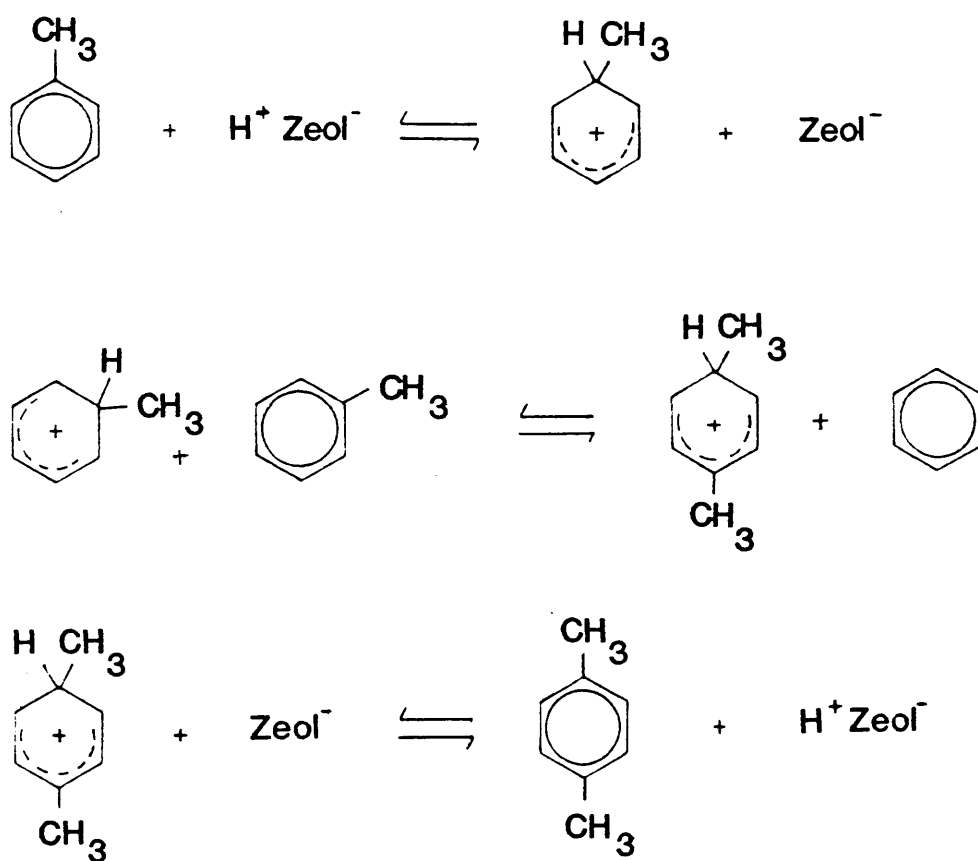
**Table 3.1 : Thermodynamic equilibrium aromatic
product distribution for toluene
disproportionation**

TEMP (°C)	BENZENE	TOLUENE	XYLENE	OTHERS
327	31.5	41.7	22.7	4.1
527	32.0	40.6	23.1	4.3

**Table 3.2 : Thermodynamic equilibrium xylene
distribution**

TEMP (°C)	PARA-XYLENE	META-XYLENE	ORTHO-XYLENE
27	23.82	59.80	16.38
127	24.24	56.82	18.94
227	24.07	54.77	21.16
327	23.81	53.24	22.95
427	23.45	52.12	24.43
527	23.09	51.35	25.56
627	22.81	50.58	26.61
727	22.49	50.06	27.45

FIGURE 3.2 : Proposed Mechanism for Toluene Disproportionation
on Zeolite ZSM5



involves the attack of a toluene molecule by a benzyl cation at the ipso position. This has the effect of weakening the carbon-methyl bond, causing it to transfer to the toluene molecule (63).

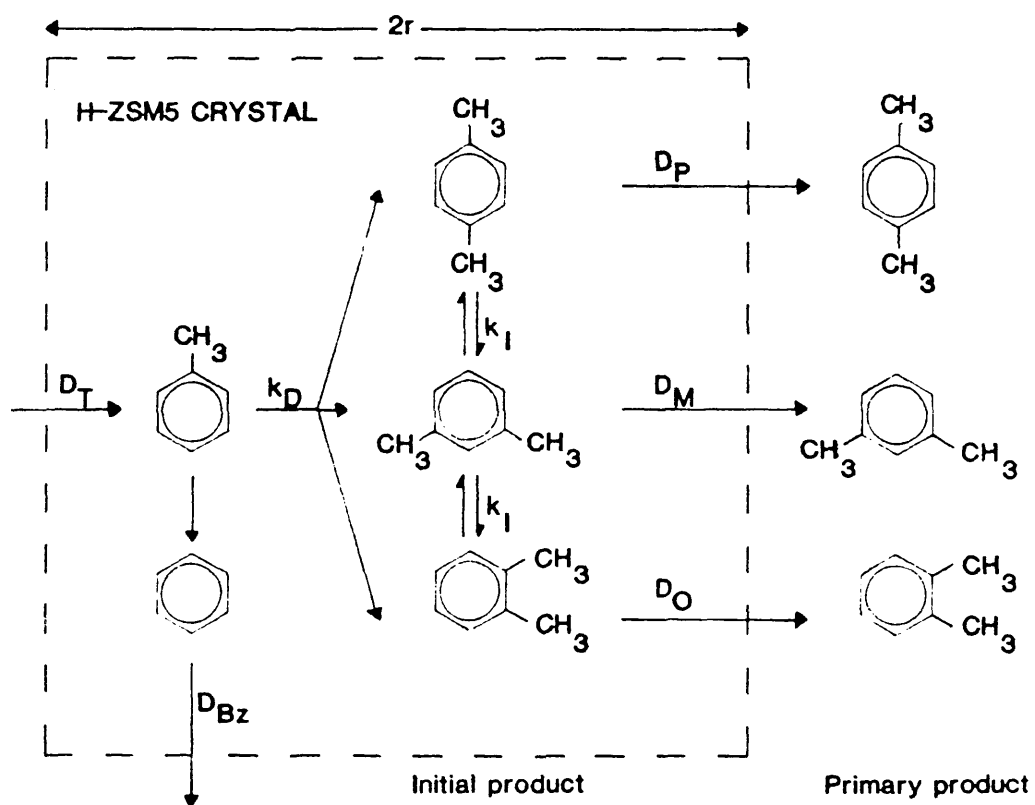
In the absence of steric constraints, para- and ortho-xylene are expected to be the primary products due to the directing influence of methyl groups on electrophilic substitution reactions. Toluene disproportionation is usually followed by a secondary isomerisation of the primary product distribution of xylenes to yield the equilibrium xylene composition.

General characteristics of selective toluene disproportionation

Figure 3.3 schematically describes the salient features of STD. Toluene diffuses through the ZSM5 channels with a diffusivity, D_T . At the acid sites within the channels, two toluene molecules disproportionate to give benzene and one of the xylene isomers, in a reaction characterised by the rate constant, k_D . The initial product distribution is unknown but it is believed to be rich in para-xylene due to transition state selectivity at the active site, which hinders the formation of the bulky bimolecular transition state leading to the ortho- and meta-xylene products. While diffusing out of the crystal, with diffusivities D_P , D_M , and D_O , the xylene isomers will undergo isomerisation to convert the initial product to a sorbed mixture, with a distribution nearer to the equilibrium composition.

At low conversions, which are experimentally realised with short contact times, the observed product distribution should approach the primary distribution because secondary isomerisation due to pore re-entry is minimised. This primary product

FIGURE 3.3 : General Characteristics of Selective Toluene Disproportionation



distribution is determined solely by the initial isomer distribution, the rate of isomerisation (k_I), the respective diffusivities of the xylene isomers (D_P , D_M , D_O) and the length of the diffusion path (r). At longer contact times, when practical conversions are realised, the primary product will undergo secondary isomerisation due to re-entry of xylene into the pore system. Hence the secondary product will be a function of conversion.

In order to maximise the fraction of para-xylene in the primary product, it is required that the initially formed meta- and ortho-xylenes should diffuse out at a slower rate ($D_{M,O}/r^2$) than their conversion to para-xylene (k_I), whilst the rate of para-xylene diffusion (D_P/r^2) out of the crystal should be faster than its rate of isomerisation (k_I). It has already been experimentally established that in both silicalite and ZSM5, para-xylene has a diffusion coefficient some thousand times greater than those of other two isomers. Hence the primary product is expected to be para-rich when the length of the diffusion paths is sufficiently long.

At a given conversion, the fraction of para-xylene in the secondary product will be maximised when the observed rate of isomerisation is lower than the observed rate of disproportionation, so that a para-rich xylene mixture is formed at a faster rate than it is isomerised to an equilibrium mixture of xylene isomers. Calculation of the intrinsic rate constants of these two processes shows that the rate of isomerisation is four orders of magnitude greater than the rate of disproportionation; obviously a severe inhibition of the isomerisation reaction is

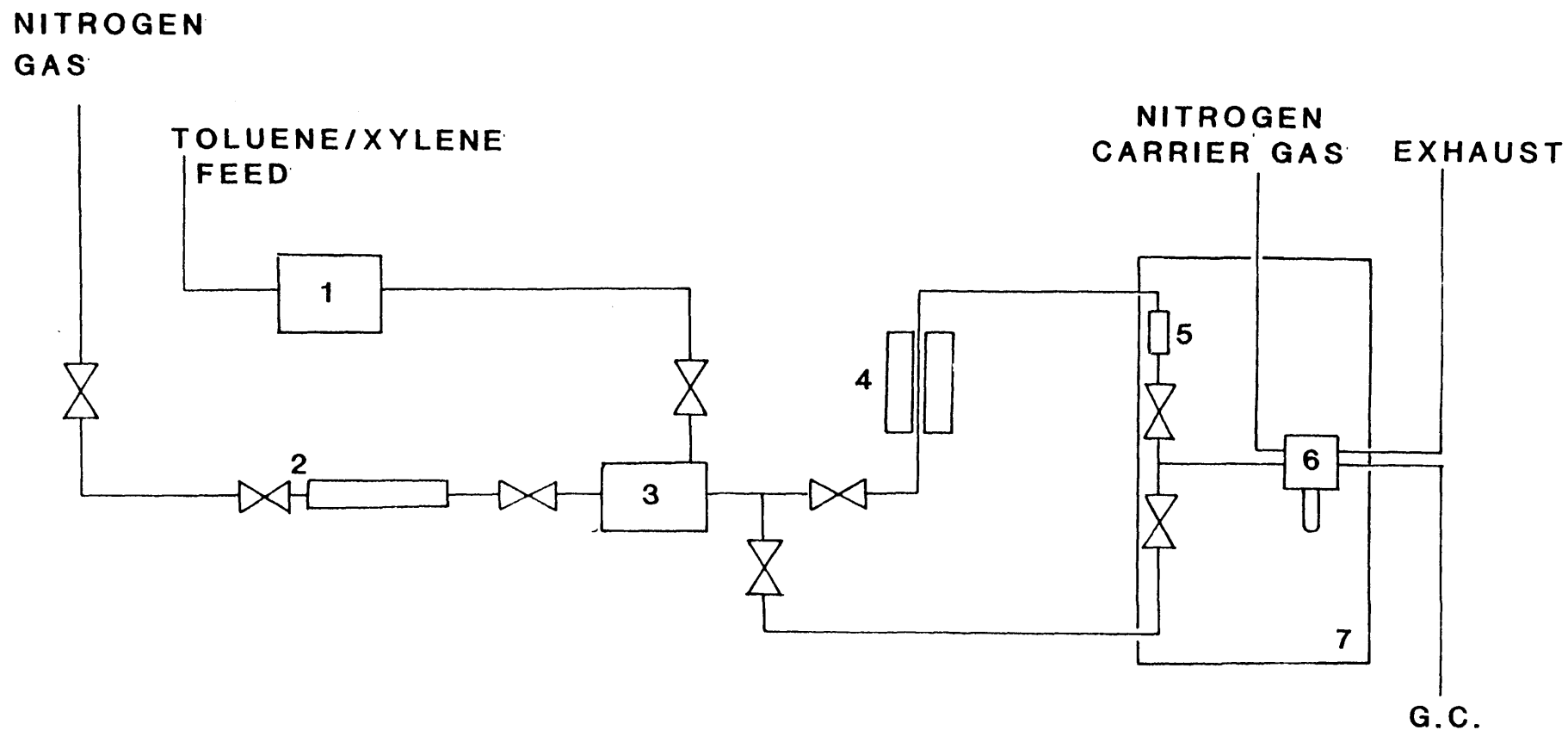
required. At low conversions this is realised by the low relative concentration of xylene with respect to toluene within the crystal. At practical conversions this condition cannot be met, however when diffusive barriers hinder the transport of ortho- and meta-xylenes relative to para-xylene this will lead to a higher "effective" concentration of ortho- and meta-xylene in the crystal. Although the relative rates of disproportionation and isomerisation are not affected by these diffusive barriers, the isomerisation of para-xylene is still effectively retarded by the concentration/diffusion effect.

The conditions for maximising the yield of para-xylene in the primary and secondary products are identical. From this discussion, it can be seen that to enhance the para-selective properties of a ZSM5 catalyst, it is required that there is either an increase in the diffusive restrictions in the ZSM5 channels, or a change in the acidic properties of the catalyst, so as to alter the relative values of the isomerisation and disproportionation rate constants.

3.4 EXPERIMENTAL

A schematic diagram of the catalytic apparatus is shown in figure 3.4. Catalytic studies were typically performed on approximately 0.1g of catalyst which was packed between silica-wool plugs and positioned around a chromel-alumel thermocouple in the reactor tube. A continuous flow of liquid reactant was fed into the spiralled vaporiser using a Gilson peristaltic pump, and the gaseous flow was maintained both before and after the bed, by a

FIGURE 3.4 : Schematic of the Catalytic Apparatus



1 Peristaltic pump

2 Flowmeter

3 Vaporiser

4 Furnace

5 Filter

6 Sample valve

7 Oven

variac-controlled, heating system surrounding all pipes and valves.

On-line gas analysis was performed using a Pye Unicam G.C.D. chromatograph, fitted with a flame ionisation detector. Separation of the aromatic products was achieved by using a 2 metre packed column, composed of 5% Bentone-34/D.I.D.P. on a Chromosorb W.A.W. support. The operating conditions for the gas chromatograph were optimised for the separation of the three xylene isomers which however could not be completely resolved:

Oven temperature = 102°C

Detector temperature = 250°C

Injector temperature = 200°C

Hydrogen pressure = 21 lb/in^2

Air pressure = 30 lb/in^2

Nitrogen carrier gas flow-rate = 45 ml/min

Sampling of the product stream and evaluation of peak areas was performed by the Pye Unicam CDP1 integrator. For each catalytic run, data were collected on a BBC microcomputer interfaced with the integrator, using the programs listed in Appendices 1 and 2. The data stored on floppy-disc were then available for manipulation using the BBC microcomputer, to yield values of the rate constants and activation energies for each system, (see the programs listed in Appendices 3 and 4).

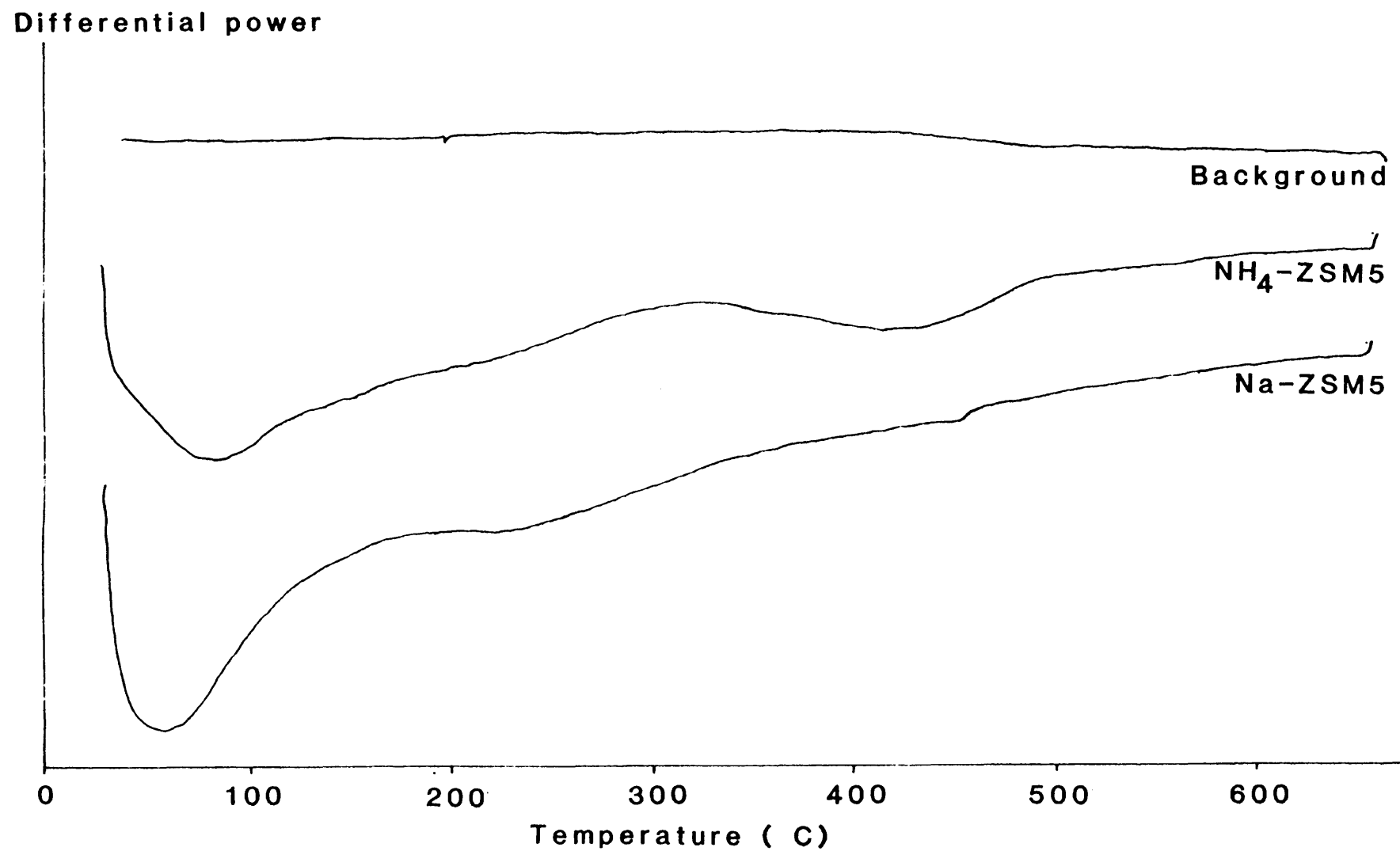
A new zeolite sample was used daily in order to avoid problems associated with catalyst aging and temperature cycling. The fresh catalyst was heated to 500°C at a rate of 10°C/min in a stream of dried nitrogen gas (flow-rate between 10 and 30 ml/min). This

removes occluded water and also forms the acid sites.

Estimates of the experimental errors were incorporated into the data manipulation programs. Small errors were known to be associated with the measurement of the mass of the zeolite bed, and with the flow-rate of liquid reactant into the catalytic system, however these were negligible in comparison with the errors found between consecutive samples of the product stream. These fluctuations were considered to be associated both with the detector, and to a small amount of pulsing and temperature variation in the reactor. To estimate the magnitude of these random errors, wherever possible the reactor was operated under each set of experimental conditions for at least one hour, so that a number of data points could be collected and their standard deviation calculated. Differences between different samples under the same conditions also occurred. This was attributed to slight variations in the position of the catalyst bed, leading to it experiencing different reaction temperatures even though the thermocouple temperature was constant. Finally, differences in the pressure of the reactor caused by blockages in the capillary tubing were shown to affect the performance of the catalyst.

Before any catalytic experiments were performed the exact value of the calcination temperature necessary to both dehydrate and deammoniate the catalysts had to be determined. DSC's of both the Na-ZSM5 and NH_4 -ZSM5 samples are shown in figure 3.5. The desorption peaks at 80°C and 230°C are attributed to physisorbed water, as they are characteristic of both samples, whilst the peak at 420°C occurs only for the NH_4 -ZSM5 sample, and is

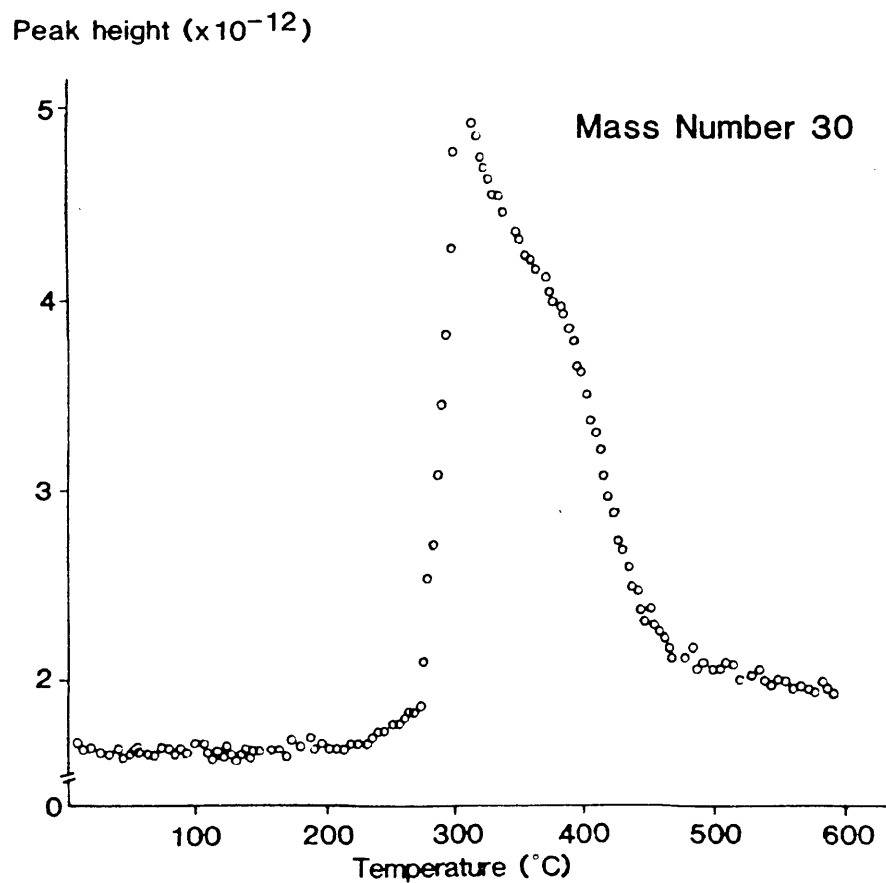
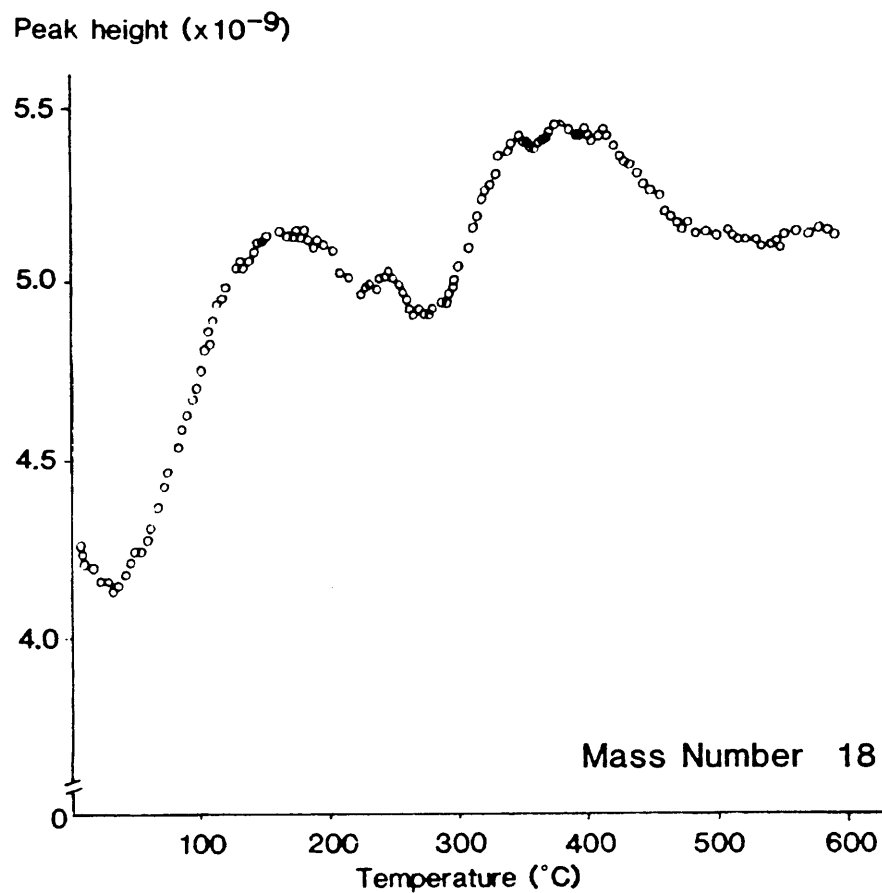
FIGURE 3.5 : Differential Scanning Calorimetry Plots of ICI Zeolite ZSM5



assigned to the desorption of ammonia and the subsequent formation of acid sites. Figure 3.6, shows the calcination of Na(20)-ZSM5 as monitored by mass spectroscopy. Mass number 18, is used to monitor the presence of both water and ammonia; the desorption temperatures correlate well with those from the DSC experiments. The second spectrum was collected under oxidising conditions, so that any liberated ammonia would be oxidised to nitrous oxide, and mass number 30, is used to monitor the evolution of this compound. The desorption temperature of 350°C is lower than expected, however the temperatures of desorption of all species were lower in the oxidising environment. This confirms the assignment of the high temperature desorption peak to that of ammonia.

Steaming of zeolites is known to cause a degree of dealumination (80), so it is possible that the removal of the zeolitic water could cause migration of aluminium from framework positions. The ^{27}Al MASNMR spectrum of a NH_4 -ZSM5 sample heated to 500°C is shown in figure 3.7. Framework tetrahedral and non-framework octahedral aluminums show shifts at about -60 ppm and 0 ppm respectively. The absence of any significant peak at 0 ppm even in the presence of acetyl-acetone, suggests that the migration of aluminium from the framework during calcination is minimal under these conditions. The stability of the catalysts over the period of six to seven hours when they were in use, was checked by the cycling of both temperatures and contact times during the collection of data. In all cases, consistent conversions and selectivities were obtained over a period of

FIGURE 3.6 : Calcination of Na(20)-ZSM5 Monitored by Mass Spectroscopy





LJB.055
PPG:
SHORTPUL.FC
DATE 29-9-87
TIME 16:10

SF 78.205
Q1 0.0
SI 8192
TD 1024
SW 125000.000
HZ/PT 30.518

AQ 4.096M
RG 20
NS 114625
RO 3793
TE 297

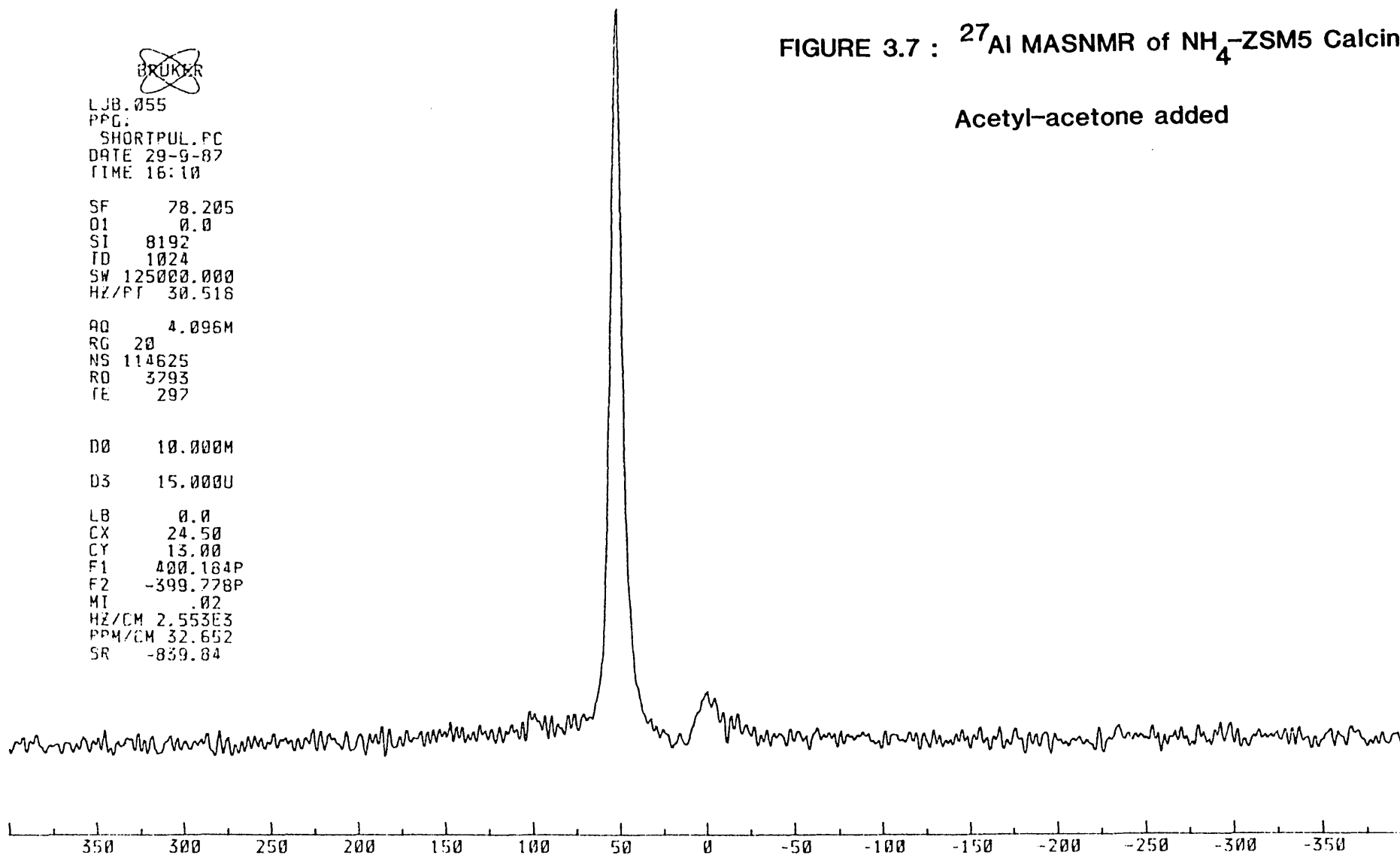
D0 10.000M

D3 15.000U

LB 0.0
CX 24.50
CY 13.00
F1 400.184P
F2 -399.778P
MI .02
HZ/CM 2.553E3
PPM/CM 32.652
SR -839.84

FIGURE 3.7 : ^{27}Al MASNMR of $\text{NH}_4\text{-ZSM5}$ Calcined at 500 C :

Acetyl-acetone added



seven to eight hours.

The detector system was calibrated with aromatic mixtures of known composition, in order to judge the accuracy of the kinetic data calculated from the catalytic experiments. The gas chromatograph was operated under the conditions given earlier and calibration xylene mixtures were made up by weighing with the masses being measured to four decimal places. The percentage concentration of each xylene isomer in the mixture, was calculated from these masses taking into account the impure nature of the xylene feedstocks. A sample of each mixture was injected onto the column, and the detector response was taken as the mean of three such injections under identical conditions. The detector response was compared to the known percentage mass composition of each of the mixtures. The results of these calibration experiments are given in tables 3.3 and 3.4.

The precision of the detector is independent of retention-time, allowing a rapid sampling rate of the the product stream, with the typical retention time of para-xylene ranging from 115 to 130 seconds in the catalytic experiments. The precision is however heavily dependent on sample size. When the signal from the gas chromatograph to the integrator generates "slope" values which exceed the maximum value which can be displayed (or stored), the computed area of that signal is found to be lower than the actual area. Such an effect is seen for the 0.10 μ l sample in table 3.3.

The accuracy of the detector system was tested in the series of calibration experiments summarised in table 3.4. The system is fully stretched having to resolve the xylene peaks when one of

Table 3.3 : Calibration of the Detector System

Variation of Detector Response with Sample Size (Constant Retention Times)

Sample Size(μ l)	% para-xylene	% meta-xylene	% ortho-xylene
(By mass	19.46	70.29	10.25)
.06	19.47	70.06	10.44
.02	19.22	70.16	10.62
.10	20.59	68.12	11.22

Variation of Detector Response with Retention Time (Constant Sample Size of .04 μ l)

Retention Time of para-xylene peak (s)	% para-xylene	% meta-xylene	% ortho-xylene
(By mass	91.69	5.79	2.50)
201	92.07	5.62	2.31
222	91.92	5.63	2.45
236	91.70	5.79	2.51
269	92.08	5.49	2.43
363	92.30	5.40	2.30
395	92.21	5.39	2.41
432	92.47	5.22	2.31

Table 3.4 : Calibration of the Detector System

Variation of Detector Response with xylene Composition (with
Constant Sample Size of .04 μ l)

	% para-xylene	% meta-xylene	% ortho-xylene
% mass	91.70	5.76	2.50
	91.92 (-.22)	5.63 (+.13)	2.45 (+.05)
% mass	94.61	3.08	2.27
	94.50 (+.11)	3.13 (-.05)	2.36 (-.09)
% mass	96.66	1.89	1.40
	96.61 (+.05)	1.93 (-.04)	1.46 (-.06)
% mass	4.92	89.69	5.36
	4.06 (+.86)	90.11 (-.42)	5.83 (-.47)
% mass	1.25	96.64	2.08
	1.13 (+.12)	96.56 (-.08)	2.31 (-.23)
% mass	3.34	4.22	91.97
	3.03 (+.31)	4.02 (+.20)	92.43 (-.46)
% mass	4.45	4.01	91.08
	4.01 (+.44)	3.77 (+.24)	91.72 (-.64)
% mass	1.20	1.45	96.86
	1.12 (+.08)	1.28 (+.17)	97.10 (-.24)

the isomers is present in large excess, and when the para- and meta-xylene peaks are not completely resolved. Generally the detector analysis is excellent, however it does have a tendency to over-estimate the area of the ortho-xylene peak. This is unexpected, as it is the isomer with the longest retention time and as a consequence is expected to have the broadest peak. When near-equilibrium mixtures of the xylene isomers are produced such an effect is insignificant, and it can be ignored in the toluene disproportionation experiments when a near-equilibrium xylene composition is usually obtained. Such an effect becomes significant in the xylene isomerisation reaction when conversions of less than 10% are routinely achieved. This requires correction to be made to the xylene compositions computed by the integrator before any meaningful kinetic analysis can be performed.

3.3 RESULTS AND DISCUSSION

A range of caesium/ammonium and sodium/ammonium exchanged forms of the ZSM5 sample supplied by ICI, were prepared using the ion exchange isotherms obtained in Chapter 2. An initial screening was performed on these samples, to determine whether or not the two cations had any effect on the course of the toluene disproportionation reaction. The experimental relationship between conversion and para-selectivity at constant temperature was obtained for each sample. The "% conversion" is defined as the percentage of reacted toluene i.e.

$$\% \text{ Conversion} = 100 - \% \text{ Area of toluene peak}$$

whilst the "para-selectivity" is defined as the percentage area of the para-xylene peak divided by the total percentage area of all the xylene peaks, i.e.;

$$\text{Para-selectivity} = \frac{\% \text{ Area of para-xylene}}{\% \text{ Area of total xylene}}$$

The samples are labelled as the percentage-fraction of cations occupying the cation/acid sites. Thus Na(60)-ZSM5 has a site distribution composed of 60% sodium and 40% hydronium ion.

Typical results showing the variation in para-selectivity with conversion at 501⁰C for two samples of identical cation loading are plotted in figure 3.8. Curves containing data points from at least three samples at the indicated cationic loading were obtained; the wide range of conversions were experimentally realised by varying the reactant flow-rate, by the addition of nitrogen diluent gas and by varying the mass of the catalyst bed. The resulting curves were fitted by eye. Particular attention was paid to the collection of data at low conversions where the distribution of xylene isomers deviates significantly from the equilibrium composition.

A more detailed account of the ratio of the xylene isomers is given in figure 3.9 for H-ZSM5 at 501⁰C. At low conversions when the initial product is expected to predominate, para-xylene is seen to approach a limiting concentration where it forms the major component in the product mixture. At intermediate conversions meta-xylene is the product formed in excess, suggesting that xylene isomerisation on ZSM5 proceeds via consecutive 1,2 methyl- shifts. At higher conversions the para-selectivity decreases until the xylene composition is identical

FIGURE 3.8 : Para-Selectivity versus Conversion curves for Na(60)-ZSM5[○]

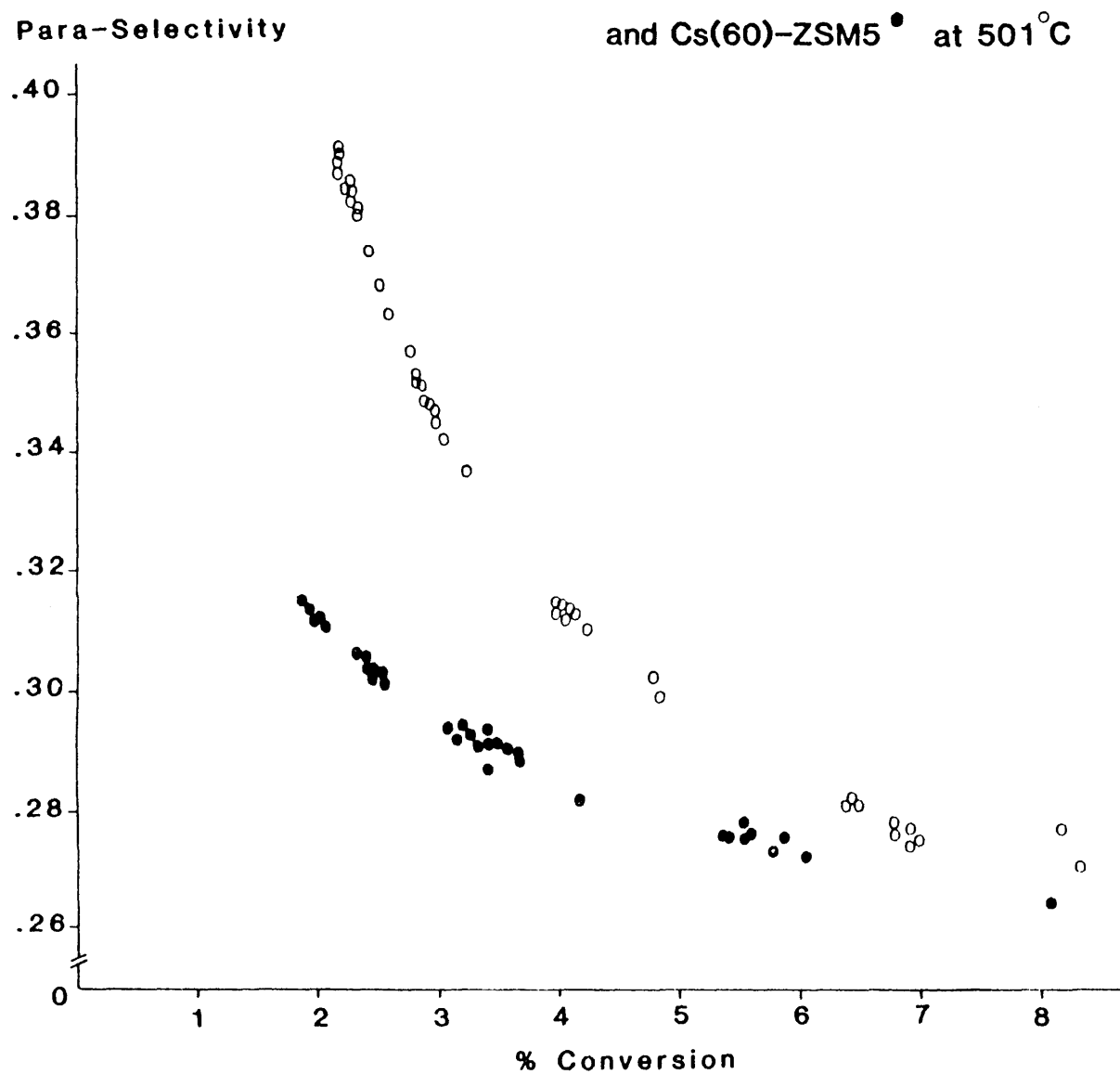
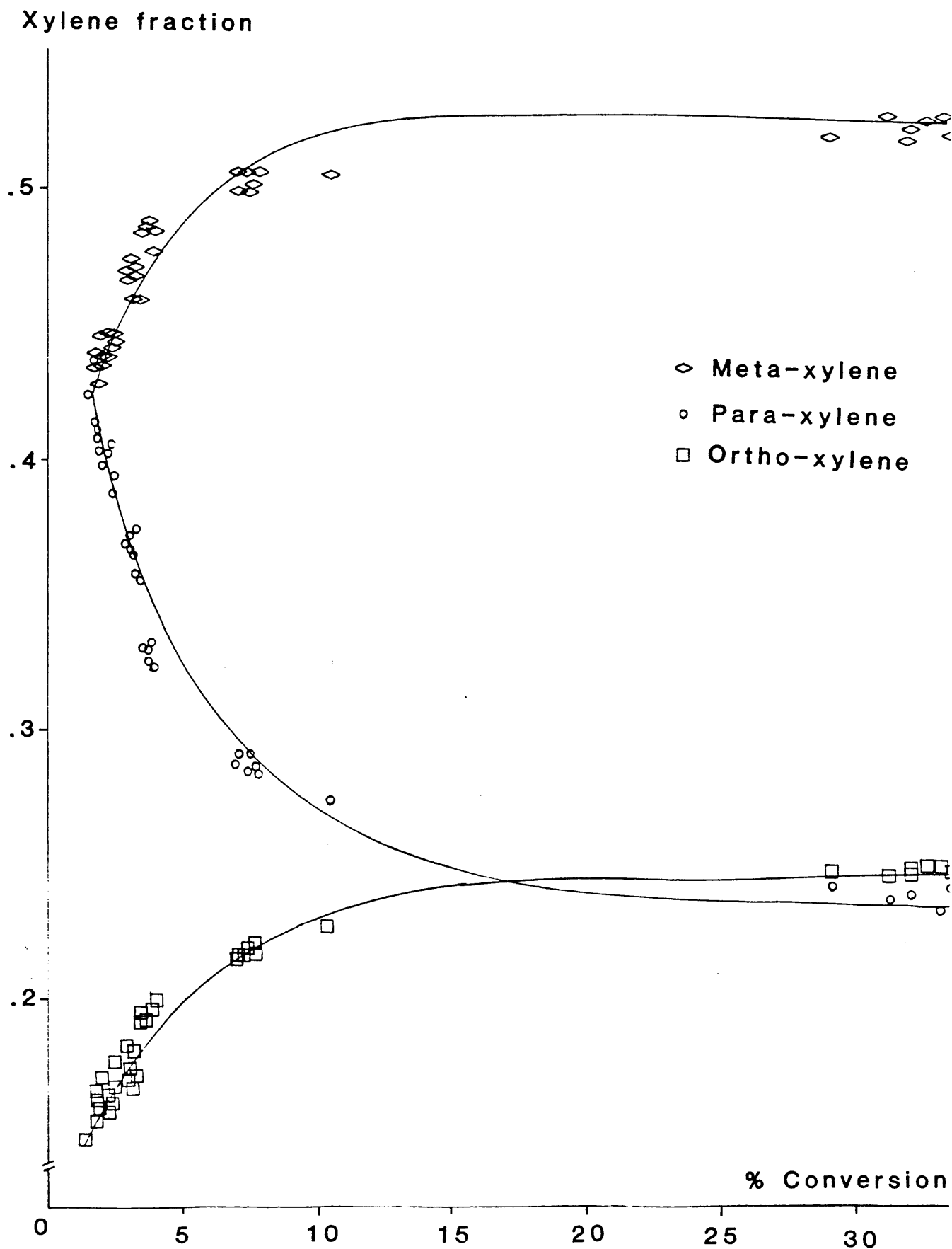


FIGURE 3.9 : Variation of the Xylene Composition with Conversion on H-ZSM5



to the equilibrium values. These observations are in accordance with the model of STD described in Section 3.2.

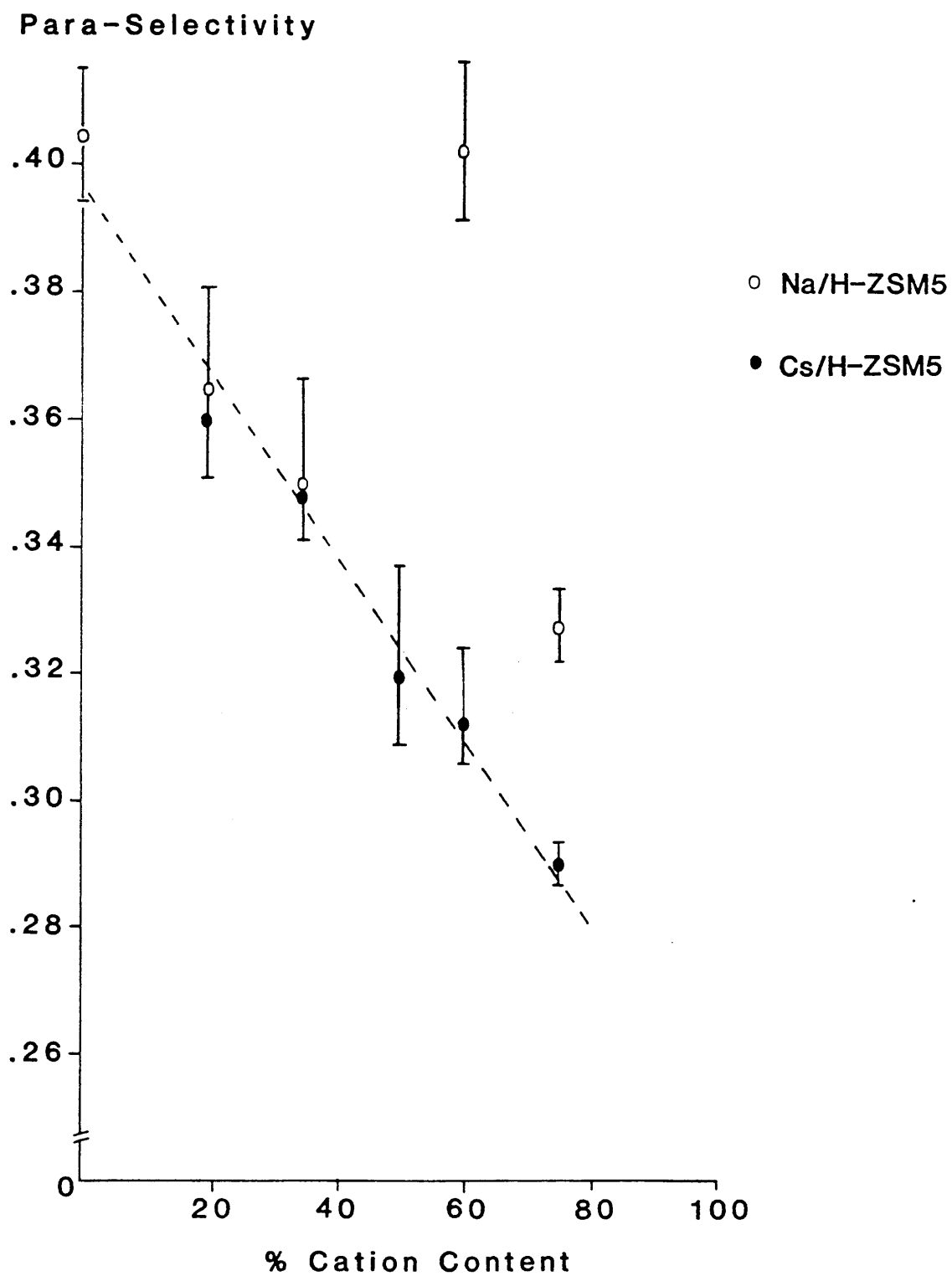
Figure 3.10 shows how the para-selectivity varies with cation loading. The para-selectivity values for each sample were obtained from the conversion versus selectivity curves at a constant conversion of 2%. The conversion versus selectivity curves lie in a decreasing series as the cation loading increases. This can be attributed to the effect of the inter-crystalline flow-rate on the relative amounts of toluene disproportionation and secondary xylene isomerisation which occurs. As the cation loading increases the number of acid sites available for catalysis must proportionally decrease. Thus, in order to achieve a desired conversion with a lower number of acid sites, there must be a compensating increase in the toluene contact time. This will also increase the probability of xylene reentry and subsequent isomerisation. The general decline in the fraction of para-xylene in the product as the cation content increases is thus an effect of contact time and not due to the shape-selective properties of the catalyst.

One would expect that if the acid site strength distribution was equivalent in all the ion-exchanged samples, and diffusion effects were insignificant, then at constant conversion the fraction of para-xylene in the product would decrease linearly as the cation content increased. This is seen to be the case for the caesium exchanged samples however at high sodium loadings a significant increase in para-selectivity is observed.

This method of screening catalysts for differences in para-selectivity is crude; it allows no quantification of the kinetic

FIGURE 3.10 : Variation of Para-Selectivity with Cation Content at

Constant Conversion : Temperature 501°C



parameters of the processes involved, and it is also found that the most significant differences in selectivity occur at low conversions, when the error involved in estimating the intercepts of steep curves is very large. An alternative approach was thus adopted, using the relationship between contact time (as measured by WHSV), and both conversion and para-selectivity for all the ion-exchanged samples. At a discrete value of WHSV, any differences between the samples will only be due to the sample itself, as all external parameters (e.g. temperature and inter-particle diffusion) will remain constant.

The relationship between conversion, para-selectivity and contact time was determined for all the cation exchanged samples studied. Typical plots are shown in figure 3.11, which represents the experimental data acquired from two samples of identical cation loading. The error bars on each point describe the standard deviation of the detector analysis, for the 10 to 15 items of data which were collected at each contact time. From a series of such plots the variation of both conversion and para-selectivity with cation content at a contact time of 0.3 seconds and a temperature of 501⁰C were determined. A diagram^matic summary of these data are shown in figures 3.12 and 3.13. The sodium and caesium forms exhibit different conversions whilst containing the same number of acid sites per unit cell. This suggests that the presence of the cation affects the strength of the acid sites of the catalyst, or that it hinders the diffusion/adsorption characteristics of the toluene/ZSM5 system. It is also apparent that the two forms exhibit different para-selectivities at high cation loadings (greater than 50% exchange), with the sodium

FIGURE 3.11 : Variation of Para-Selectivity and Conversion with Contact Time
for Na(75)-ZSM5 at 515°C

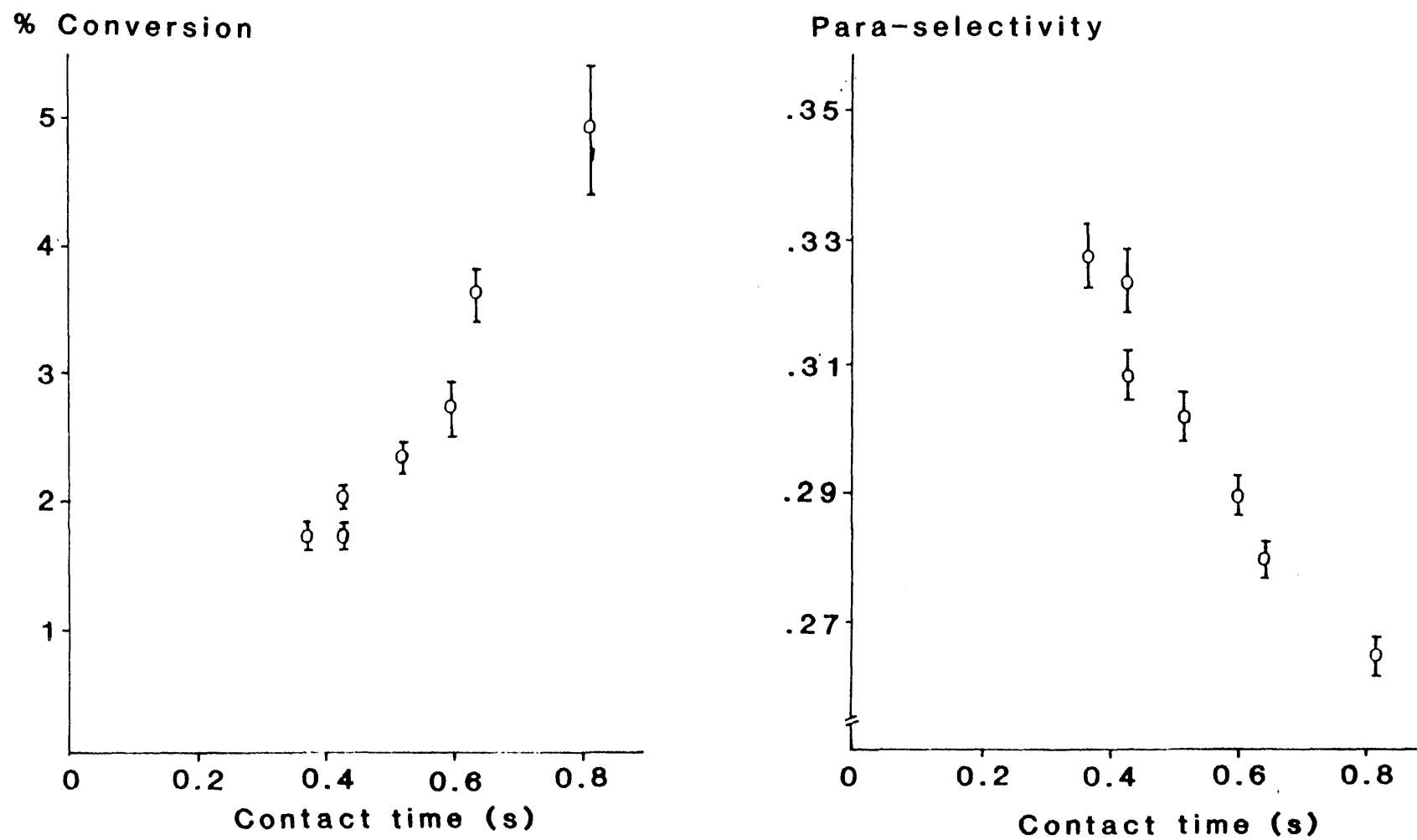
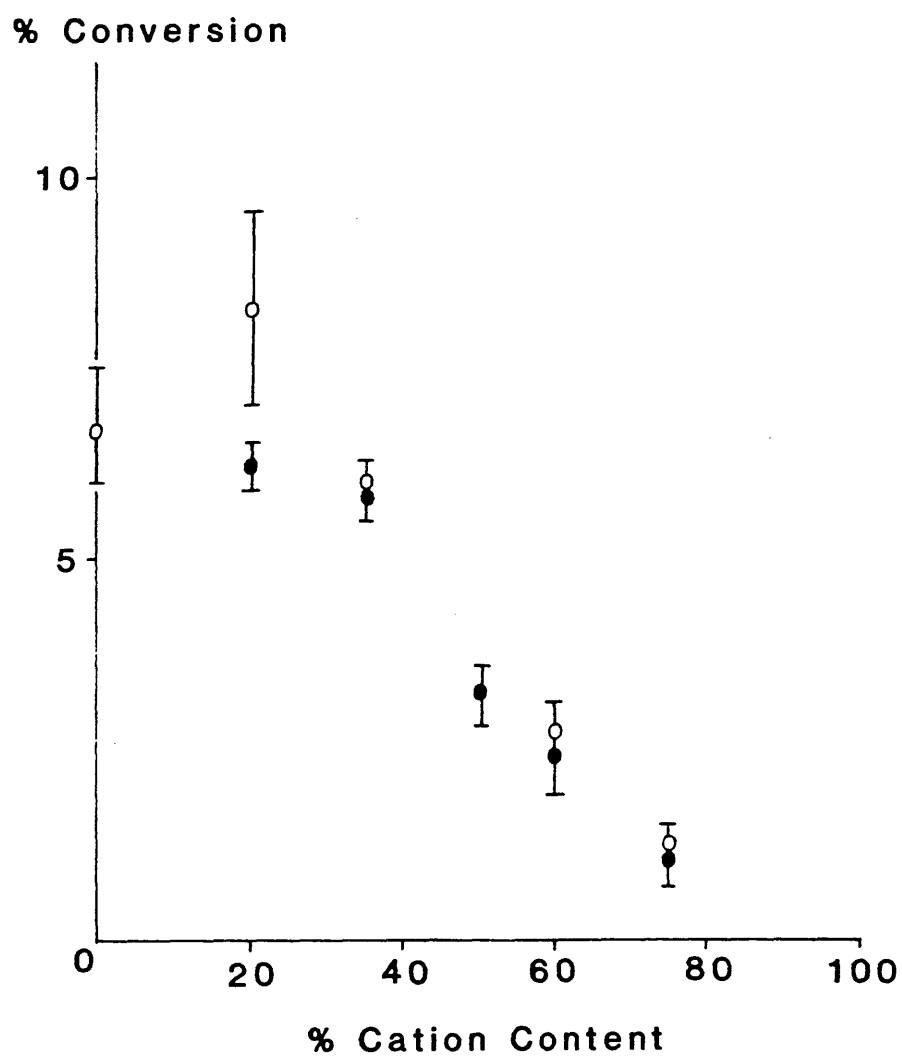


FIGURE 3.12 : Variation of Conversion with Cation Content at Constant

Contact Time : Temperature 501°C

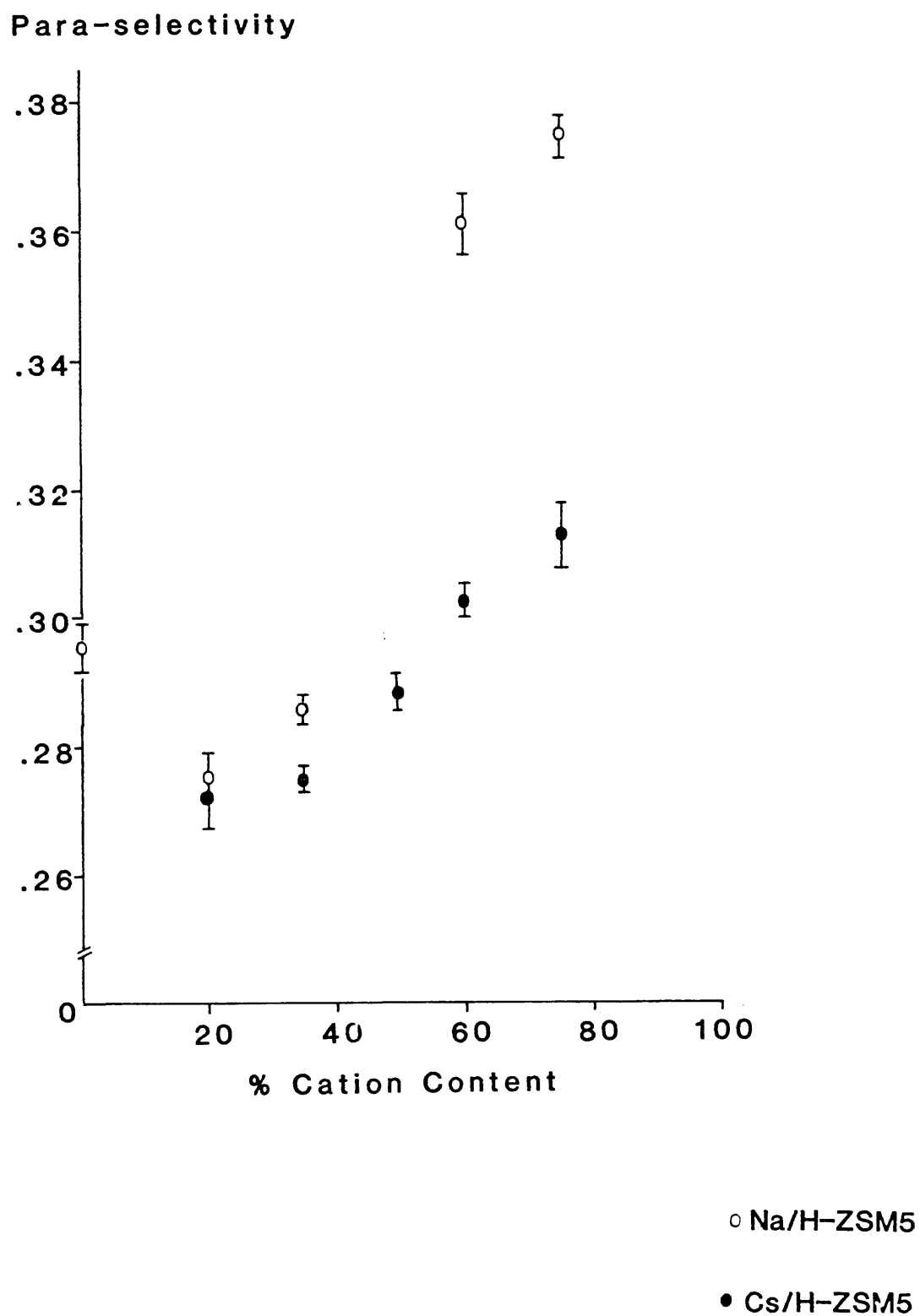


○ Na/H-ZSM5

● Cs/H-ZSM5

FIGURE 3.13 : Variation of Para-Selectivity with Cation Content at

Constant Contact Time : Temperature 501°C



forms being much more para-selective than the equivalent caesium forms. This result contradicts the original proposition of this project, i.e. that if any effect was observed the caesium forms would be more para-selective. It is possible that the answer to this apparent contradiction might lie in the kinetics of the xylene isomerisation reaction, i.e. the cations affect the ability of the acid sites to isomerise the xylene isomers. Alternatively, the caesium and sodium ions could be located at different sites within the ZSM5 framework, resulting in the cations having a more complicated effect on the diffusivities than a simple steric model would suggest.

From the conversion data obtained at various contact times, the first and second order rate constants for toluene disproportionation can be calculated for all the catalysts, using integral rate analysis methods. Figure 3.14 shows the results of both a first and second order rate analysis treatment for one sample. A small discrepancy between results from experiments with different samples of identical cation loading is observed, which is attributed to a variation in the position of the catalyst bed within the reactor; nevertheless, the data for each run is highly consistent, indicating the high degree of control on the experimental variables within each rate analysis.

The data for the sample represented in figure 3.14 has been fitted to a least-squares refinement program to test the linearity of both integrated rate equations. The fitting parameters, given in table 3.5, show that toluene disproportionation is best described by a first order rate equation, the correlation coefficient for this fit being closer

FIGURE 3.14 : Integrated Rate Analysis for Toluene Disproportionation
on Na(20)-ZSM5 at 515°C

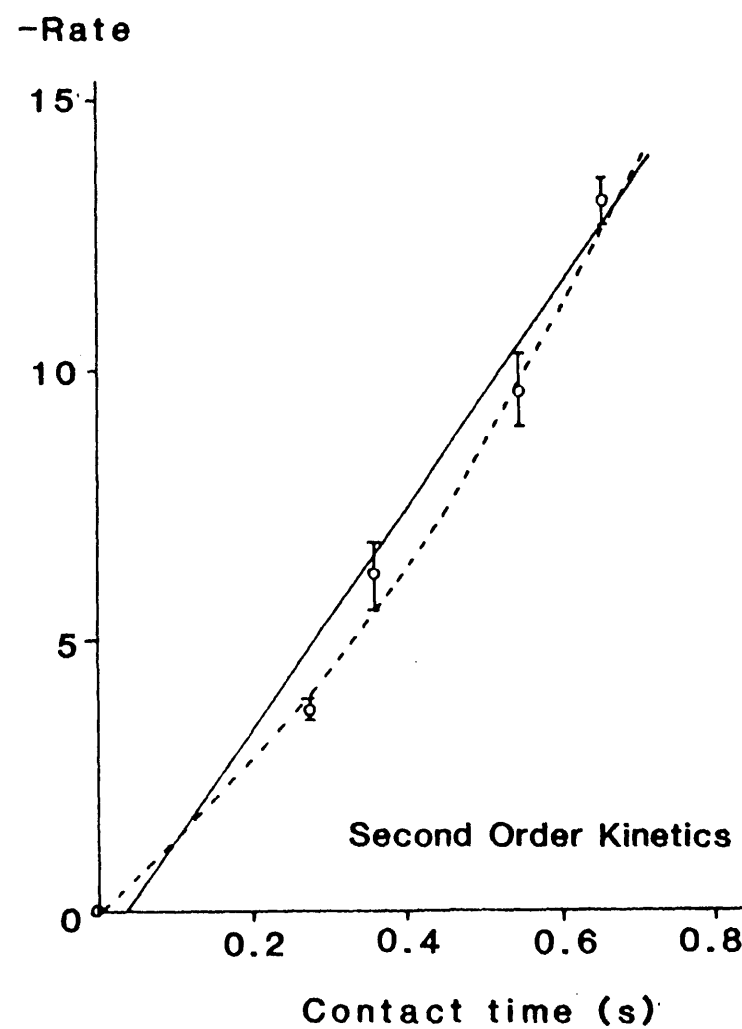
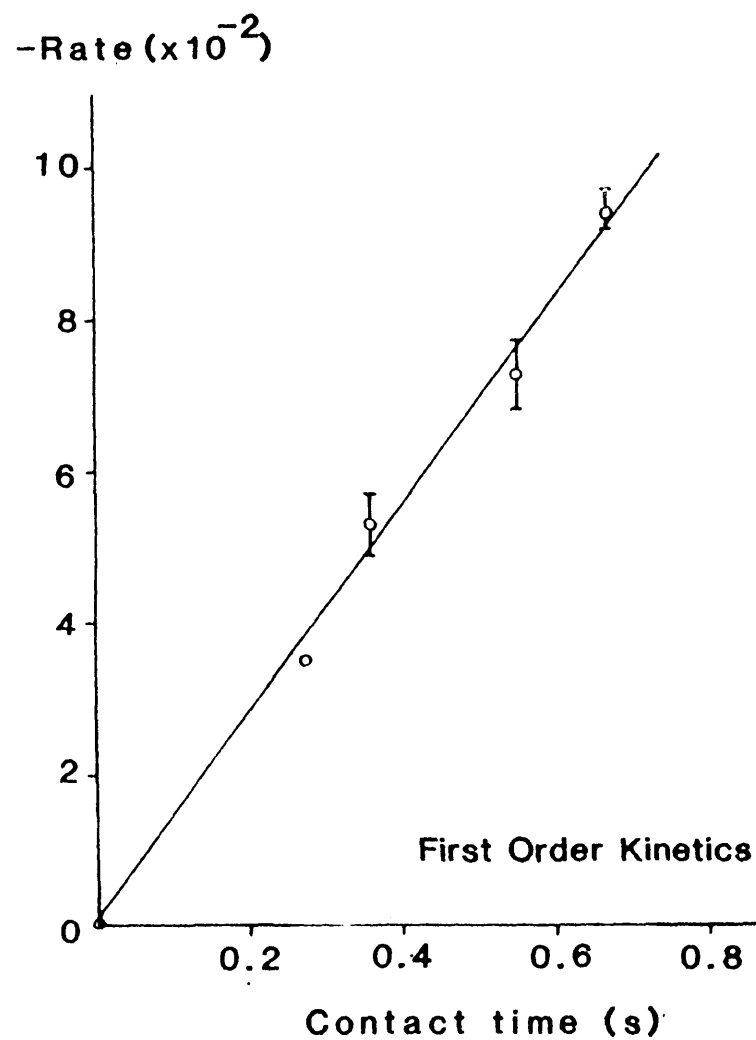


**Table 3.5 : Integrated rate analysis for toluene
disproportionation on Na(20)-ZSM5**

Data for the first and second order integrated rate equations fitted by a least squares method to a straight line

	First Order	Second Order
Gradient	-0.14	-19
Intercept	0.049	0.65
Correlation Coefficient	0.9926	0.9787

The second order kinetics data fitted to a linear and quadratic polynomial

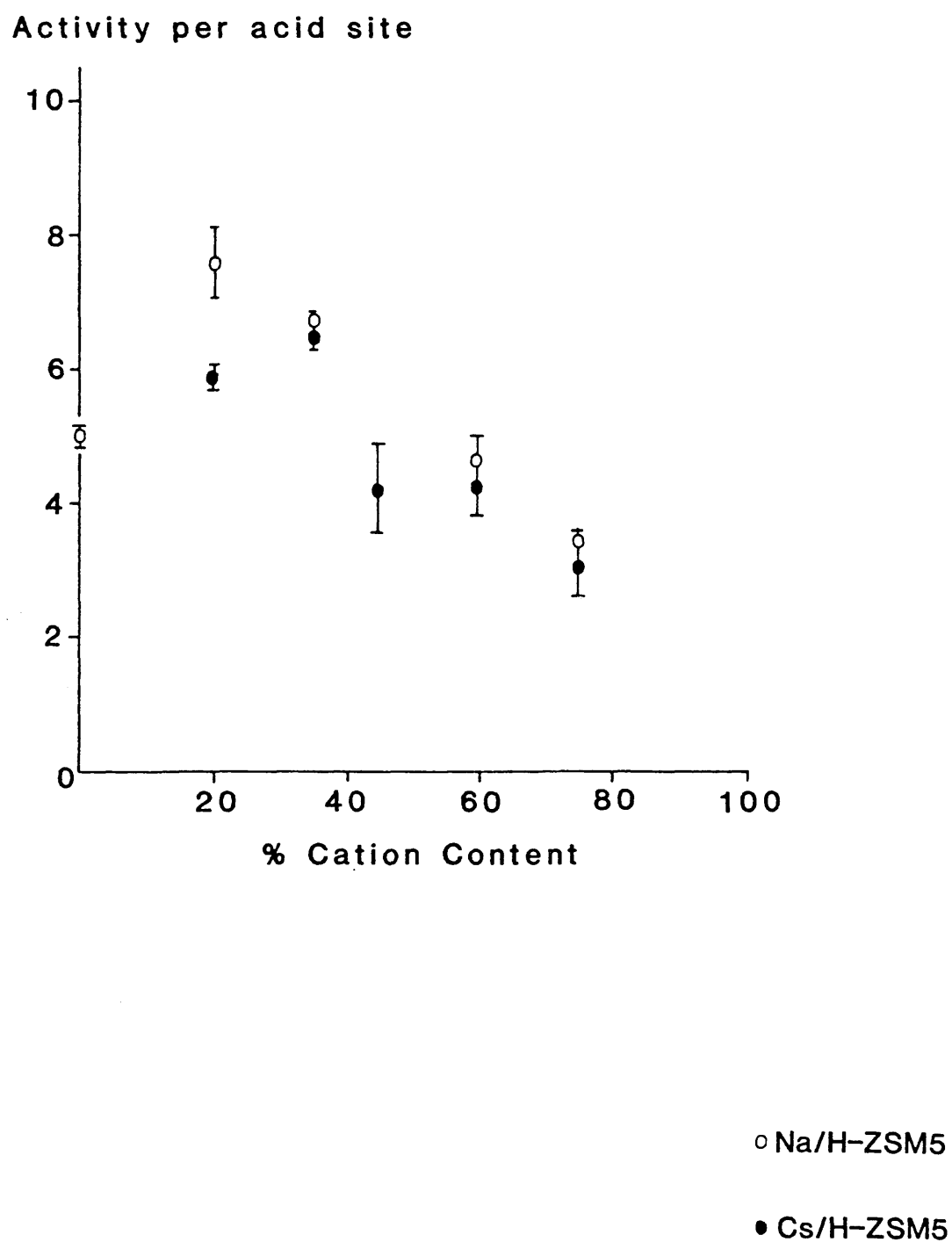
polynomial	R factor
$y = 0.65 - 19.42x$	0.858
$y = 0.0058 - 11.807x - 11.363x^2$	0.569

to unity. The data for the second order rate analysis was fitted to both linear and quadratic equations, to further emphasise the non-linear nature of this data. Both of the polynomials are represented in figure 3.14 and their respective fitting parameters given in table 3.5. The R-factor is substantially lower for the second order polynomial, indicating a much closer fit to the calculated data.

The first order rate constant for each cation exchanged sample was calculated using the program listed in Appendix 4. The data were corrected to take into account the different number of acid sites per unit cell at varying levels of cation exchange and plotted in figure 3.15. The error bars stem principally from the standard deviation in the detector analysis for the 8 to 12 rates which were determined at various contact times.

The decrease in activity at high cation-loadings, could indicate a degree of mass-transport control in these samples; this would correlate with their increased para-selectivity. Toluene and para-xylene have approximately the same cross-sectional diameter, which is less than that of both meta- and ortho-xylene. Any diffusional restrictions experienced by toluene and para-xylene will be amplified in their effect on the other two xylene isomers, causing the increased para-selectivity observed. Establishing that toluene disproportionation is a first order process on ZSM5, points to diffusion to the active site or its subsequent adsorption as possible rate-determining steps. It is possible to investigate the extent of mass-transport control on toluene disproportionation by measuring the activation energies for the various samples. As mentioned previously, when

FIGURE 3.15 : Variation of Activity per Acid Site with Cation Content



the influence of mass-transport on a reaction becomes more pronounced, it is reflected in a lowering of the apparent activation energy for the reaction.

Arrhenius plots were constructed for samples of different cation loadings over a temperature range of approximately 100°C. Two such plots for samples of Na(20)-ZSM5 are shown in figure 3.16 which clearly demonstrates the precision of these experiments. The rate data were fitted by a least-squares minimisation program, and the calculated Arrhenius parameters for each sample are summarised in table 3.6. As the cation loading increases so does the activation energy for the reaction. This eliminates the possibility of mass-transport inhibition of the toluene disproportionation reaction at high cation loadings; an effect which would have produced a decrease not an increase in the activation energy.

For a chemical reaction, an increase in the activation energy is indicative of an increase in the stability of the starting material, or a decrease in the stability of the reaction intermediates. The postulated reaction mechanism for acid catalysed toluene disproportionation is given in figure 3.2. If the formation of the protonated toluene molecule is the rate determining step in this reaction, then the strength of the zeolite Bronsted acid site, will be of major significance in the energetics of the reaction. Hence the increase in activation energy at high cation loading, points to these catalysts possessing weaker Bronsted acid sites.

The samples of intermediate cation content exhibit some unusual behaviour; they show both higher activation energies and

FIGURE 3.16 : Arrhenius Plots for two samples of Na(20)-ZSM5

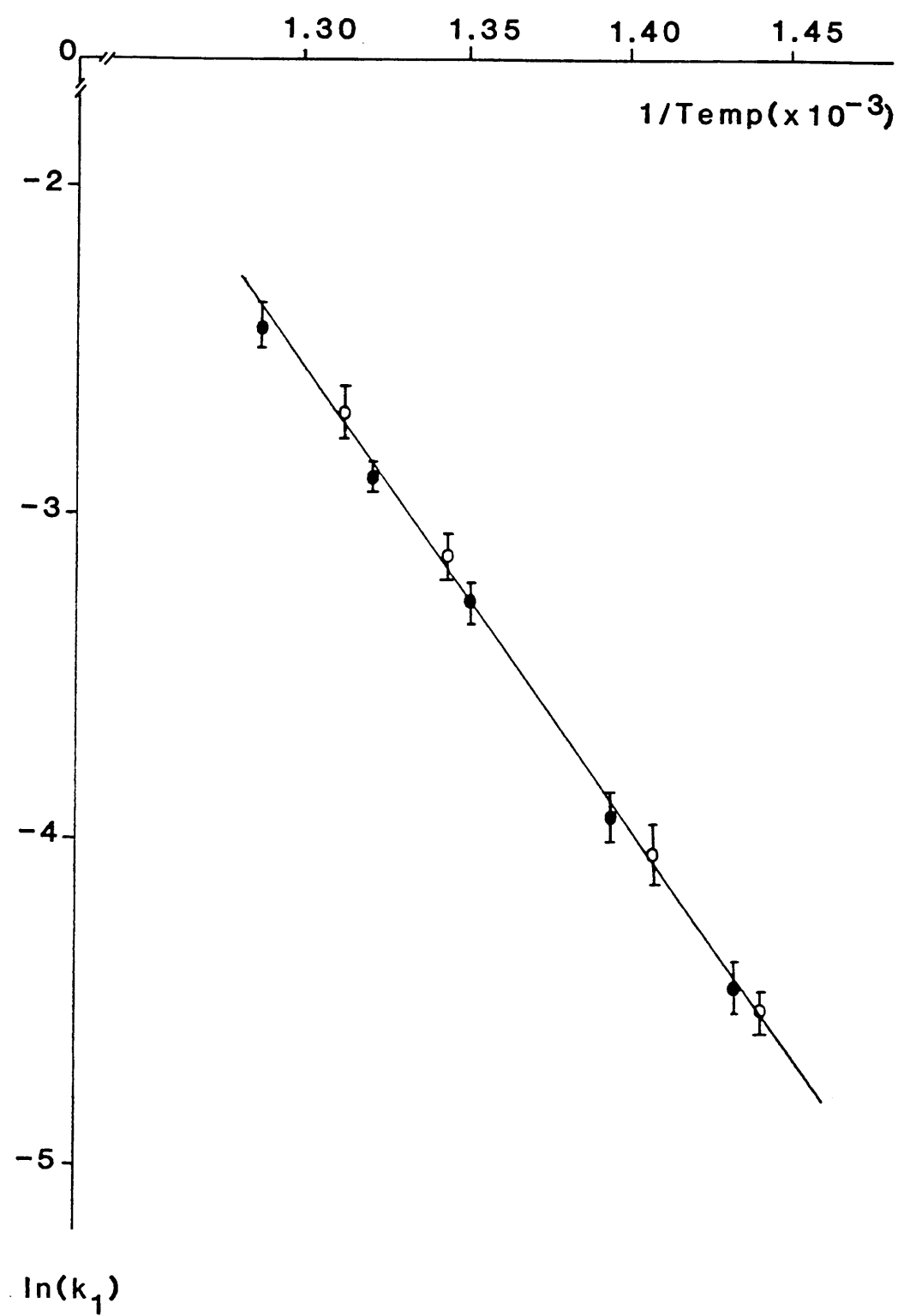


Table 3.6 : Arrhenius parameters for toluene
disproportionation on cation-exchanged ZSM5

Sample	E_{Act} (kJ/mol)	$\ln (A)$	Correlation Coefficient
H-ZSM5	94.5 $\pm$ 2.9	12.4 $\pm$ 0.5	.998
Na(20)-ZSM5	118.2 $\pm$ 0.9	16.0 $\pm$ 0.1	.999
Na(20)-ZSM5	116.3 $\pm$ 1.8	15.6 $\pm$ 0.3	.999
Na(35)-ZSM5	122.0 $\pm$ 2.2	16.2 $\pm$ 0.4	.999
Cs(35)-ZSM5	114.0 $\pm$ 1.6	15.4 $\pm$ 0.3	.999
Na(75)-ZSM5	103.4 $\pm$ 4.5	12.0 $\pm$ 0.7	.994
Cs(75)-ZSM5	101.0 $\pm$ 1.7	11.4 $\pm$ 0.3	.999

larger pre-exponential factors than H-ZSM5 for the reaction. A higher activation energy has already been used as a pointer to the presence of weaker active sites. From a knowledge of collision theory, the pre-exponential factor can be thought of as a collision frequency multiplied by a reaction probability, i.e. the likelihood that a collision between two molecules will result in a reaction. Any change in the pre-exponential factor can be thought of as a variation in the reaction probability. It appears that at intermediate cation loadings, the active site is orientated so as to increase the reaction probability.

To summarise the kinetic data; analysis of the effect of contact time on the reaction rate, reveals the reaction to be first order with respect to toluene, and it appears that the formation of the protonated toluene molecule at the active site is the rate-determining step in the disproportionation of toluene on zeolite ZSM5. Activation energies for the reaction are approximately 100kJ/mol, which eliminates the possibility of mass-transport control on the reaction kinetics. The activation energies increase at high cation loadings which also show reduced activity per unit acid site. These observations point to a decrease in acid site strength at high cation contents.

The variation of acid site strength with cation loading explains the differing activities per acid site illustrated in figure 3.15, however the unexpected para-selective properties of the sodium exchanged samples has not been satisfactorily explained. This too, could be an acid site effect, but the xylene isomerisation reaction is facile in comparison with toluene disproportionation, and xylene is therefore less able than

toluene to discriminate between acid sites of differing strengths, especially if the differences are only minor. The possibility cannot be entirely overlooked, however. The kinetic investigation of the xylene isomerisation reaction will definitely yield information on the selectivities of the cation-exchanged samples towards all of the xylene isomers.

XYLENE ISOMERISATION ON ION EXCHANGED ZSM5

4.1 INTRODUCTION

The results of the toluene disproportionation experiments on the ion exchanged ZSM5 samples, show that the cation does have a significant effect on the course of the reaction. The cause is not known, although the originally proposed explanation, concerning the steric effect of the differently sized cations on the diffusion of the xylene isomers in the ZSM5 channels, is not valid. The para-xylene sorption capacities, given in table 2.1, show that the caesium form possesses a lower sorption capacity, than either the sodium or hydronium exchanged forms. This suggests that the cations are sited in the zeolite channels, such that the caesium ions occupy more free space than the sodium or hydronium ions. These sorption data further imply that the steric effect of the cations on the diffusion coefficients, would be in the predicted order, leading to the caesium exchanged samples being more para-selective than those exchanged with sodium.

The kinetic data for toluene disproportionation, suggests that the introduction of cations causes the characteristics of the acid sites to be changed; indicated by a variation in rate constants and activation energies. As toluene disproportionation in ZSM5 is a multi-stage process, it is conceivable that the cation could be influencing the kinetics of the xylene isomerisation reaction, and in this way affecting the para-selective properties of the various samples. To investigate this possibility further, a kinetic model is developed to obtain rate constants and activation energies for the xylene isomerisation

reaction, and selected ion exchanged samples are kinetically analysed.

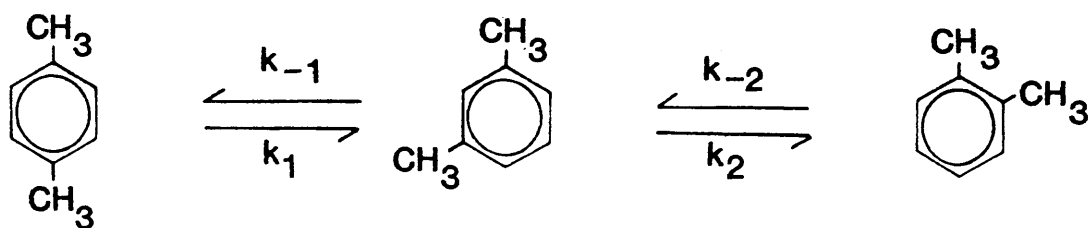
4.2 KINETIC MODEL FOR XYLENE ISOMERISATION

The kinetics of the xylene isomerisation reaction have attracted interest in the literature, due to its role as the secondary reaction determining the selectivity in a number of aromatic reactions, including toluene disproportionation. Three-component reversible reactions may be most simply described by one of two reaction schemes; a consecutive reaction entirely consistent with stepwise 1,2-methyl shifts, or by parallel reaction paths involving both 1,2-methyl and 1,4-methyl shifts (76). Both of these schemes are illustrated in figure 4.1

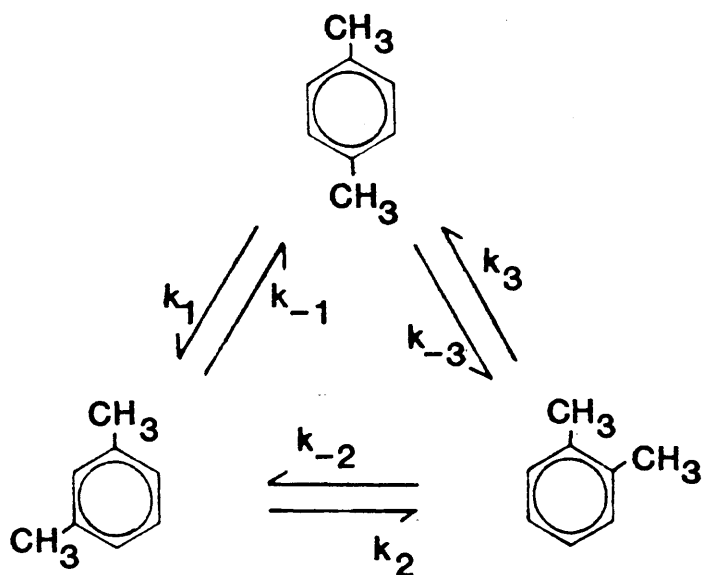
The observed xylene product distributions for a number of different acid catalysts have been related to these three-component reaction schemes (56,81,82,83). The presence of various isomerisation pathways was noted, dependent on the nature of the catalyst. Over non-shape selective acidic catalysts such as $\text{SiO}_2\text{-Al}_2\text{O}_3$, the observed kinetics appear to be consistent with a consecutive reaction mechanism. This is in agreement with the generally accepted mechanism for xylene isomerisation proceeding via 1,2-methyl shifts. AP type zeolites displayed several reaction paths, being dependent on the temperature and crystal size. An increase in either of these parameters resulted in the reaction path shifting from that of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ samples, towards that observed for para-selective ZSM5 zeolite catalysts. These shifts were accompanied by an apparent change in the kinetics of the reaction; for small crystal AP zeolite at 200°C,

FIGURE 4.1 : Three-Component Reversible Reaction Mechanisms

Consecutive Reactions



Parallel Reactions



the kinetics were entirely consistent with stepwise 1,2-methyl shifts. However, when the crystallite size or temperature increased, the apparent kinetics required a contribution from the direct ortho- to para-xylene path, i.e. the parallel reaction scheme was observed.

These results were explained in terms of a diffusional alteration of the intrinsic kinetics, so that the observed reaction scheme was no longer directly related to the reaction mechanism at the active site. With the larger crystals, the xylene isomers remain longer in the zeolite pores, and several isomerisation steps may occur. The observed products are thus the result of multistep reactions, and the apparent kinetics change from those consistent with a consecutive reaction mechanism, to those of the more complex reaction scheme incorporating an apparent 1,4-methyl shift (ortho- to para-xylene).

By mathematically describing consecutive reactions in a porous crystal whilst under conditions of plug-flow (84,85), it has been shown that in the presence of diffusion effects, a reversible series reaction can show the apparent kinetics of a reversible parallel reaction. Hence the observation of apparent kinetics consistent with a parallel reaction in a porous crystal, could point to the influence of diffusion-control on an intrinsically consecutive reaction. Kinetically describing the xylene isomerisation reaction on ZSM5 as a parallel reaction, may yield information on the amount of diffusion-control occurring during the xylene isomerisation reaction, and hence that occurring during the toluene disproportionation reaction.

The three-component parallel reversible reaction scheme on

which the kinetic analysis is based is illustrated in figure 4.1. Assuming that all the reactions are first order, the rate equations for isomerisation starting from each of the pure xylene isomers can be set up (86,87). For example starting with pure para-xylene (A):

$$\frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - k_{-1}[B] - k_2[B] \quad \{4.1\}$$

and
$$\frac{d[C]}{dt} = k_{-3}[A] + k_2[B] - k_3[C] - k_{-2}[C] \quad \{4.2\}$$

At low conversions, the concentrations of both components B and C (where B is meta- and C is ortho-xylene) will be small, and the corresponding terms in the rate equation can be neglected. Equations 4.1 and 4.2 then simplify to:

$$\frac{d[B]}{dt} = k_1[A] \quad \text{and} \quad \frac{d[C]}{dt} = k_{-3}[A] \quad \{4.3\}$$

Dividing the two equations and applying the limiting conditions of zero conversion or contact time, leads to the useful relationship:

$$\lim \{ [B]/[C] \}_{t \rightarrow 0} = k_1/k_{-3} \quad \{4.4\}$$

Similar expressions can be obtained for the ratio of rate constants starting with pure meta-xylene and pure ortho-xylene:

$$\lim \{ [A]/[C] \}_{t \rightarrow 0} = k_{-1}/k_2 \quad \{4.5\}$$

$$\lim \{ [A]/[B] \}_{t \rightarrow 0} = k_3/k_{-2} \quad \{4.6\}$$

Thus, by experimentally determining the ratio of $[B]/[C]$, $[A]/[C]$, and $[A]/[B]$ at low total conversion, and extrapolating these ratios to zero conversion, the ratios of the rate constants k_1/k_{-3} , k_{-1}/k_2 , and k_3/k_{-2} are obtained.

At equilibrium the concentrations of the three xylene isomers are constant at the values given in table 3.2. This yields a further set of relations consistent with the expression for the thermodynamic equilibrium constant:

$$k_1/k_{-1} = 2.3 \quad k_2/k_{-2} = 0.4 \quad k_3/k_{-3} = 1.0 \quad \{4.7\}$$

Equations 4.4 to 4.7 provide six equations for the six unknown rate constants; the equations are not however independent, and so they only allow the calculation of relative rate constants by this method of analysis.

By the use of the design-equation for plug-flow, equation 3.8, it is possible to obtain the absolute rate constants and activation energies from these data. For example starting with pure para-xylene (A), a rate equation for the loss of para-xylene can be set up in an analogous manner to those of equations 4.1 and 4.2:

$$-\frac{d[A]}{dt} = k_1[A] + k_{-3}[A] - k_{-1}[B] - k_3[C] \quad \{4.8\}$$

At low conversions, the concentrations of components B and C become negligible in comparison to that of the reactant A, and equation 4.7 can be simplified to:

$$-\frac{d[A]}{dt} = k_1[A] + k_{-3}[A] \quad \{4.9\}$$

Substituting this rate equation into the design-equation for plug-flow, equation 3.8, and assuming first order kinetics gives:

$$-(k_1 + k_{-3}) \frac{V}{u} = \log \left\{ \frac{A_0}{A} \right\} \quad \{4.10\}$$

Thus a plot of contact time versus $\log (A/A_0)$ will have a gradient of $-(k_1 + k_{-3})$. Combining the value of this gradient with the relative values of k_1 and k_{-3} , previously obtained, allows the calculation of the absolute values of all the isomerisation rate constants.

In a similar manner it is possible to substitute the observed rate constant $k_0 (= k_1 + k_{-3})$ into the Arrhenius equation, equation 3.5:

$$(k_1 + k_{-3}) = A_1 \exp \left\{ -\frac{E_1}{RT} \right\} + A_{-3} \exp \left\{ -\frac{E_{-3}}{RT} \right\} \quad \{4.11\}$$

$$\text{so:} \quad \ln (k_1 + k_{-3}) = \ln (A_1 A_{-3}) - \frac{E_1 + E_{-3}}{RT} \quad \{4.12\}$$

A plot of $\ln (k_0)$ versus reciprocal temperature will have a gradient of $-(E_1 + E_{-3})/R$. This yields the combined activation energies where:

$$E_{\text{para}} = E_1 + E_{-3} \quad \{4.13\}$$

$$E_{\text{meta}} = E_{-1} + E_2 \quad \{4.14\}$$

$$E_{\text{ortho}} = E_{-2} + E_3 \quad \{4.15\}$$

4.3 EXPERIMENTAL

The xylene isomerisation experiments used the same techniques that were developed for the study of toluene disproportionation. Each sample was calcined at $10^{\circ}\text{C}/\text{min}$ to 500°C in a flow of dried nitrogen, and the reaction temperature was established by cooling, again with a continuous flow of nitrogen gas through the catalyst bed. The conversion of the reactant xylene was varied by adjusting the reaction temperature, whilst always being maintained at a level below 10% in order for the kinetic analysis to be meaningful. The purities of the reactant xylenes were determined by gas chromatography^{at} and are tabulated in table 4.1. The impurities in the reactant xylenes were taken into account in the kinetic analysis, by assuming that at the low concentrations in which they were encountered, their effect on the kinetics of the reaction would be negligible. They were treated as "inert" impurities, and their contribution to the experimentally observed product concentrations were negated, by the subtraction of the percentage concentration of each impurity from the appropriate product peak. The presence of impurities in the reactant implies that the conversion will also need to be corrected, by the addition of the sum of the impurities to the percentage concentration of the reactant.

4.4 RESULTS AND DISCUSSION

Initial xylene isomerisation experiments were performed at or near 500°C , however at all experimentally realisable contact times, a near equilibrium mixture of xylene isomers was obtained. In order to achieve the low conversions (<10%) necessary to

Table 4.1 : Analysis of the Xylene Reactant by Gas
Chromatography

Sample	% para-xylene	% meta-xylene	% ortho-xylene
Ortho-xylene	0.021	0.334	99.141
Meta-xylene	0.244	99.301	0.416
Para-xylene	98.980	0.751	0.235

obtain meaningful kinetic data, the reaction temperature was reduced to lie within the range 220°C - 300°C . This gives an indication of the relative ease with which ZSM5 can isomerise xylenes in comparison with the disproportionation of toluene. The performance of the xylene isomerisation reactions at much lower temperatures than those for toluene disproportionation, does not allow direct comparison of the para-selectivity of different samples caused by mass transfer effects. They do however, yield a minimum factor for such phenomena, as the effects of diffusional resistance increase with temperature.

The raw experimental data consisted of xylene isomer distributions, which could be plotted as the percentage-concentration of the products versus that of the reactant, as illustrated in figure 4.2 for para-xylene isomerisation on H-ZSM5. The detector is unable to fully resolve the xylene peaks below a conversion of about 2%, which limits the amount of data available when it is kinetically most important. Data manipulation to correct for the impure nature of the reactant, was performed by the BBC microcomputer, which then used the corrected data to produce the conversion versus product distribution plots shown in figures 4.3 to 4.6. In these experiments each point is unique, and averaging of deviations in the gas chromatograph response cannot occur as is usual. This accounts for the large scatter observed in this set of experiments.

It can be seen from the ortho- and meta-xylene isomerisation data, that differences between the Na(75)-ZSM5 and the Cs(75)-ZSM5 samples exist, with the sodium form being more para-

FIGURE 4.2 : "Raw" Product Distribution for Ortho-xylene Isomerisation
on Na(20)-ZSM5

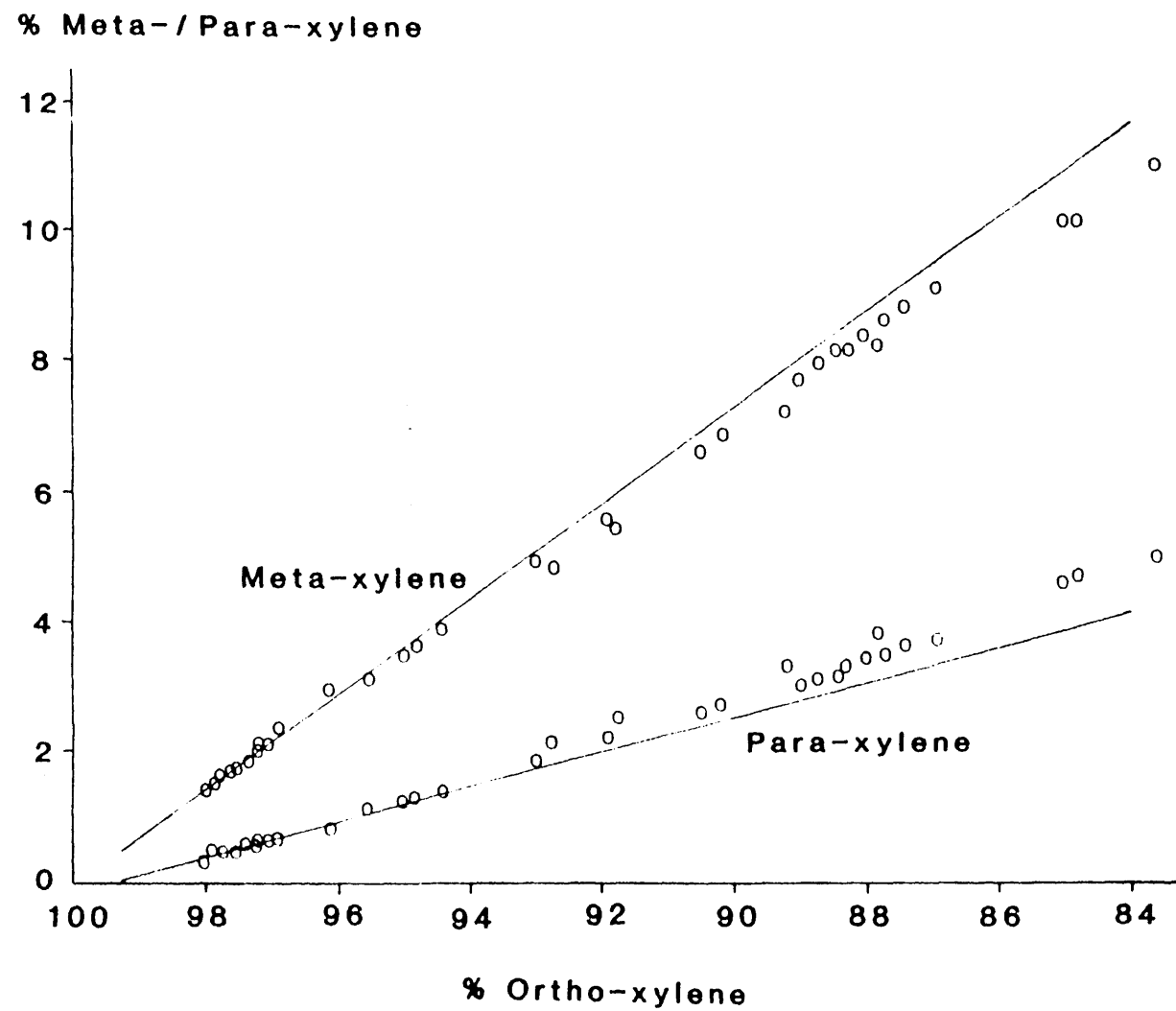
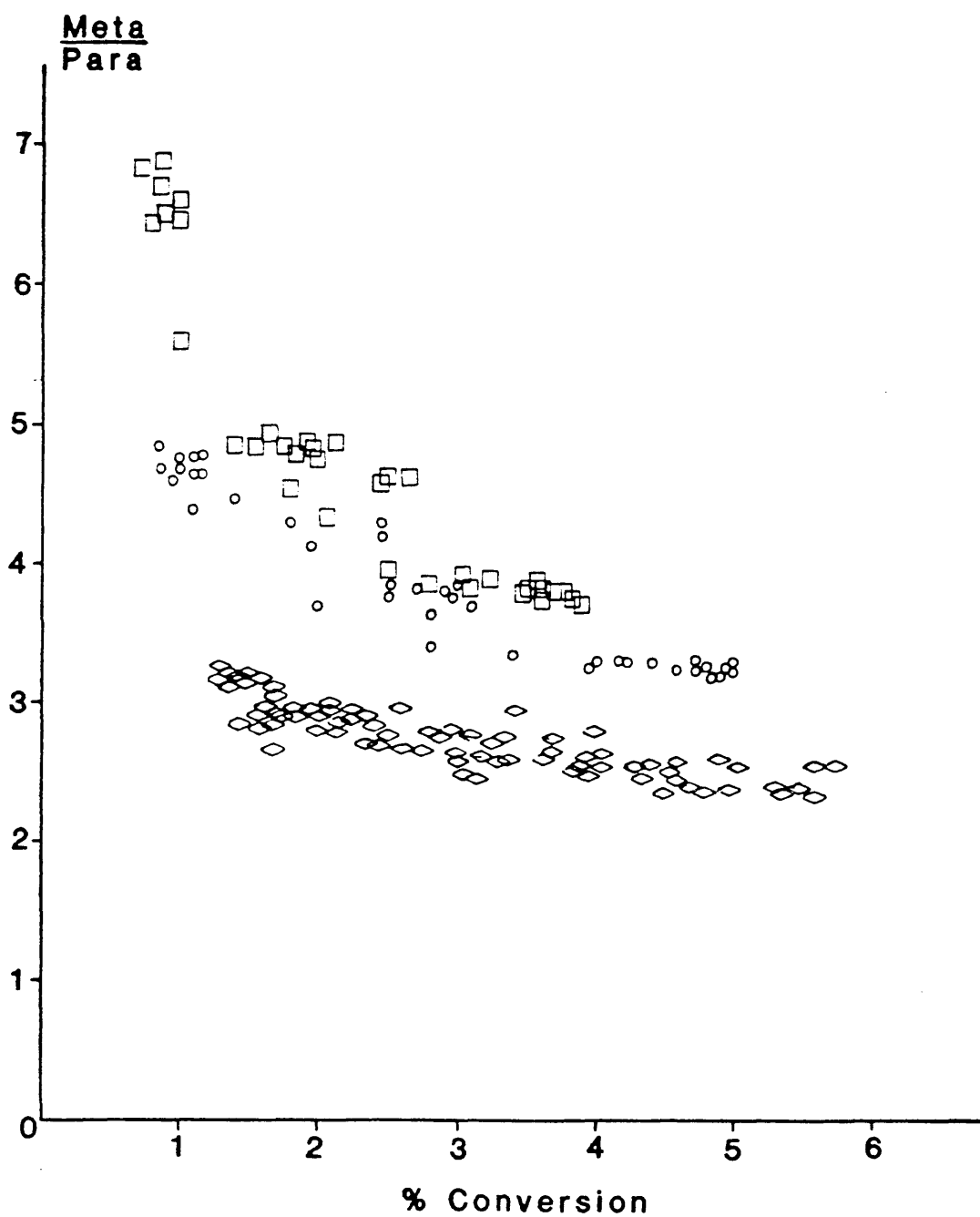


FIGURE 4.3 : Product Distribution for Ortho-xylene Isomerisation

on Cation exchanged ZSM5

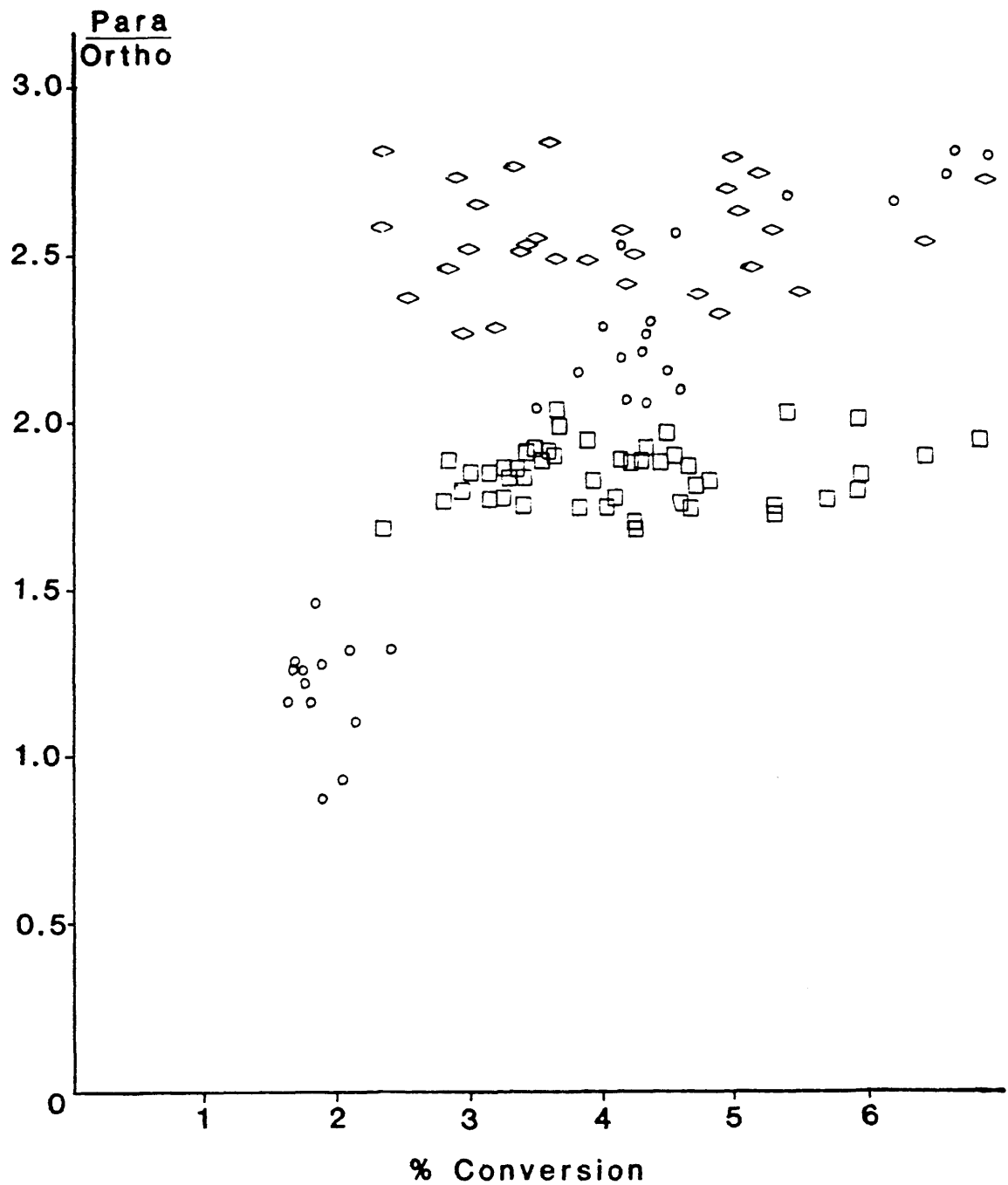


○ H-ZSM5

◇ Na(75)-ZSM5

□ Cs(75)-ZSM5

on Cation exchanged ZSM5



○ H-ZSM5

◇ Na(75)-ZSM5

□ Cs(75)-ZSM5

on Cation exchanged ZSM5

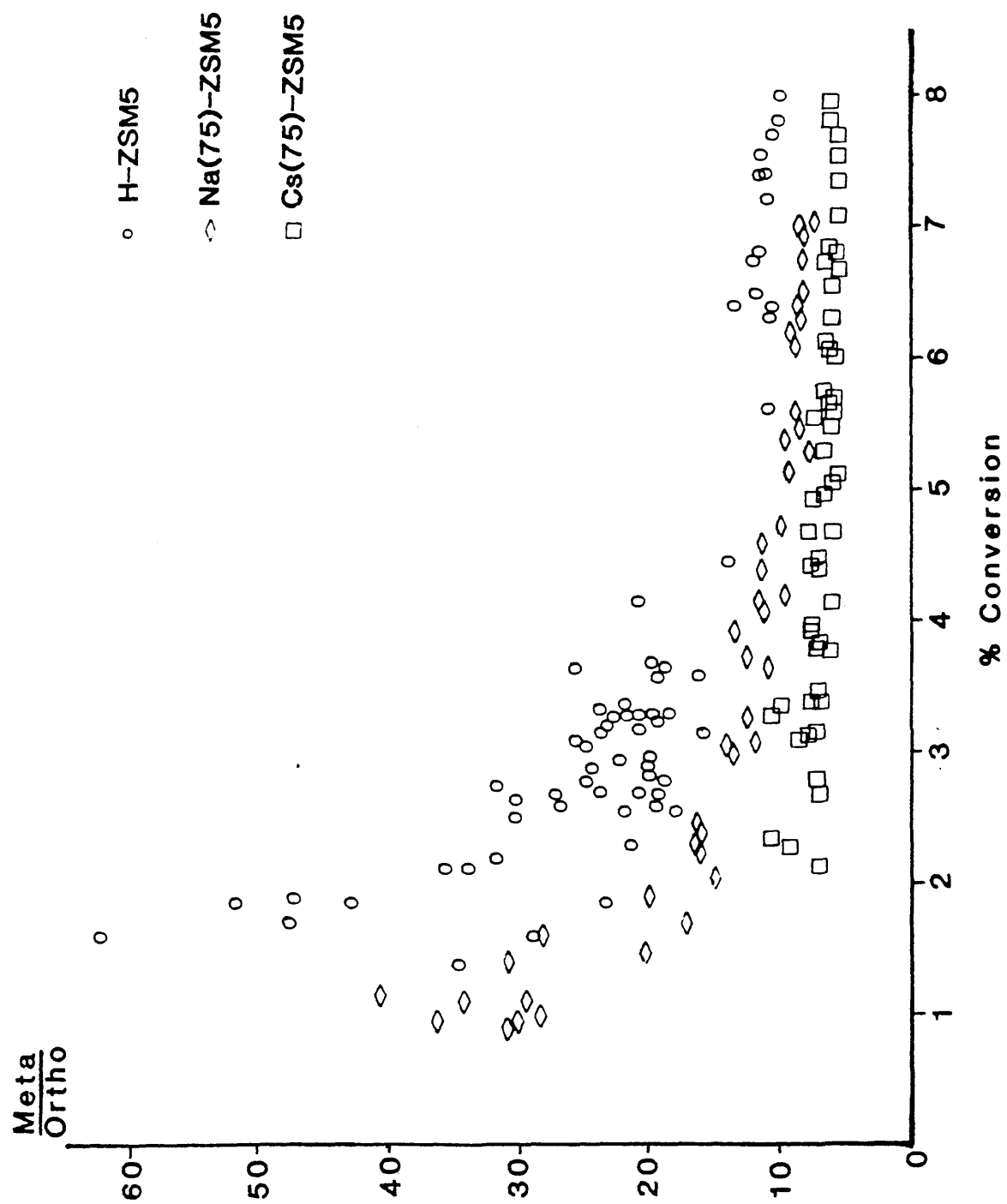
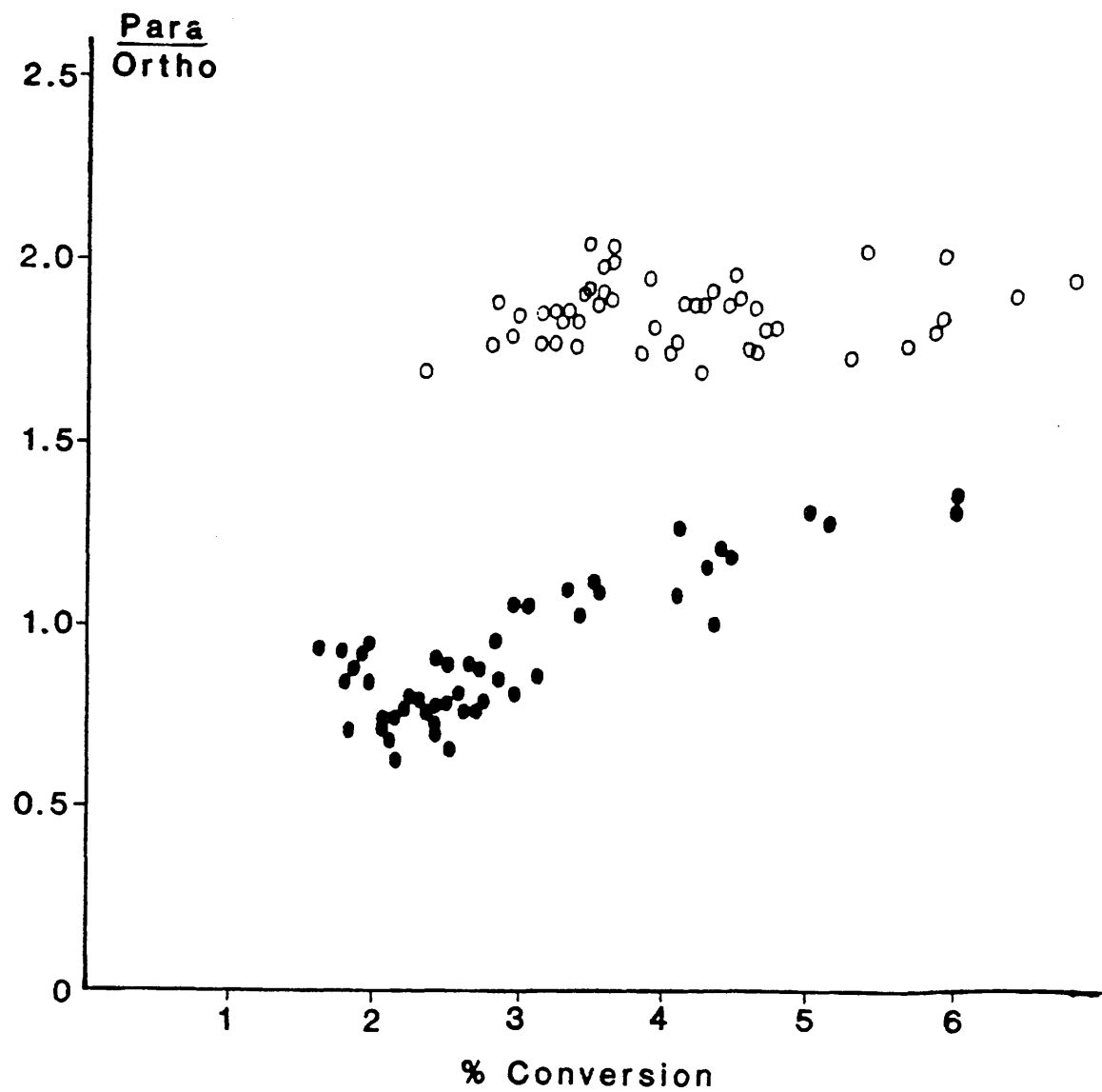


FIGURE 4.6 : Product Distribution for Meta-xylene Isomerisation on ¹²⁴

Cs(75)-ZSM5 with different Calcination Procedures



○ Calcined at 10 C/min to 500°C

● Calcined rapidly to 500°C

selective than the caesium form. This is in accordance with the data from the toluene disproportionation experiments, which attributed greater para-selectivity to the sodium form.

The evaluation of the product distribution ratios for the isomerisation of all three xylene isomers, gives a means of comparing the precision of the rate data to be calculated. The multiplication of the product ratios of the ortho- and meta-xylene isomerisation data, will yield a theoretical product ratio for the isomerisation of para-xylene, which can be compared to the experimentally determined ratios:

$$\frac{\text{Meta}}{\text{Para}} \times \frac{\text{Para}}{\text{Ortho}} = \frac{\text{Meta}}{\text{Ortho}}$$

The agreement between the calculated and experimental ratios is reasonable at conversions greater than 5%, however at low conversion the experimental ratio is much greater than that predicted. This has been attributed to the errors involved in calculating the product distribution ratio for the para-xylene isomerisation reaction. The selectivity to meta-xylene is very high, and at low conversions the percentage concentration of the ortho-xylene component approaches zero. The large errors inherent in dividing a large number by a much smaller number become overwhelming, and effectively discount the para-xylene data collected at low conversions.

The data in figure 4.6 show the difference in selectivity which occurs when the calcination conditions are varied. The sample calcined at 10⁰C/min in a flow of dried nitrogen gas, shows the expected selectivity of para-xylene over ortho-xylene. When the

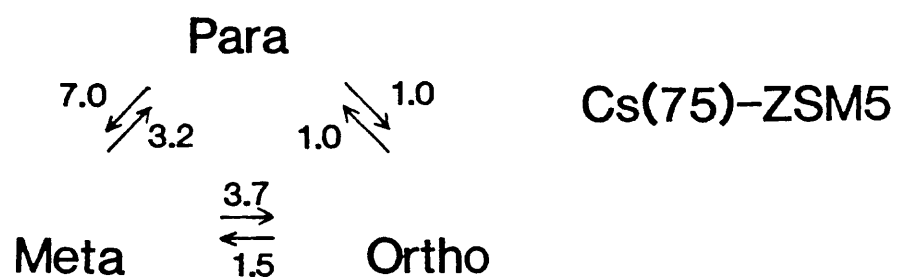
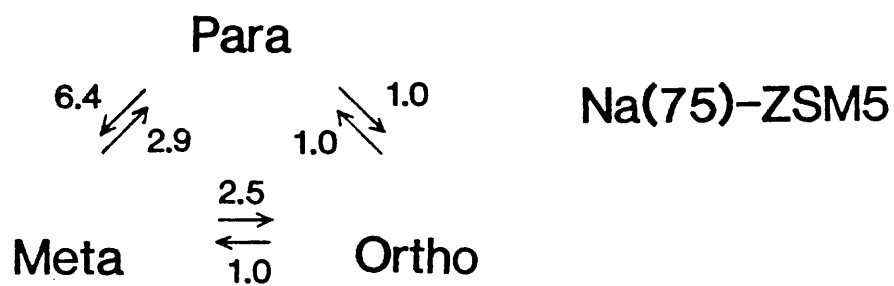
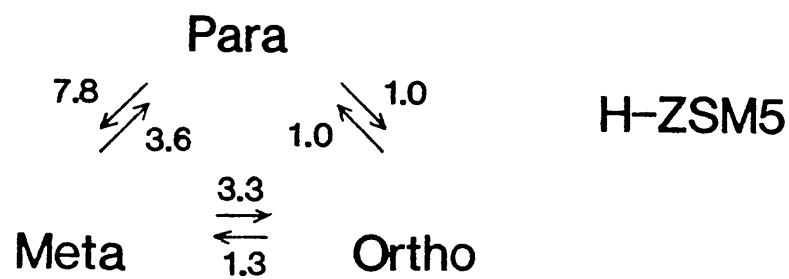
sample is calcined very rapidly to reaction temperature, as occurred with the second sample, a complete reversal of the selectivity occurs, with the sample now being selective to ortho-xylene; no significant loss of activity was observed. Framework dealumination would be expected to increase diffusional resistance, and hence para-selectivity, so such an explanation is not valid in this situation.

The xylene product ratios of figures 4.3 to 4.5, can be used to calculate the six relative rate constants using the method described in Section 4.2. Equations 4.4 to 4.6 show that the product ratios of $[\text{Meta}]/[\text{Ortho}]$, $[\text{Para}]/[\text{Ortho}]$ and $[\text{Para}]/[\text{Meta}]$ are equivalent to the ratios of the rate constants, k_1/k_{-3} , k_{-1}/k_2 and k_3/k_{-2} respectively. Product ratios were estimated for the three samples at various conversions for meta- and ortho-xylene isomerisation, whilst the ratios for para-xylene isomerisation were calculated by multiplying the first two ratios. This was considered to produce more accurate results than the direct estimation of the product distribution from the para-xylene data. Combining these ratios with the data from equation 4.7 allowed the calculation of the six relative rate constants for the three samples which are represented in figure 4.7. It was found that for all three samples, at whatever conversion the product distributions were estimated, the error in the calculated relative rate constants was only ± 0.2 .

The introduction of caesium increases the rate of the meta- to ortho-xylene pathway at the expense of the para- to meta-xylene transformation. This change is not particularly large and is probably not a very significant effect. Of more significance is

FIGURE 4.7 : Relative Rate Constants for xylene Isomerisation

on Cation exchanged ZSM5



the change brought about by the introduction of sodium into the sample; this causes a decrease in all of the observed rate constants relative to the para- to ortho-xylene transformation. Alternatively this may be considered as an increase in the contribution of the "forbidden" para- to ortho-xylene pathway relative to all other pathways. The relative rate constants of figure 4.7, are the observed and not the intrinsic rate constants, and as such they include any effect due to the diffusion of the xylene isomers within the ZSM5 channels. Mathematically it has already been shown, that when the effects of diffusion become significant in a reversible three-component series reaction, the apparent kinetics exhibit the properties of a three-component reversible parallel reaction. Thus the enhancement of the ortho- to meta-xylene transformation, during isomerisation on the Na(75)-ZSM5 sample, is indicative of greater diffusion control which is not apparent on the Cs(75)-ZSM5 sample.

In order to apply the kinetic equations developed in Section 4.2, the assumption of first order kinetics must be tested. Figure 4.8 shows the integrated rate analysis treatment for para-xylene isomerisation on Na(75)-ZSM5 at 300°C. The data was fitted by a least-squares refinement program to test the linearity of both the first and second order integrated rate equations. The fitting parameters given in table 4.2, show that the xylene isomerisation rate data is best described by a first order rate equation, the correlation coefficient for this fit being closer to unity. The data for the second order rate analysis was also

FIGURE 4.8 : Integrated Rate Analysis for Para-xylene Isomerisation

on Na(75)-ZSM5

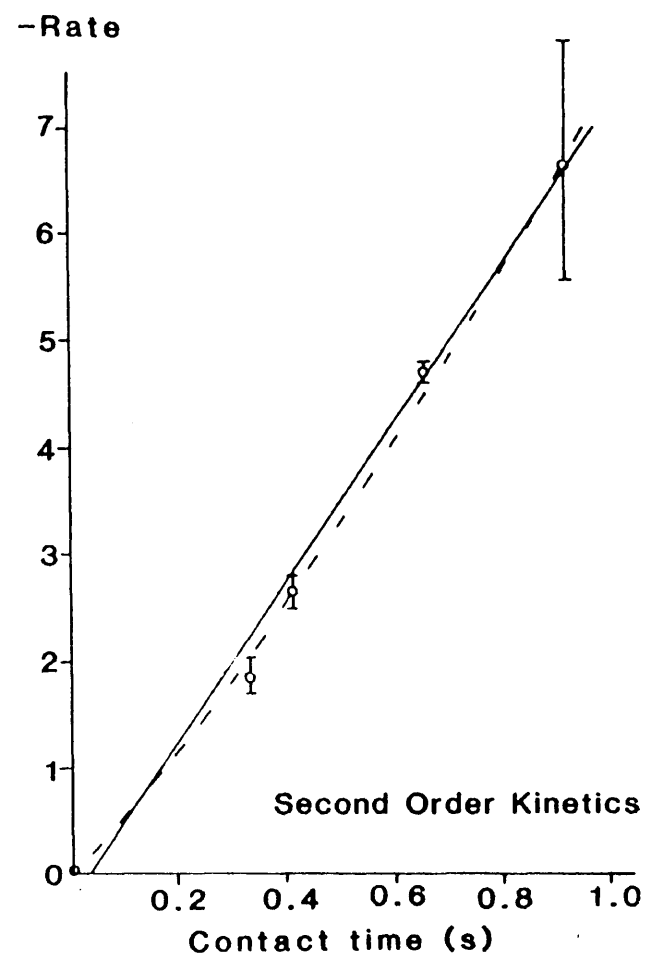
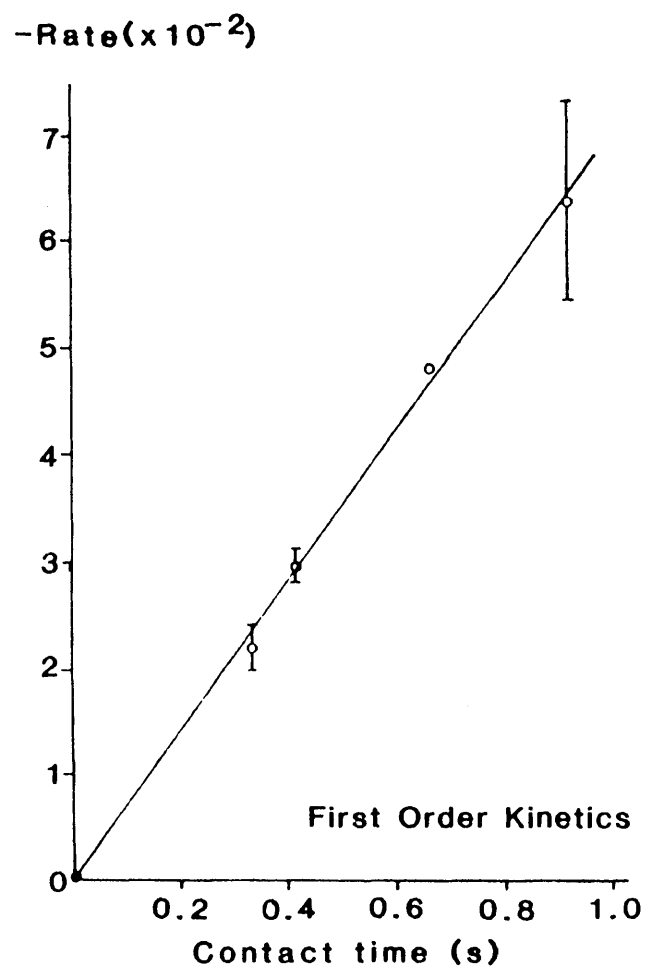


Table 4.2 : Integrated rate analysis for para-xylene
isomerisation on Na(75)-ZSM5

Data for the first and second order integrated rate equations
 fitted by a least squares method to a straight line

	First Order	Second Order
Gradient	-7.03×10^{-2}	-7.41
Intercept	1.30×10^{-4}	0.27
Correlation Coefficient	0.9970	0.9905

The second order kinetics data fitted to a linear and quadratic
 polynomial

polynomial	R factor
$y = 0.27 - 7.41x$	0.291
$y = 0.0674 - 5.813x - 1.710x^2$	0.244

fitted to both linear and quadratic rate equations, to further emphasise the non-linear nature of this analysis. Both of the polynomials are represented in figure 4.8 and their respective fitting parameters given in table 4.2. The R-factor is lower for the second order polynomial, indicating a closer fit to the experimental data.

Experimentally the conversion versus product distribution plots were produced by variation of the reactor temperature, thus the same data can be used, to calculate the activation energies for xylene isomerisation, by the use of equation 4.12. The combined activation energies, pre-exponential factors, and the associated correlation coefficients are tabulated in table 4.3. The correlation coefficients are low, which is attributed to the scatter in the data which can be seen in figures 4.3 to 4.6. Substantial differences do occur between the activation energies of different samples which are larger than the standard deviations, and so meaningful comparisons between the different samples can be made.

In order to comment on the activation energies for xylene isomerisation, a means of splitting the observed combined activation energies into their individual components must be found. The free energies of formation of the three xylene isomers are given in table 4.4 (88). The energies are virtually identical, which leads to the approximation that the activation energies for the forward and reverse reactions are the same. Hence the three combined activation energies can be solved simultaneously to calculate the six separate activation energies:

Table 4.3 : Arrhenius parameters for xylene isomerisation
on cation-exchanged ZSM5

	E_A (kJ/mol)	$\ln(A)$	Correlation Coefficient
<u>Ortho-xylene isomerisation:</u>			
H-ZSM5	143 ± 24	31 ± 6	.974
Na(75)-ZSM5	114 ± 3	22 ± 1	.998
Na(75)-ZSM5	114 ± 20	22 ± 5	.940
Cs(75)-ZSM5	178 ± 19	36 ± 4	.989
<u>Meta-xylene isomerisation:</u>			
H-ZSM5	99 ± 14	20 ± 3	.960
Na(75)-ZSM5	166 ± 22	32 ± 5	.982
Cs(75)-ZSM5	129 ± 6	24 ± 1	.993
* Cs(75)-ZSM5	76 ± 9	12 ± 2	.974
<u>Para-xylene isomerisation:</u>			
H-ZSM5	107 ± 5	22 ± 1	.994
Na(75)-ZSM5	128 ± 8	25 ± 2	.990
Cs(75)-ZSM5	113 ± 5	21 ± 1	.993

* Sample calcined rapidly to 500°C

Table 4.4 : Standard Free Energies of Formation
of Para-, Meta- and Ortho-Xylene

	ΔG_f° (kJ/mol)
Para-xylene	110.3
Meta-xylene	107.6
Ortho-xylene	110.1

$$E_{\text{Para}} = E_1 + E_3$$

$$E_{\text{Meta}} = E_1 + E_2$$

$$E_{\text{Ortho}} = E_2 + E_3$$

where E_1 is equal to E_{-1} , E_2 is equal to E_{-2} , and E_3 is equal to E_{-3} .

This is a reasonable assumption to make when the xylene isomerisation is occurring in an environment which is not diffusion-controlled. This may not be the case for the reaction in ZSM5; the increased diffusivity of the para-xylene isomer may cause the activation energy for the meta- to para-xylene transformation not to be the same as that for the para- to meta-xylene transformation.

The activation energies calculated by assuming that the energies of the forward and reverse reactions are identical are given in table 4.5, model 1. The experimental error is large, however tentative conclusions can still be drawn from these data. Two distinct activation energy ranges can be observed; one from 80 to 90 kJ/mol and the other from 20 to 40 kJ/mol. The higher activation energy range is that typical of a chemical reaction; whilst the lower activation energy range, is characteristic of the activation energy for the chemical reaction which has been modified by the presence of diffusion effects; this typically halves the observed activation energy as stated in Section 2.2.

Both the H-ZSM5 and the Cs(75)-ZSM5 samples show "diffusion-modified" activation energies for the para- to meta-xylene isomerisation reaction, whilst the Na(75)-ZSM5 sample exhibits a

**Table 4.5 : Activation Energies for xylene isomerisation
on cation-exchanged ZSM5**

Model One

Sample	E_1, E_{-1} (kJ/mol)	E_2, E_{-2} (kJ/mol)	E_3, E_{-3} (kJ/mol)
H-ZSM5	31 ± 15	68 ± 20	76 ± 14
Na(75)-ZSM5	90 ± 14	76 ± 12	38 ± 12
Cs(75)-ZSM5	24 ± 11	105 ± 13	89 ± 10

Model Two

Sample	E_1, E_{-3} (kJ/mol)	$E_{\text{meta}} - E_{\text{ortho}}$ (kJ/mol)
H-ZSM5	54 ± 3	-44 ± 28
Na(75)-ZSM5	64 ± 4	52 ± 22
Cs(75)-ZSM5	57 ± 3	-49 ± 20

high activation energy for this transformation, and a low activation energy for that of the ortho- to para-xylene reaction. Thus in Na(75)-ZSM5, the apparent kinetics suggest that not only is the direct ortho- to para-xylene reaction observed, but that it has an activation energy characteristic of a diffusion-controlled reaction.

A second method of splitting the combined activation energies involves taking into account the kinetic diameter of the three xylene isomers and relating this to the observed activation energies modified by diffusion in the ZSM5 channels. The kinetic diameters of the three xylene isomers are given in Section 1.4. Assuming that meta- and ortho-xylene have the same kinetic diameter which is different to that of para-xylene, then they can be considered to be subject to the same extent of diffusion-control in the zeolite channels. This assumption imposes restrictions on pairs of reactions so that they will always be under the same degree of diffusion control. It is however reasonable to expect, that if the meta- to para-xylene isomerisation reaction is diffusion controlled, then the ortho- to para-xylene transformation will also be under the same control. This assumption produces the following approximations:

$$E_1 = E_{-3}$$

$$E_2 = E_{-2}$$

$$E_3 = E_{-1}$$

Substituting these approximations into equations 4.13 to 4.15, yields the relationships:

$$E_{\text{meta}} - E_{\text{ortho}} = 0$$

$$E_{\text{para}} = 2E_1$$

The first relationship can easily be compared with the values calculated from the experimental data and are given in table 4.5, model 2. Not only is the difference of E_{meta} and E_{para} not equal to zero for all three samples, but it is not even equal to a constant, which would allow the possibility of a systematic error explaining their deviation from model behaviour. The values of E_1 and E_{-3} are also given for completeness.

The study of the xylene isomerisation reactions on cation exchanged ZSM5 samples, has emphasised the results of the toluene disproportionation experiments. The raw data describing the product distribution as a function of conversion, clearly show that the Na(75)-ZSM5 sample is more para-selective than either the H-ZSM5 or Cs(75)-ZSM5 samples. Kinetic analysis of the observed relative rate constants using a three-component reversible reaction scheme, indicate that the reason for this enhanced para-selectivity is diffusive in nature; there is an increase in the "forbidden" para- to ortho-xylene transformation, which in other systems has been attributed to an increase in diffusion control. Activation energies for the xylene isomerisation reactions were calculated, and two models used to separate the combined activation energies. The models were selected to describe the limits of the effect of product selectivity on the course of the xylene isomerisation reaction. Model 1 assumed that the rates, and hence the activation energies, of the forward and reverse reactions were identical,

whilst model 2 assumed that the rates and their associated activation energies were dependent on the kinetic diameters of the xylene isomers. It is model 1 which produces the more comprehensible results, and leads again to the implication that it is a diffusion-related phenomenon which is causing the increased para-selectivity of the sodium exchanged forms over the corresponding caesium exchanged forms.

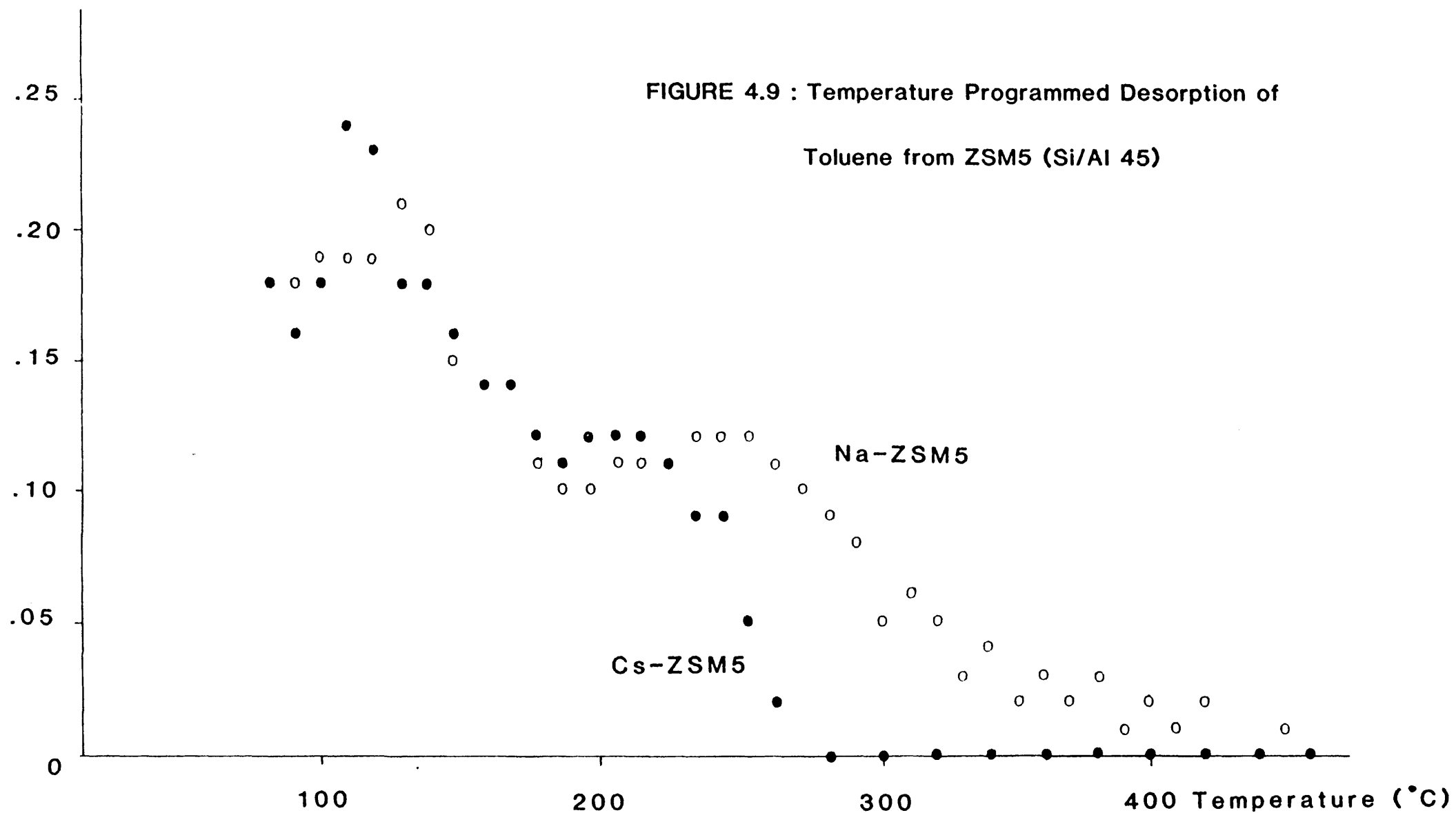
Adsorption data for the two ion-exchanged forms of the ZSM5 sample, have shown that the observed diffusion effect is not steric in nature. Using Sandersons concept of intermediate electronegativity (89), it has been established that the introduction of sodium into a zeolite produces a more-highly polarised framework than the introduction of caesium (90). This results in the the formation of stronger sorption complexes with the sodium cation. The strength of the sorption complex will depend on the dipole moment of the sorbates, which in the case of the three xylene isomers is in the order:

$$\eta_p \ll \eta_m < \eta_o$$

The dipole moment of para-xylene is zero, hence to a first approximation its sorption characteristics will not be dependent on the nature of the cation. The other two xylene isomers with non-zero dipole moments will interact more strongly with the sodium ion than with the caesium ion, leading to longer retention times within the channels of the sodium-exchanged zeolite sample. Hence the diffusive effect seen in the toluene disproportionation and xylene isomerisation reactions is electrostatic not steric in nature. This increase in the strength of the sorption complex

Differential Weight Loss (mg/g)

FIGURE 4.9 : Temperature Programmed Desorption of
Toluene from ZSM5 (Si/Al 45)



formed between a polar aromatic molecule and the sodium cation, is illustrated in figure 4.9, which shows the TPD profiles for the desorption of toluene from the ZSM5 samples fully-exchanged by both sodium and caesium.

HIGH ALUMINA ZSM5 CATALYSTS

5.1 PERCOLATION THEORY AND ZEOLITES

The zeolite framework is characterised by a regular system of intracrystalline cages and windows, with typical cross-sectional diameters lying between 3 and 10 Å. This network can contain various chemical entities such as coke, cations or inorganic molecules, which diminish the size of the cages and windows and modify the diffusion characteristics of that particular region of the network. The effectiveness of these blockages in modifying both the diffusion and adsorption characteristics of the zeolite, has been studied experimentally, and the results interpreted by using percolation theory (91,92,93).

A porous solid such as a zeolite may be considered as a regular arrangement of cages sited on the intersections of a network, with all the cages being connected by windows or channels. Percolation theory addresses the problem of transport within the porous media, when the cages or windows are randomly blocked. The likelihood of all the cages in the network being accessible to a diffusing species, is dependent on the proportion of cages or windows that are blocked; the more blockages the less likely that this criterion will be met. The relationship between the proportion of blocked sites and the probability of complete accessibility, is best described by a step-function with the probability changing dramatically over a small change in the number of blockages. The value corresponding to this significant change in the probability is known as the critical value, and it tends to be higher for blockages occurring in the windows rather

than the cages.

The critical probability is dependent on the geometry of the network. For a number of two-dimensional lattices, the values of the critical probabilities have been solved exactly, however the three-dimensional lattices rely on numerical computation, involving either Monte Carlo simulation or series expansion methods. Such Monte Carlo simulation techniques have been used to solve diffusion and adsorption related problems in zeolitic systems (94).

Percolation theory might be useful in mathematically investigating the effect of cations, on the para-selective properties of ZSM5 in the toluene disproportionation reaction. The values of the critical probabilities for the ZSM5 network could be used to predict the number of cations per unit cell which would give rise to a percolation effect, and to compare this with the experimentally-determined number of cations which leads to an increase in the para-selectivity of the ZSM5 sample. If a correlation is found to exist then the increase in para-selectivity may be attributed to the effect of the cations on the diffusion characteristics of the sample.

Monte Carlo simulations of diffusion within the ZSM5 lattice were not performed; instead it was hoped to approximate the ZSM5 framework to a network that had already been solved and its critical probabilities calculated. This would directly lead to an approximate value for the cation-loading required to observe a percolation effect, provided that the cation completely blocks the site at which it is positioned.

The ZSM5 lattice is three-dimensional and each channel

intersection is four coordinate, thus the obvious approximation for the ZSM5 structure is to a diamond-type lattice. From the literature (94), critical probabilities for this lattice were found to be:

Critical probability for blocking at intersections = 0.425

Critical probability for blocking in the channels = 0.388

The critical probabilities refer to the smallest fraction of channels or intersections which must be unblocked to allow complete accessibility. Relating these figures to the ZSM5 structure, it is possible to calculate the number of cations per unit cell which would be required to induce a percolation effect, when the cations are randomly located in one or other of these sites:

Blocking of intersections

Fractional number of blockages = $1 - 0.425 = 0.575$

Number of blockages per unit cell = $0.575 \times 4 = 2.3$

Blocking of channels

Fractional number of blockages = $1 - 0.388 = 0.612$

Number of blockages per unit cell = $0.612 \times 8 = 4.9$

These calculations assume:

1. Both the aluminium and the charge-balancing cations are randomly arranged throughout the ZSM5 crystal.
2. The cation completely blocks the channel or intersection.
3. The adsorbate shows no preference for diffusion through the sinusoidal or straight channels.

The ZSM5 sample supplied by ICI has a maximum imposed by the bulk Si/Al ratio, of two cations per unit cell, hence if the above criteria are true the differences in para-selectivity at high cation loadings already observed, can not be attributed to a percolation effect. Obviously within the bounds of the above criteria, a catalyst of lower Si/Al ratio must be employed in order to observe a percolation effect. Two methods of tackling this problem were investigated. First the direct synthesis of a high-alumina ZSM5 sample and secondly the modification of the ICI sample to introduce more aluminium into the ZSM5 framework.

5.2 ALUMINATION OF ZEOLITES

The substitution of aluminium into zeolite frameworks, has until fairly recently attracted little attention, with the main thrust of research into the modification of the chemical composition of zeolites, concentrating on the dealumination of the framework. This was principally fuelled by the finding that catalysts of higher Si/Al ratios, exhibited enhanced thermal and chemical stabilities (1).

During the late 1970's, synthetic routes were discovered leading to the production of "zeolite" frameworks incorporating other elements besides silicon and aluminium, e.g. iron (95), gallium (96) and phosphorus (97). Such work directly produced open crystalline structures, some of which were isostructural with known zeolites, whilst others have not, so far, been encountered in the zeolite world e.g. ALPO-5 (98). Concurrent with this work, research also proceeded on the modification of

existing zeolites, by their reaction with a volatile compound of an appropriate element, including aluminium.

The introduction of aluminium into zeolite ZSM5 has been accomplished by reaction at high temperature, with such compounds as sodium aluminate, ammoniacal aluminium fluoride, and the aluminium halides. All of these processes have been reported in the patent literature (97,98), and the zeolites produced have shown enhanced activities for a wide range of acid-catalysed reactions. Alumination of ZSM5 has typically been performed on high silica samples, with Si/Al ratios of approximately 20,000:1, and the most common method of preparation has involved the direct reaction with aluminium chloride vapour.

The nature of the aluminium sites introduced into the zeolite by this treatment, have been elucidated by various physicochemical techniques, complemented by catalytic testing. ²⁷Al MASNMR gives direct evidence for the nature of the aluminium in the zeolite. After treatment with aluminium chloride, the signal at 55 ppm, assigned to framework tetrahedral aluminium, greatly increases in intensity. Signals at 5 and 70 ppm are also seen to appear, indicating the formation of γ -alumina, believed to result from the hydrothermal treatment of the product to remove unreacted aluminium chloride. In such samples, the hexane sorption capacities remained essentially constant indicating that the channels were largely free from occluded material. The existence of such non-framework aluminium species, is also suggested by discrepancies between the bulk Si/Al ratio, and that calculated from cation exchange capacities or the ²⁹Si MASNMR spectra (101).

The introduction of aluminium into the ZSM5 framework, creates acid sites which can be studied by conventional methods. FTIR analysis, demonstrates that this treatment introduces Bronsted acid sites into the zeolite. The band at 3610 cm^{-1} , characteristic of Bronsted acid sites, is seen to appear, whilst the intensity of the band at 3740 cm^{-1} , associated with internal silanol groups, decreases. This is consistent with the insertion of aluminium into the framework at silanol defect sites (102). The acid strength distribution on these treated samples, can be determined by the TPD of ammonia. Relative to synthetic ZSM5 samples of the same framework Si/Al ratio, the treated samples exhibit high temperature peaks, indicating that some of the acid sites in the aluminated ZSM5 are much stronger than in the as-synthesised samples. The number of acid sites can be evaluated from the amount of ammonia desorbed during the TPD. The aluminated zeolites, possess more acid sites than the framework aluminium concentration suggests, but less than that characteristic of the bulk Si/Al ratio. This suggests that the framework, and part of the non-framework aluminium, are responsible for the acid sites on the aluminated ZSM5.

Insertion of aluminium into the zeolite framework, by methods other than reaction with a volatile aluminium compound, have received little attention so far. One such process involves the reinsertion of aluminium into the framework of ultrastable-Y, by the low temperature reaction with potassium hydroxide solutions (103). ^{29}Si MASNMR has shown that on reaction, the framework Si/Al ratio increases, however no chemical analysis or mass-balance calculations were reported. It seems probable that at the

high experimental pH conditions employed, the framework is partially degraded and either an aluminium rich core is revealed, or migration of extra lattice aluminium is occurring into framework sites. Such a low temperature method of aluminium insertion is worth investigating further, as it may lead to a greater retention of framework integrity than the high temperature processes discussed previously.

5.3 PRODUCTION OF HIGH ALUMINIUM CONTENT ZSM5 ZEOLITES

Direct synthesis method

The initial attempts at synthesising ZSM5, involved the adaptation of a method previously used to produce siliceous samples with typical Si/Al ratios of 60 to 100. The composition of the reactant gel is given in table 5.1, method 1. This mixture was heated in an autoclave at 170°C and at autogeneous pressure for two weeks. On removal from the autoclave, crystals were observed which gave an XRD pattern characteristic of ZSM5. These were calcined at 550°C under flowing nitrogen for eight hours, followed by calcination in air at 600°C for a further twenty-four hours.

Chemical analysis of the resulting ion exchanged samples involved the same methods described in Chapter 2, employed in the analysis of the ICI sample. During the determination of the aluminium contents, complete dissolution in HF was found not to be possible, and so the insoluble residue was collected and its dry mass determined. This accounted for approximately 12% of the total mass of the sample. The molar Si/Al ratios of the dissolved

**Table 5.1 : Composition of synthesis mixture for
production of high alumina ZSM5**

	Method 1	Method 2
SiO_2	47.1g	14g
NaAlO_2	----	8ml
Al_2O_3	4.0g	----
NaOH	5.0g	2.0g
KOH	----	0.18g
TPA	50g	15g
H_2O	240ml	120ml
Na-citrate	----	10g
$(\text{NH}_4)_2\text{CO}_3$	24.7g	----

component ranged between 75 and 80, depending on the aluminium content of the synthesis gel. Considering that the Si/Al ratio of the reacting mixtures was between 10 and 20, it is likely that the undissolved residue is composed of acid-insoluble α -alumina.

It is obvious that the straight introduction of solid alumina into the synthesis mixture used in the preparation of siliceous ZSM5, does not increase the framework Si/Al ratio. A means of dissolving the alumina prior to reaction with the silica source was required. This was achieved by the preparation of an alkaline sodium aluminate solution, by the reaction of the following mixture in an autoclave at 170⁰ C:

Al(OH)₃ ... 0.80g

NaOH ... 1.20g

H₂O ... 10ml

After eight hours the mixture had completely dissolved, and was subsequently used as the aluminium source in the synthesis gel given in table 5.1, method 2. Identical reaction conditions were employed as for the previous synthesis. Electron micrographs of the resulting crystals showed no sign of amorphous impurities, with the sample formed into aggregates composed of crystals approximately 1 micron in diameter.

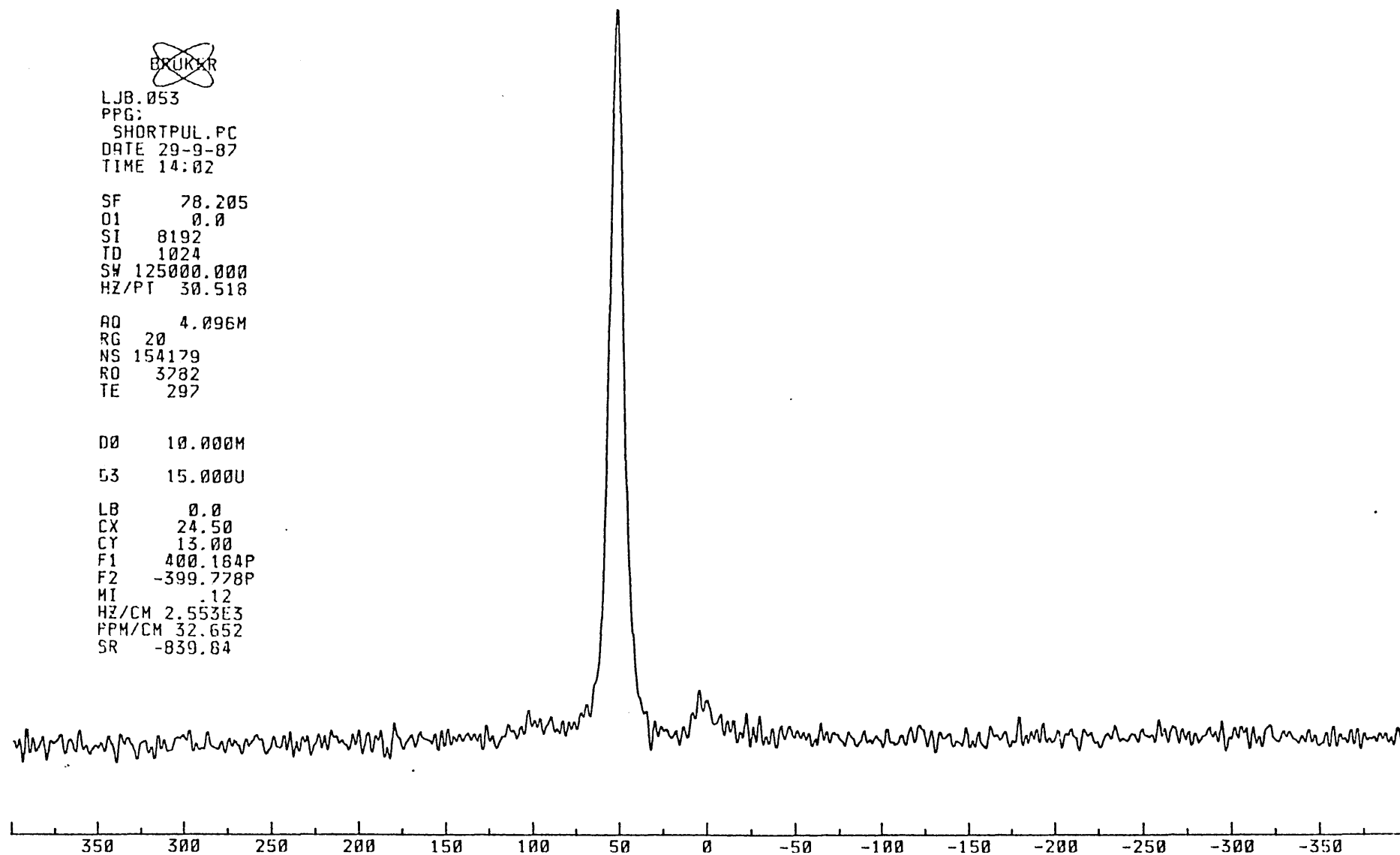
Chemical analysis of the resulting ion exchanged samples are given in table 5.2. The Si/Al ratio determined by wet chemical analysis is equal to that of the starting gel, indicating that the problem of unreacted alumina has been avoided by the use of a soluble alumina source. The ²⁷Al MASNMR spectrum of the calcined sample is shown in figure 5.1, which demonstrates that all the

Table 5.2 : Chemical analysis of the synthesised ZSM5 sample

	Cs-ZSM5	Na-ZSM5	NH ₄ -ZSM5
C.E.C (meq/g)	0.57	0.54	---
H ₂ O (mol./U.C.)	22.0	26.6	23.9
M ⁺ (ions/U.C.)		3.3	
Al (atoms/U.C.)		3.31	
Si (atoms/U.C.)		92.69	
Si/Al		28.0	
Para-xylene sorption capacity (mol./U.C.)	11.0	12.2	12.5 [*]

* H-ZSM5

FIGURE 5.1 : ^{27}Al MASNMR of ZSM5 (Si/Al 28): Acetyl-acetone added



aluminium is in framework positions.

Alumination of the ICI ZSM5 zeolite

An alumination mechanism based on the low temperature occlusion of an aluminium species into the ZSM5 channels followed by insertion by treatment with KOH solution was postulated. Prior to such work being attempted a more detailed investigation of the effect of an alkaline environment on ZSM5 was required. Samples of the parent ZSM5 sample were contacted for 24 hours with 0.25M (pH=13.4) or 0.025M (pH=12.4) potassium hydroxide solutions at 80°C. After centrifugation and drying, the mass of the sample treated with the 0.25M potassium hydroxide solution had decreased by 34%, whilst no mass-loss was found for the sample treated with the 0.025M solution. Structural changes were monitored by the use of XRD and ^{29}Si MASNMR. Comparison of the remaining solids showed that the sample treated with 0.25M KOH exhibited a less intense XRD pattern than either the parent or the sample treated with 0.025M KOH, indicating a loss of crystallinity, whilst ^{29}Si MASNMR showed an increase in the fine structure of the Si(0Al) peak which has previously been attributed to framework dealumination.

It appears that treatment with alkaline solutions can cause structural degradation and dissolution, however this may not always be unwanted. In order to incorporate aluminium into the framework, the experimental conditions must cause the framework to exhibit some "mobility", and a controlled reaction in an alkaline environment might provide just this framework mobility.

In addition to conditions leading to a labile framework,

alumination requires a source of non-framework aluminium to be present in the ZSM5 channels. The least severe method of introducing this was considered to be the ion exchange of H-ZSM5 with a solution of aluminium sulphate. Ion exchange was followed by the rotation of the solids with either a 0.25M or 0.025M potassium hydroxide solution for 24 hours, washing, exchange with ammonium chloride and drying. The course of the reaction was followed by ^{27}Al MASNMR. Only the spectrum taken after the exchange with aluminium sulphate showed a peak at 1.1 ppm characteristic of non-framework octahedral aluminium. The intensity of this peak was very low, and this was attributed to the low selectivity of ZSM5 for the exchange of multivalent cations. After treatment with the potassium hydroxide solutions this peak was no longer present indicating either dissolution or ion exchange with the potassium ion.

Considering the low selectivity of the zeolite towards the aluminium ion, it was considered that exchange of the cation sites followed by treatment with potassium hydroxide solution, would not realistically yield structurally crystalline sample with the required framework aluminium content. The direct alumination with a volatile aluminium containing compound at elevated temperatures was thus investigated as a means of increasing the framework aluminium concentration to the desired level.

Approximately 5g of the parent ZSM5 zeolite, was placed into porcelain boats inside a muffle furnace. Dry nitrogen was flowed through the furnace which was heated at $10^{\circ}\text{C}/\text{min}$ to 350°C to remove zeolitic water. The reactor was cooled to room

temperature, and 1g of aluminium chloride (GPR) was rapidly mixed into the zeolite bed. The nitrogen flow was resumed and the reactor was heated to 180°C , where it was maintained for two hours in a static environment. After cooling, the samples were transferred to an air oven, and heated to 450°C for twelve hours to remove any residual aluminium chloride.

The product was washed in 400ml aliquots of distilled water until the pH of the washings was equal to 7. The sample was divided and the sodium, caesium and ammonium forms were prepared by repeated exchange with concentrated solutions of the appropriate chloride salts (i.e. NaCl , CsCl and NH_4Cl). In the case of the sodium and caesium exchanges, the pH of the exchanged solutions never reached 7. The final exchanges were performed in the presence of $\text{Na}_2\text{H}(\text{PO}_4)$ which acts as a buffer at pH 9. In the case of the caesium exchange, this introduces a possible sodium "impurity" into the exchange equilibria. The concentration of buffer was kept to a minimum, and the selectivity of zeolite ZSM5 to caesium over sodium, was expected to produce an essentially homoionic zeolite. It was considered that this method of preparing Cs-ZSM5, would produce a sample with a higher concentration of caesium than exchange with CsCl , which appeared to be exchanging hydronium ions as well as caesium. The chemical analysis of the ion exchanged samples are given in table 5.3 and the ^{27}Al MASNMR spectrum of the calcined product is given in figure 5.2. From the integrated intensities of the peaks assigned to tetrahedral framework and octahedral non-framework aluminium, the framework aluminium content can be calculated from the bulk

Table 5.3 : Chemical analysis of the aluminated ZSM5 sample

	Cs-ZSM5	Na-ZSM5	NH ₄ -ZSM5
C.E.C (meq/g)	0.53	0.38	28.1
H ₂ O (mol./U.C.)	34.7	32.1	
M ⁺ (ions/U.C.)	3.39	2.36	
Al (atoms/U.C.)		8.49	
Si (atoms/U.C.)		87.51	
Si/Al		10.3	
Para-xylene sorption capacity (mol./unit cell)	10.1	9.9	10.6 [*]

* H-ZSM5



LJB.057
PPG:
SHORTPUL.PC
DATE 3-9-87
TIME 9.04

SF 78.205
Q1 0.0
SI 8192
TD 4096
SW 125000.000
HZ/PT 30.518

AQ 16.384M
RG 20
NS 2.794E6
RO 3781
TE 297

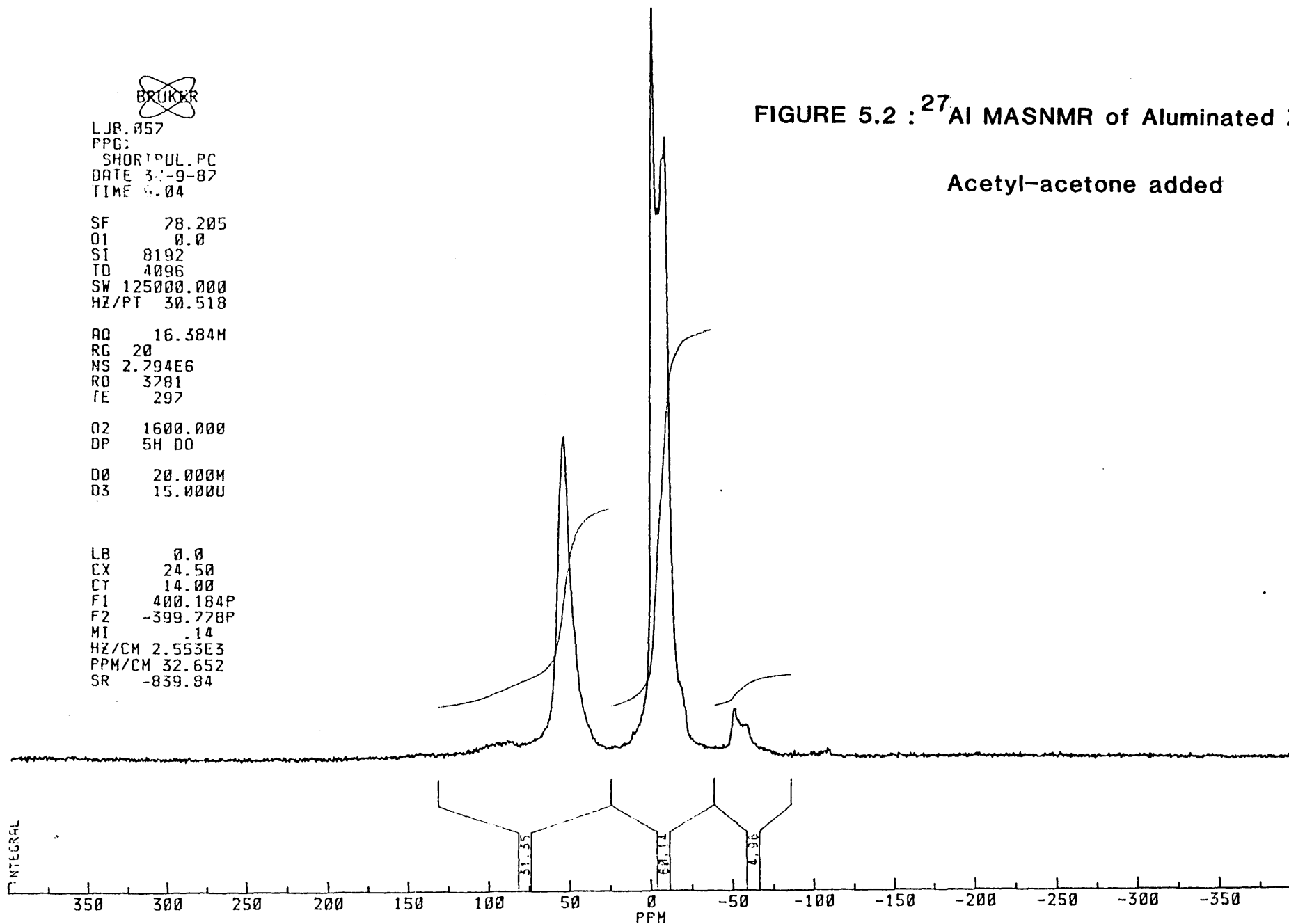
O2 1600.000
DP 5H D0

D0 20.000M
D3 15.000U

LB 0.0
CX 24.50
CY 14.00
F1 400.184P
F2 -399.778P
MI .14
HZ/CM 2.553E3
PPM/CM 32.652
SR -839.84

FIGURE 5.2 : ^{27}Al MASNMR of Aluminated ZSM5 :

Acetyl-acetone added



Si/Al ratio given in table 5.3. The ratio of the octahedral to tetrahedral signal is found to vary with the length of the excitation pulse. True quantitative intensities are obtained only if short pulses are employed; the 0.35 μ s pulse used to obtain figure 5.2, should be quantitative to 10%. This gives a framework Si/Al ratio of 35, corresponding to 2.7 aluminium atoms per unit cell.

5.3 TOLUENE DISPROPORTIONATION ON ALUMINATED ZSM5 SAMPLES

The ZSM5 samples prepared in the previous section both have higher framework aluminium contents than the ICI sample investigated in the preceeding chapters. Screening experiments can be performed to investigate the suitability of the two methods of preparation, in producing cation-rich ZSM5 for the enhancement of para-selectivity in xylene-producing reactions.

To be able to unambiguously assign changes in observed para-selectivity to a cation-induced effect the ZSM5 channels must be free of occluded species. The presence of such species will increase the diffusional resistance within the channels and affect the para-selectivity, even in the absence of a cation effect. The para-xylene sorption capacities for the cation exchanged forms of the two ZSM5 samples are given in tables 5.2 and 5.3. The directly synthesised sample exhibits a sorption order consistent with the size of the exchanged cations. The aluminated sample however, possesses a sorption capacity order which is anomalous for the sodium exchanged form. Furthermore the ^{27}Al MASNMR spectrum has already indicated that much of the aluminium

in this sample is present in non-framework positions, and as such could directly influence its diffusional properties.

The effect of the occluded aluminium species on the course of the toluene disproportionation reaction, was assessed by a comparison of the performance of the pure acid forms of the aluminated and parent ICI samples. These samples have no cations present in the channels, and so any variation in their performance can be attributed to the alumination procedure. Figure 5.3 shows the para-selectivity versus conversion curves at various temperatures for both samples. As expected both samples become more para-selective as the temperature increases, however overall the aluminated sample is more para-selective than the parent ICI sample. This enhanced para-selectivity is directly attributable to the occluded aluminium species in the channels of the zeolite modifying the diffusion characteristics of the samples.

The Arrhenius parameters for toluene disproportionation on the pure H-ZSM5 forms of the two samples were experimentally determined. This yields information on the thermodynamics and para-selectivity over a large temperature and conversion range which may be compared with the data obtained on the ICI sample. The observed Arrhenius parameters are given in table 5.4. Comparison of these values with those of the ICI sample given in table 3.6, emphasises the effect of the occluded aluminium on the energetics of the toluene disproportionation reaction. This modification of the thermodynamics of the reaction, combined with the enhanced para-selectivity of the aluminated sample, suggest that any further investigation on the effect of different cations

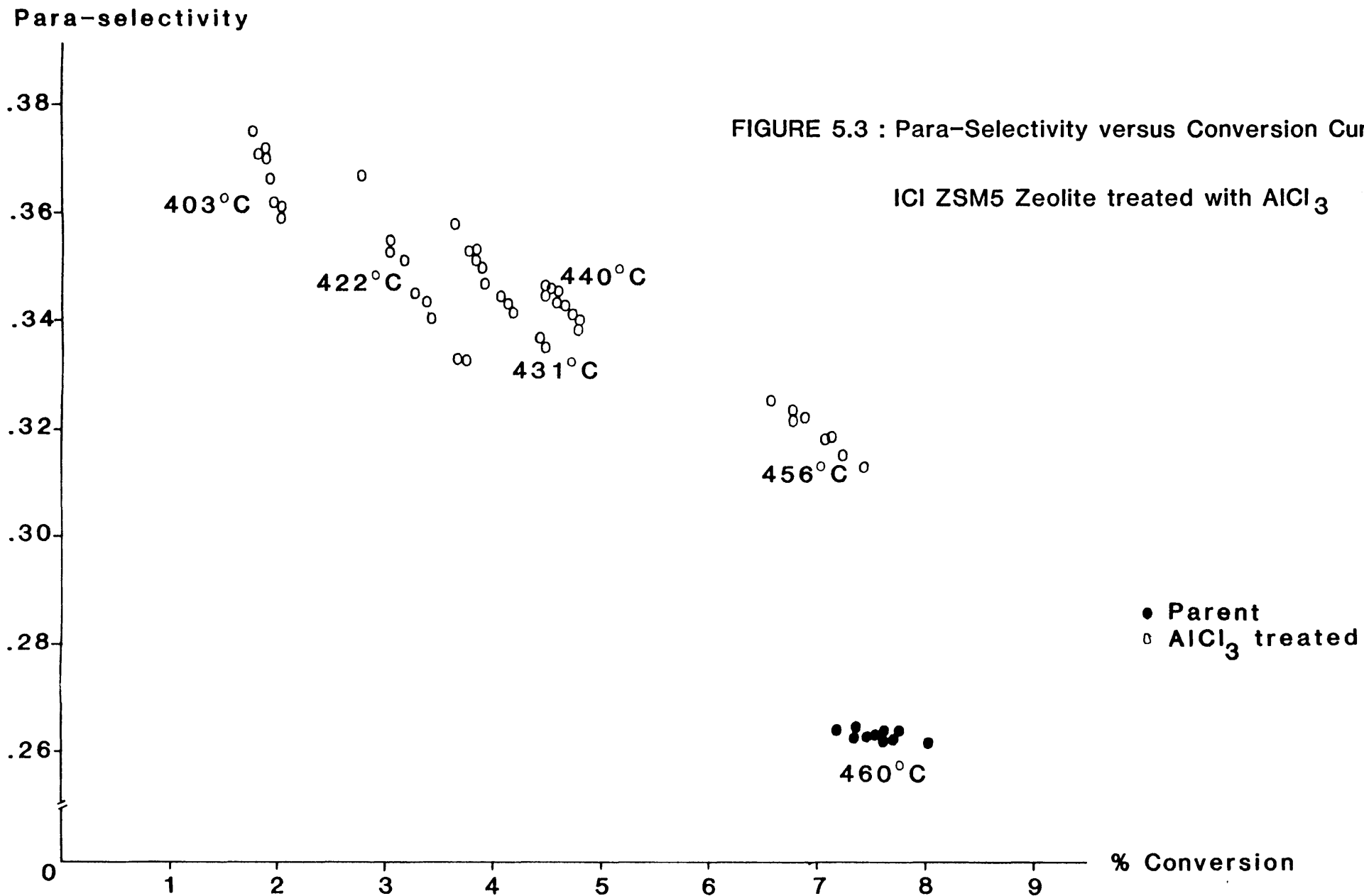


**Table 5.4 : Arrhenius parameters for toluene disproportion
on high-alumina ZSM5 samples**

Directly Synthesised ZSM5 (Si/Al=28)

Sample	E_{Act} (kJ/mol)	$\ln (A)$	Correlation Coefficient
H-ZSM5	90.8 $\pm$ 2.4	12.8 $\pm$ 0.4	.998
Na(50)-ZSM5	124.0 $\pm$ 0.7	16.5 $\pm$ 0.1	.999
Cs(50)-ZSM5	113.0 $\pm$ 0.2	15.1 $\pm$ 0.2	.999
Na(80)-ZSM5	131.1 $\pm$ 0.8	15.5 $\pm$ 0.1	.999
Cs(80)-ZSM5	96.2 $\pm$ 1.2	9.5 $\pm$ 0.2	.999

Parent ICI sample treated with aluminium chloride

Sample	E_{Act} (kJ/mol)	$\ln (A)$	Correlation Coefficient
H-ZSM5	104.0 $\pm$ 4.5	14.0 $\pm$ 0.8	.994

on the course of the reaction on this sample will be inappropriate, due to the inability to uncouple the effect of the cation from that of the occluded aluminium species.

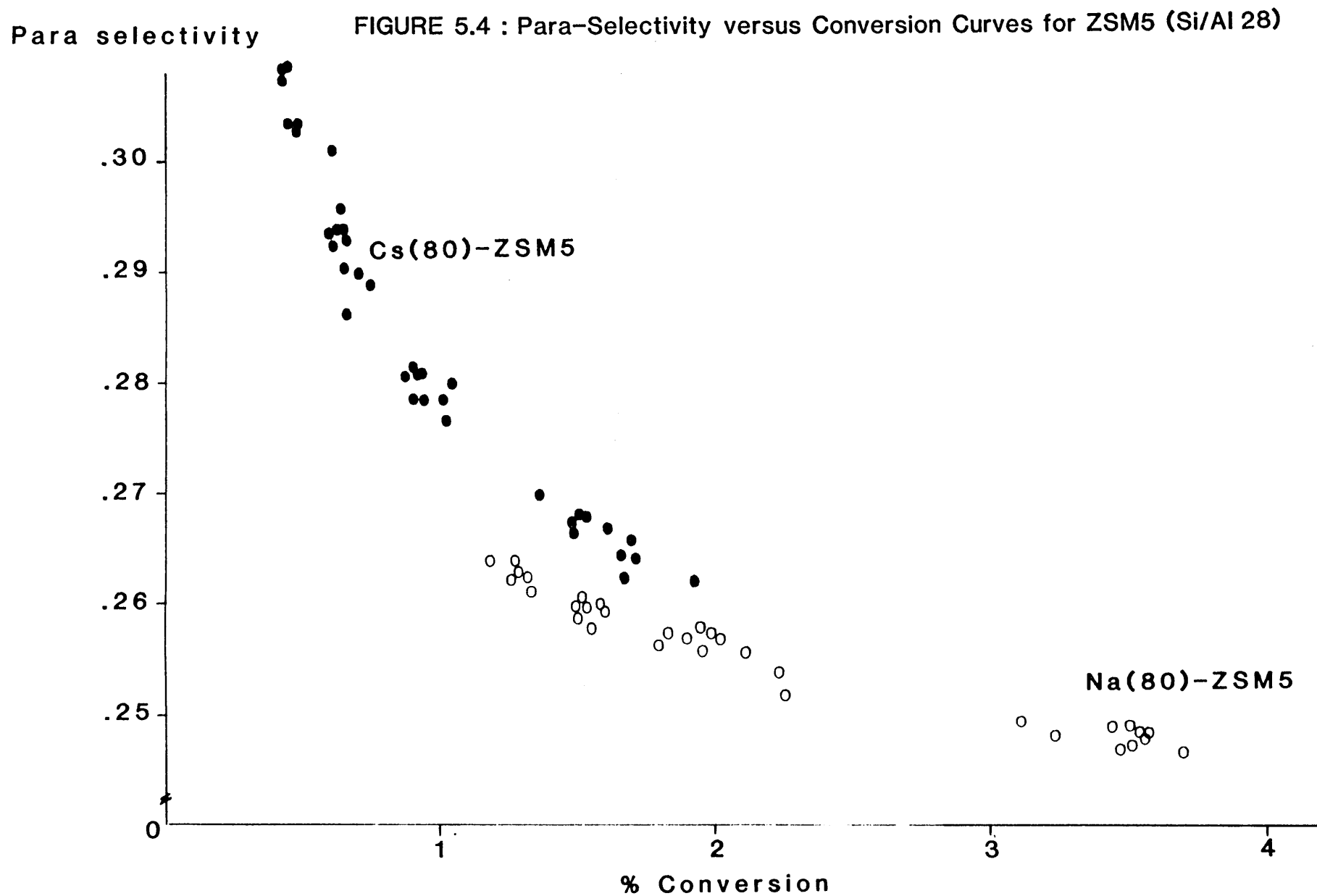
The Arrhenius data permits the calculation of the activity per acid site for each sample at arbitrary temperatures. The activity per acid site was defined as the first order rate constant divided by the number of acid sites per unit cell. The results of these calculations for a temperature of 500°C are given in table 5.5 for a number of cation-exchanged forms of the directly synthesised ZSM5 sample. The pure hydronium exchanged form exhibits a higher activity per acid site than the ICI sample, however the introduction of cations into the system causes a rapid decline in the activity of the remaining acid sites.

Isothermal toluene disproportionation experiments yielded para-selectivity versus conversion curves for the directly synthesised ZSM5 sample after cation exchange. These are shown in figure 5.4. A comparison of the para-selectivity values for these samples at 2% conversion with those for the ICI sample (figure 3.10) demonstrates the overall lack of para-selectivity even at very high cation content. The fully hydronium exchanged ICI sample exhibits greater para-selectivity than these samples even though the reaction on these samples is performed at higher temperatures. Section 3.2 showed that the para-selectivity should theoretically increase with temperature if diffusion effects are relevant, so the above comparison should be flattering to the directly synthesised sample.

The absence of any difference in the para-selectivities with cation type is tentatively attributed to aluminium zoning. It is

Table 5.5 : Activities per acid site for toluene
disproportionation

Sample	Activity per acid site
H-ZSM5 (Si/Al=45)	0.051
H-ZSM5 (Si/Al=28)	0.080
Na(50)-ZSM5 (Si/Al=28)	0.037
Cs(50)-ZSM5 (Si/Al=28)	0.050
Na(80)-ZSM5 (Si/Al=28)	0.011
Cs(80)-ZSM5 (Si/Al=28)	0.006



postulated that most of the framework aluminium atoms and hence the charge-balancing cations are located on the outer surface of the ZSM5 crystals. This would have the effect of decreasing the effective crystal size, and inhibiting any diffusional role of the cations. In order to investigate this suggestion, XPS studies were performed on the caesium exchanged forms of the three ZSM5 samples. XPS is a surface-sensitive technique with an approximate analysis depth of 50 Å. The results of the analysis are summarised in table 5.6. The sample treated with AlCl_3 displays a surface Si/Al ratio of 3:1. A signal from chlorine is also detected, however the nature of the charge shift is uncertain and there is consequent doubt about its origin. The other two ZSM5 samples exhibited no aluminium signals, whilst single silicon and oxygen species were detected. The detection limit of the XPS technique has been estimated by the operator, to yield a maximum Si/Al ratio of 100:1. Hence both the ZSM5 samples appear to contain aluminium-deficient surfaces, and the relative aluminium zoning of the two samples cannot be estimated from this technique.

In conclusion, both direct synthesis and alumination techniques, can be used to produce ZSM5 samples with higher framework aluminium concentrations, than the sample with a Si/Al ratio of 45 supplied by ICI. Both techniques yielded samples which made them inappropriate for the investigation of a cation-induced percolation effect. The aluminated sample contained occluded aluminium species which exhibited a diffusional effect which would be difficult to uncouple from any cation effect. The directly synthesised sample although free from such species,

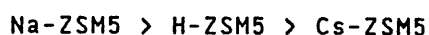
Table 5.6 : Elemental Compositions of Zeolite Samples
Relative to the Si(2p) Signal

	O(1s)	Si(2p)	Al(2p)	Na(2s)	Cs(3d)	Cl(2p)
Na-Y(Si/Al=5)	1.10	1	0.20	0.17		
ZSM-5(Si/Al=45)	1.5	1			0.04	
ZSM-5(Si/Al=28)	1.5	1			0.03	
ZSM-5(Si/Al=10)	1.10	1	0.32		0.03	0.03

suffered from aluminium zoning, which caused any increase in the diffusional resistance to be overwhelmed by the decline in effective crystal size.

CONCLUSION

The parent ZSM5 sample with a Si/Al ratio of 45, exhibits an increase in para-selectivity for the toluene disproportionation and xylene isomerisation reactions on cation exchange which is in the order of:



This is the opposite to the order anticipated, based on the assumption of increasing diffusional resistance with ionic radius. The increased selectivity of the sodium exchanged form is attributed to an electrostatic effect; the electropositive sodium cation more strongly sorbs the polar meta- and ortho-xylenes relative to the non-polar para-xylene. This exaggerates the differences between the diffusion coefficients of the three xylene isomers, and increases the para-selectivity. The TPD of toluene from sodium and caesium exchanged ZSM5 shows that toluene desorbs from the caesium form at a lower temperature than the sodium form. Further sorption or diffusion measurements are needed to test this hypothesis.

The introduction of cations into ZSM5 has an effect on the activity of the remaining acid sites. At high cation loadings the activity per acid site declines, accompanied by an increase in the observed activation energy. This is attributed to cation exchange into the strong acid sites. At intermediate cation loadings, the activity and Arrhenius parameters are increased relative to H-ZSM5. The activation energy is increasing implying lower acidic strength, however the pre-exponential factor is also increasing, leading to the suggestion that the reaction probability is

increased at intermediate cation loading.

An increase in diffusional resistance due to pore-blockage by cations is predicted by percolation theory to occur at low Si/Al ratios. No success was found in producing such high-alumina ZSM5 samples of appropriate crystal size for meaningful comparison, however the production of such high-alumina samples should be worth pursuing.

APPENDIX 1 : PROGRAM PYE/02

```

10 REM The assembled program "ASSEM" is loaded
20 REM and the label of the clock "MINS" is
30 REM printed in the top right hand corner of
40 REM the screen. Stop is set to zero until
50 REM the timelimit is exceeded when it is
60 REM set to unity in PROCend
70
80 *A:
90 PROCaddress
100 PRINT CHR$(15)
110 *LOAD "ASSEM"
120 *B:
130 PRINT CHR$(12)
140 ?&7C24=&4D : ?&7C25=&49 : ?&7C26=&4E : ?&7C27=&53
150 VDU 28,0,24,39,8
160 PROCfile
170 TIME=0
180 time=INT((TIME/100)/60)
190 PROCtime
200 stop=0
210 PROCrun
220 END
230
240 DEF PROCaddress
250
260 REM The addresses of the assembly language
270 REM routines are defined for the "CALL"
280 REM statements in the program.
290
300 SET=&2001 : ENTER=&200F : OF=&202C
310 CLR=&2039 : TEST=&2053 : ZERO=&2091
320 TRED=&209F
330 PTD=&218D : RESET=&21B2
340 CLF=&21C4
350 ENDPROC
360
370 DEF PROCfile
380
390 REM A time limit and filename is supplied
400 REM by the user. The data file is opened
410 REM and initialisation occurs.
420
430 PRINT "PUT DATA DISC ""IN DRIVE B"
440 PRINT
450 INPUT "ENTER RUN TIME""IN MINUTES ONLY",timelimit
460 PRINT
470 PRINT "ENTER FILE NAME""SIX CHARACTERS ONLY"
480 CALL SET
490 CALL ENTER
500 CALL OF
510 PRINT
520 CALL CLR
530 CALL TEST
540 CALL ZERO
550 ENDPROC

```

```

560
570 DEF PROCrun
580
590 REM The clock is constantly updated and
600 REM the timelimit condition checked
610 REM until an interrupt is detected (both
620 REM count1 and count2 are set to zero)
630 REM After the interrupt is serviced, a
640 REM delay loop is entered (TRED). When
650 REM the end of a data block is detected
660 REM (enddata=61) PROCinput is called
670 REM to write the data block to file
680
690 REPEAT
700   CALL TRED
710   enddata=?&20F2
720   IF enddata=61 THEN PROCinput
730   time=INT((TIME/100)/60)
740   IF time>=timelimit THEN PROCend
750   REPEAT
760     REPEAT
770       time=INT((TIME/100)/60)
780       PROCtime
790       IF time>=timelimit THEN PROCend
800       count1=?&2176
810     UNTIL count1=0
820     time=INT((TIME/100)/60)
830     IF time>=timelimit THEN PROCend
840     PROCtime
850     count2=?&2175
860   UNTIL count2=0
870 UNTIL stop=1
880 ENDPROC
890
900 DEF PROCend
910
920 REM When the timelimit has been exceeded,
930 REM the data file is closed and the
940 REM interface is disabled (at location &FCFE)
950
960 CALL CLF
970 ?64766=01
980 stop=1
990 END
1000 ENDPROC
1010
1020 DEF PROCinput
1030
1040 REM When the end of a data block is recognised
1050 REM it is written to file and the memory
1060 REM locations are reinitialised.
1070
1080 enddata=0
1090 CALL PTD : CALL RESET
1100 PRINT:PRINT
1110 ENDPROC

```

```
1120
1130 DEFPROCtime
1140
1150 REM Divides the time into it's constituent
1160 REM digits, then prints them out as ASCII
1170 REM characters in the top right hand
1180 REM corner of the screen.
1190
1200 X=time
1210 thous=0 : hund=0 : ten=0 : unit=0
1220 thous=X DIV 1000
1230 X=X MOD 1000
1240 hund=X DIV 100
1250 X=X MOD 100
1260 ten=X DIV 10
1270 X=X MOD 10
1280 unit=X
1290 ?&7C1F=(thous+48) : ?&7C20=(hund+48)
1300 ?&7C21=(ten+48) : ?&7C22=(unit+48)
1310 ENDPROC
```

APPENDIX 2 : PROGRAM ASSEM

```

10 U=0
20 P%=&2000
30 [:OPT U
40 .SV1 NOP
50 .SET
60
70 /Initialises the variable SV1 which counts
80 /the number of inputted characters forming
90 /the filename.
100
110 LDA #&0
120 STA SV1
130 RTS
140
150 .S1 NOP
160 .S2 NOP
170 .S3 NOP
180 .S4 NOP
190 .S5 NOP
200 .S6 NOP
210 .S7 NOP
220 .S8 NOP
230 .ENTER
240
250 /Reads in the characters forming the
260 /filename from the keyboard. After the
270 /sixth character, a carriage return is
280 /added (ASCII code &0D). The filename is
290 /stored in locations S1 to S8.
300
310 .LOOP
320 JSR &FFEO
330 JSR &FFEE
340 LDX SV1
350 STA S1,X
360 INC SV1
370 CPX #&05 : BNE LOOP
380 LDX SV1
390 LDA #&0D
400 STA S1,X
410 RTS
420
430 .H1 NOP
440 .OF
450
460 /Creates an input file, where X and Y
470 /point to the address of the filename.
480 /H1 holds the channel number allocated to
490 /the file, for writing.
500
510 LDX #(S1 MOD 256): LDY #(S1 DIV 256): LDA #&80
520 JSR &FFCE
530 STA H1
540 RTS

```

```

550
560 .CLR
570
580 /Uses the zero page locations, &82 and &83,
590 /as indirection addresses to the data
600 /storage locations (pages after &2300).
610 /These locations are filled with blanks
620 /(ASCII code &20).
630
640 LDA #&0
650 STA &82
660 LDA #&23
670 STA &83
680 LDY #&0
690 .KAS1
700 LDA #&20
710 .KAS2
720 STA (&82),Y
730 INY : BNE KAS2
740 INC &83
750 LDA #&40
760 CMP &83 : BNE KAS1
770 RTS
780
790 .TEST
800
810 /Initialises the program variables, and
820 /sets up interface (via &FCFE). Redirects
830 /the interrupt routine by setting up
840 /&206 and &207 to send the program to
850 /the instructions labelled by .TEA.
860
870 LDA #00
880 STA R4
890 LDA #00
900 STA &80
910 LDA #&23
920 STA &81
930 LDA #&0
940 STA F3
950 LDA #00: STA F1 : STA F2
960 LDA #3
970 STA &FCFE
980 LDA #&81 : STA &FCFE
990 SEI
1000 LDX #(TEA MOD 256)
1010 LDY #(TEA DIV 256)
1020 STX &206
1030 STY &207
1040 CLI
1050 RTS
1060
1070 .C0 NOP
1080 .C1 NOP
1090 .C2 NOP
1100 .C3 NOP

```

```

1110 .C4 NOP
1120 .C5 NOP
1130 .C6 NOP
1140 .C7 NOP
1150 .C8 NOP
1160 .C9 NOP
1170 .C10 NOP
1180 .C11 NOP
1190 .C12 NOP
1200 .ZERO
1210
1220 /Fills the control block, C0 to C12
1230 /with zeros.
1240
1250 LDY #0
1260 .Z2
1270 LDA #0
1280 STA C0,Y
1290 INY
1300 TYA
1310 CMP #&0D : BNE Z2
1320 RTS
1330
1340 .TRED
1350
1360 /A time-wasting routine, entered when
1370 /waiting for consecutive interrupts.
1380
1390 INC F1
1400 LDA F1
1410 CMP #&FF : BNE TRED
1420 INC F2
1430 LDA F2
1440 CMP #&FF : BNE TRED
1450 RTS
1460
1470 .TEA
1480
1490 /Procedure entered when an interrupt from
1500 /the interface is received. Reads in the
1510 /the interrupt and compares it with a
1520 /linefeed and "=" (ASCII code &0A and &3D).
1530 /When the end of a run is indicated by
1540 /an "=", R4 is set to 0 and X1 to &3D.
1550
1560 PHA:TXA:PHA:TYA:PHA
1570 LDA #&0
1580 STA F1 : STA F2
1590 LDA &FCFF
1600 JSR &FFEE
1610 CMP #&0A : BEQ EXIT
1620 JSR STRING
1630 LDX #&FF
1640 CPX R4 : BNE EXIT
1650 CMP #&3D : BNE YES
1660 STA X1

```

```

1670 LDA #&0
1680 STA R4
1690 JMP EXIT
1700 .YES
1710
1720 /When a valid character is received.
1730 /after the string "RUN" has been detected
1740 /it is stored in the next free memory
1750 /locations.
1760
1770 LDY F3
1780 STA (&80),Y
1790 JSR TIPLE
1800 .EXIT
1810
1820 /Recovers the program variables from
1830 /the stack at the end of the interrupt
1840 /routine.
1850
1860 PLA:TAY:PLA:TAX:PLA
1870 RTI
1880
1890 .X1 NOP
1900 .R0 NOP
1910 .R1 NOP
1920 .R2 NOP
1930 .R3 NOP
1940 .R4 NOP
1950 .STRING
1960
1970 /Compares the interrupt data in R0 to
1980 /R2 with the string "RUN". If true then
1990 /R4 is set to &FF and R0 to R2 are zeroed.
2000
2010 PHA
2020 STA R3
2030 LDA #&52
2040 CMP R0 : BNE NO
2050 LDA #&55
2060 CMP R1 : BNE NO
2070 LDA #&4E
2080 CMP R2 : BNE NO
2090 LDA #&FF
2100 STA R4
2110 JSR SRUN
2120 LDA #&0
2130 STA R0 : STA R1 : STA R2
2140 PLA
2150 RTS
2160
2170 .NO
2180
2190 /If R0 to R2 are not equal to the string
2200 /"RUN", the data is shifted.
2210
2220 LDA R1 : STA R0

```

```

2230 LDA R2 : STA R1
2240 LDA R3 : STA R2
2250 PLA
2260 RTS
2270
2280 .SRUN
2290
2300 /If R0 to R2 are equal to "RUN", these
2310 /data are stored in the next free memory
2320 /locations.
2330
2340 PHA
2350 LDY F3
2360 LDA #&0D:STA (&80),Y
2370 JSR TIPLE:LDY F3
2380 LDA R0:STA (&80),Y
2390 JSR TIPLE:LDY F3
2400 LDA R1:STA (&80),Y
2410 JSR TIPLE:LDY F3
2420 LDA R2:STA (&80),Y
2430 JSR TIPLE:LDY F3
2440 LDA #&20:STA (&80),Y
2450 JSR TIPLE:LDY F3
2460 PLA
2470 RTS
2480
2490 .F1 NOP
2500 .F2 NOP
2510 .F3 NOP
2520 .TIPLE
2530
2540 /Increments the value of the next free
2550 /memory location for data storage.
2560 /F3 holds a counter (0 to &FF). When
2570 /a page boundary is reached (F3=&FF),
2580 /the address in &81 is incrementedand
2590 /F3 is set to zero.
2600
2610 LDA F3
2620 CMP #&FF : BNE TRIP
2630 LDA #0
2640 STA F3
2650 INC &81
2660 JMP TENT
2670 .TRIP
2680 INC F3
2690 .TENT RTS
2700
2710 .PTD
2720
2730 /Transfers data from the memory to file.
2740
2750 LDA H1
2760 STA C0
2770 SEC
2780 LDA F3

```

```
2790 SBC &80
2800 STA C5
2810 LDA &81
2820 SBC &23
2830 STA C6
2840 LDA &23
2850 STA C2
2860 LDX #(C0 MOD 256) : LDY #(C0 DIV 256) : LDA &2
2870 JSR &FFD1
2880 RTS
2890
2900 .RESET
2910
2920 /Resets the values for the next free
2930 /memory locations to their initial
2940 /values after data transfer.
2950
2960 LDA &23
2970 STA &81
2980 LDA #0
2990 STA &80 : STA F3 : STA C1 : STA X1
3000 RTS
3010
3020 .CLF
3030
3040 /Closes the data file.
3050
3060 LDA #0
3070 LDY C0
3080 JSR &FFCE
3090 RTS
3100 .ETS RTS:]
3110 U=U+3 : IF U=3 THEN 20
```

APPENDIX 3 : PROGRAM SEARCH

```

10 REM Condenses the information on the raw
20 REM data disc by picking out the %areas
30 REM of the user-selected G.C. peaks for
40 REM each runnumber.
50
60 @%-10
70 CLS
80 *B:
90 PROCinput
100 PROCtitle
110 REPEAT
120   FOR count=0 TO num-1
130     area(count)=0
140   NEXT count
150   runnum$=FNrunnum
160   PROCstart
170   IF char<>0 THEN PROCsearch
180   PROCcontrol
190 UNTIL EOF#chan
200 PROCend
210 END
220
230 DEF PROCsearch
240
250 REM Sifts through the data for each runnumber,
260 REM searching for the specified peaks,
270 REM held in the array 'time'. 'Sign' is set
280 REM to unity if a peak of higher R.T.
290 REM than that searched for is found.
300 REM This allows for comparison with later
310 REM peaks in 'time' before searching
320 REM for more peaks using PROCnewline
330
340   FOR count=0 TO num-1
350     sign=0
360     IF sign=0 THEN PROCnewline
370     ret_time(count)=char
380     IF ret_time(count)<((time(count)+10) AND (ret
_time(count)>time(count)-10) THEN PROCarea:area(count)=area:sign=0
390     IF ret_time(count)>(time(count)+10) THEN sign=1
400     IF ret_time(count)<((time(count)-10) THEN count=count-1
410   NEXT count
420 ENDPROC
430
440 DEF PROCinput
450
460 REM Opens the raw data file specified,
470 REM prompts for the R.T.'s of interest in
480 REM the chromatographs(stored in 'time'),
490 REM and prompts for the desired outputs to
500 REM disc and printer.
510

```

```

520 PRINT "This program condenses the information"
    "on your data discs by searching for the""peaks wh
ich you request"
530 PRINT
540 INPUT "    What name did you give to""    you
r data file",file$
550 chan=OPENIN(file$)
560 PRINT
570 PRINT "You'll be asked to supply the retention
""times of all the peaks you wish to be""searched
for. These will have tolerance""limits of +/-10 seco
nds attached to them."
580 PRINT "THESE RETENTION TIMES MUST BE SUPPLIED"
    "IN THE ORDER OF SHORTEST R.T. FIRST!"
590 PRINT
600 INPUT "    How many peaks are to be""    sear
ched for",num
610 DIM time(num+1)
620 time(num)=0
630 PRINT
640 FOR I=0 TO num-1
650   INPUT "    The retention time of the""    pe
ak to be searched for is",time(I)
660   PRINT
670 NEXT I
680 PRINT "    Do you want the data""    stored o
n disc (Y/N)?"
690 disc$=GET$
700 IF disc$="Y" THEN PROCfile(num)
710 IF disc$="Y" THEN FOR I=0 TO num-1:PRINT#chan1
,time(I):NEXT I
720 PRINT
730 PRINT "    Do you want the data ""    printed
(y/n)?"
740 ans$=GET$
750 ENDPROC
760
770 DEF PROCtitle
780
790 REM Prints the title of the data table,
800 REM and dimensions the arrays 'ret_time'
810 REM and 'area' to store the R.T.'s and %areas
820 REM of the G.C. peaks.
830
840 CLS
850 IF ans$="Y" THEN VDU2 ELSE VDU3
860 PRINT "*****"
870 PRINT "***DATA FILE IS ";file$;***"
880 PRINT "*****"
890 PRINT:PRINT
900 PRINT TAB(3) "RUN NUM";
910 FOR I=0 TO num-1
920   PRINT TAB(13+(11*I));time(I);"s";
930 NEXT I
940 FOR I=0 TO num
950   PRINT TAB(11*I);"_____";
960 NEXT I
970 PRINT

```

```

980 DIM ret_time(num)
990 DIM area(num)
1000 DIM unit(5)
1010 @%=&0102030B
1020 ENDPROC
1030
1040 DEF PROCcontrol
1050
1060 REM Organises the output to the screen.
1070 REM printer and disc.
1080
1090 PRINT TAB(4);runnum$;
1100 IF disc$="Y" THEN PROCprint(runnum$)
1110 FOR count=0 TO num-1
1120   PRINT area(count);
1130   IF disc$="Y" THEN PROCprintarea(area(count))
1140 NEXT count
1150 PRINT
1160 ENDPROC
1170
1180 DEF PROCend
1190
1200 REM Closes all data files and runs the
1210 REM program'CHOSE' outlining the alternatives
1220 REM available for further data manipulation.
1230
1240 CLOSE #chan
1250 IF disc$="Y" THEN CLOSE#chan1
1260 VDU3
1270 *A:
1280 CHAIN"CHOSE"
1290 END
1300 ENDPROC
1310
1320 DEF FNrunnum
1330
1340 REM Reads in characters from the data file
1350 REM until the string 'RUN' is recognised.
1360 REM A search for carriage return (ASCII
1370 REM code 13) is made, the previous two
1380 REM digits form the runnumber.
1390
1400 char1$=CHR$(BGET#(chan))
1410 char2$=CHR$(BGET#(chan))
1420 char3$=CHR$(BGET#(chan))
1430 REPEAT
1440   char1$=char2$
1450   char2$=char3$
1460   char3$=CHR$(BGET#(chan))
1470   IF EOF#chan THEN PROCend
1480 UNTIL char1$="R" AND char2$="U" AND char3$="N"
1490 REPEAT
1500   char1$=char2$
1510   char2$=char3$
1520   char3$=CHR$(BGET#(chan))
1530   char3=ASC(char3$)
1540 UNTIL char3=13
1550 char$=char1$+char2$
1560 =char$

```

```

1570
1580 DEF PROCstart
1590
1600 REM Reads in characters from the data file.
1610 REM until the string 'CONC' is recognised,
1620 REM signifying the start of the %area data.
1630 REM If 'NO' is found, char is set to zero
1640 REM indicating that there are no peaks
1650 REM in the run.
1660
1670 char=1
1680 char1$=CHR$(BGET#(chan))
1690 char2$=CHR$(BGET#(chan))
1700 char3$=CHR$(BGET#(chan))
1710 char4$=CHR$(BGET#(chan))
1720 REPEAT
1730 IF char1$="N" AND char2$="O" THEN char=0
1740 char1$=char2$
1750 char2$=char3$
1760 char3$=char4$
1770 char4$=CHR$(BGET#(chan))
1780 UNTIL (char1$="C" AND char2$="O" AND char3$="N"
AND char4$="C")OR(char=0)
1790 ENDPROC
1800
1810 DEF PROCnewline
1820
1830 REM Reads in characters until the end of
1840 REM a series of numbers is recognised
1850 REM (ASCII code 32). This is converted
1860 REM to the R.T. of the peak.
1870
1880 char1$=CHR$(BGET#(chan))
1890 char2$=CHR$(BGET#(chan))
1900 char3$=CHR$(BGET#(chan))
1910 char4$=CHR$(BGET#(chan))
1920 REPEAT
1930 char1$=char2$
1940 char2$=char3$
1950 char3$=char4$
1960 char4$=CHR$(BGET#(chan))
1970 char2=ASC(char2$)
1980 char3=ASC(char3$)
1990 char4=ASC(char4$)
2000 UNTIL char3>=48 AND char3<=58 AND char4=32
2010 char1=ASC(char1$)-48
2020 char2=ASC(char2$)-48
2030 char3=ASC(char3$)-48
2040 IF char1<0 THEN char=char2*10+char3 ELSE char=ch
ar1*100+char2*10+char3
2050 ENDPROC
2060
2070 DEF PROCarea
2080
2090 REM Reads in characters until a decimal
2100 REM point is recognised in char3 (ASCII
2110 REM code 46). The characters are converted
2120 REM to the %area for the G.C. peak.
2130

```

```

2140 char1$=CHR$(BGET#(chan))
2150 char2$=CHR$(BGET#(chan))
2160 char3$=CHR$(BGET#(chan))
2170 char4$=CHR$(BGET#(chan))
2180 char5$=CHR$(BGET#(chan))
2190 char6$=CHR$(BGET#(chan))
2200 char7$=CHR$(BGET#(chan))
2210 REPEAT
2220   char1$=char2$
2230   char2$=char3$
2240   char3$=char4$
2250   char4$=char5$
2260   char5$=char6$
2270   char6$=char7$
2280   char7$=CHR$(BGET#(chan))
2290   char3=ASC(char3$)
2300 UNTIL char3=46
2310 char1=ASC(char1$)-48
2320 char2=ASC(char2$)-48
2330 char4=ASC(char4$)-48
2340 char5=ASC(char5$)-48
2350 char6=ASC(char6$)-48
2360 IF char1<0 THEN area=char2*1+char4*.1+char5*.01+
char6*.001 ELSE area=char1*10+char2*1+char4*.1+char5*.
01+char6*.001
2370 ENDPROC
2380
2390 DEF PROCfile(num)
2400
2410 REM Opens a data file for the storage
2420 REM of the condensed G.C. data.
2430
2440 PRINT
2450 PRINT "    What file name do you"
2460 PRINT "    wish to store the data"
2470 INPUT "    under",file1$
2480 chan1=OPENOUT(file1$)
2490 PRINT#chan1,file$,num
2500 ENDPROC
2510
2520 DEF PROCprint(value$)
2530 PRINT#chan1,value$
2540 ENDPROC
2550
2560 DEF PROCprintarea(area)
2570 PRINT#chan1,area
2580 ENDPROC

```

APPENDIX 4 : PROGRAM KINETIC

```

10 REM Allows the calculation of mean areas
20 REM and standard deviations of G.C. peaks
30 REM from data files created by the program
40 REM "SEARCH". If required kinetic data can
50 REM be calculated in conjunction with user
60 REM supplied experimental conditions.
70
80 @%-10
90 *B:
100 CLS
110 PRINT "      What name did you give to "
120 INPUT "      your data file",file$
130 chan=OPENIN(file$)
140 PROCinput
150 PROCtitle
160 PROCvalue
170 PRINT:PRINT
180 VDU3
190 PRINT "      Do you want to calculate "
200 PRINT "      rate constants?(Y/N)"
210 VDU2
220 ans$=GET$
230 IF ans$="Y" THEN PROCKinetic
240 PROCend
250 END
260
270 DEF PROCinput
280
290 REM Dimensions arrays to hold the various
300 REM experimental conditions and asks for
310 REM the initial and final runnumbers
320 REM corresponding to each set of conditions.
330
340 PRINT
350 INPUT "      Number of times that conditions were
varied",num
360 DIM WHSV(num)
370 DIM DELTAWHSV(num)
380 DIM T(num)
390 DIM i_runnum(num)
400 DIM f_runnum(num)
410 FOR I=0 TO num-1
420 PRINT
430 INPUT "      Initial run number is",i_runnum(I)

440 INPUT "      Final run number is",f_runnum(I)
450 dim=f_runnum(I)-i_runnum(I)
460 IF I=0 THEN size=dim
470 IF I<>0 AND dim>size THEN size=dim
480 IF f_runnum(I)-i_runnum(I)<=1 THEN PRINT"      A
larger range is required,please enter another set of
values":I=I-1
490 NEXT I
500 CLS
510 ENDPROC

```

```

520
530 DEF PROCtitle
540
550 REM Prints the title of the data table,
560 REM and dimensions the arrays 'store' and
570 REM 'buffer' to store peak areas and
580 REM the array 'peak' to store the retention
590 REM times of the G.C. peaks.
600
610 INPUT#chan,title$
620 VDU2
630 PRINT:PRINT
640 PRINT"*****"
650 PRINT "**DATA FILE IS ";title$;"**"
660 PRINT"*****"
670 PRINT
680 PRINT TAB(27);"MEAN AREAS AND STANDARD DEVIATIO
NS"
690 INPUT#chan,peaknum
700 DIM store(peaknum,size)
710 DIM peak(peaknum)
720 DIM buffer(peaknum)
730 PRINT TAB(8);"RANGE ";
740 FOR I=0 TO (peaknum-1)
750 INPUT#chan,peak(I)
760 PRINT TAB((22*I)+20) peak(I);"s";
770 NEXT I
780 PRINT TAB(8);"_____";
790 FOR I=1 TO peaknum
800 PRINT TAB(22*I);"_____";
810 NEXT I
820 PRINT:PRINT
830 ENDPROC
840
850 DEF PROCvalue
860
870 REM For each runnumber range, calls PROCmean
880 REM to calculate and print the mean %areas
890 REM of the G.C. peaks. At the end of the
900 REM calculations, ends the data table.
910
920 DIM mean(peaknum,num):DIM error(peaknum,num)
930 FOR I=0 TO num-1
940 FOR J=0 TO peaknum-1
950 mean(J,I)=0:error(J,I)=0
960 NEXT J
970 NEXT I
980 FOR count=0 TO num-1
990 IF count=0 THEN PROCmean(0,i_runnum(count),f_r
unnum(count)) ELSE PROCmean(f_runnum(count-1),i_runnu
m(count),f_runnum(count))
1000 NEXT count
1010 PRINT TAB(8);"_____";
1020 FOR I=1 TO peaknum
1030 PRINT TAB(22*I);"_____";
1040 NEXT I
1050 ENDPROC

```

```

1060
1070 DEF PROCend
1080
1090 REM Closes the data file and turns off printer.
1100
1110 CLOSE#chan
1120 VDU3
1130 END
1140 ENDPROC
1150
1160 DEF PROCmean(end,initial,final)
1170
1180 REM Calls PROCsearch to find the first
1190 REM runnumber in the range specified.
1200 REM Reads in the runnumber and %areas for
1210 REM each chromatograph in the range specified.
1220
1230 LOCAL I
1240 range=final-initial
1250 start=initial-1
1260 div=0
1270 IF initial-end>1 THEN PROCsearch
1280 FOR I=0 TO final-initial
1290   stop=1
1300   INPUT#chan,RUNNUM$
1310   FOR J=0 TO peaknum-1
1320     INPUT#chan,buffer(J)
1330   NEXT J
1340   FOR K=0 TO peaknum-1
1350     store(K,I)=buffer(K)
1360   NEXT K
1370 NEXT I
1380 PROCcalc(initial,final)
1390 IF div<>0 THEN PROCprint ELSE PRINT initial;"-";
;final;"      ";      ----NO PEAKS DETECTED----"
1400 ENDPROC
1410
1420 DEF PROCprint
1430
1440 REM Prints out the mean and standard
1450 REM deviations for the peaks in each
1460 REM range specified.
1470
1480 PRINT initial;"-";final;"      ";
1490 IF final<10 THEN PRINT" ";
1500 @%=&02030A
1510 FOR I=0 TO peaknum-1
1520   PRINT TAB((22*I)+20) mean(I,count);"+/-";error
(I,count);"      ";
1530 NEXT I
1540 @%=10
1550 PRINT
1560 ENDPROC
1570

```

```

1580 DEF PROCsearch
1590
1600 REM Searches for the initial runnumber
1610 REM in the range specified by user.
1620 REM If an end of data occurs the program
1630 REM jumps to the end (PROCend)
1640
1650 REPEAT
1660   INPUT#chan,RUNNUM$
1670   FOR I=0 TO peaknum-1
1680     INPUT#chan,buffer
1690   NEXT I
1700   IF start<10 THEN start$=" "+STR$(start) ELSE s
tart$=STR$(start)
1710 UNTIL RUNNUM$=start$ OR EOF#chan
1720 X=EOF#chan
1730 IF X=-1 THEN PROCend
1740 ENDPROC
1750
1760 DEF PROCret_time
1770
1780 REM Searches for the retention-time
1790 REM corresponding to the reactant(RT)
1800
1810 LOCAL I
1820 det=0
1830 FOR I=0 TO peaknum-1
1840   IF peak(I)=RT THEN I=peaknum+1
1850   IF I<(peaknum+1) THEN det=det+1
1860 NEXT I
1870 ENDPROC
1880
1890 DEF PROCKinetic
1900
1910 REM Calculates the flow-rates,pressures,
1920 REM concentrations and integrated rates
1930 REM for each set of experimental conditions.
1940
1950 VDU3
1960 PRINT
1970 PRINT TAB(4);"The retention times of the peaks"
1980 PRINT "which have been stored are:"
1990 PRINT
2000 FOR I=0 TO peaknum-1
2010   PRINT TAB(4);I;". ";peak(I);"sec"
2020   PRINT
2030 NEXT I
2040 REPEAT
2050   PRINT TAB(4) "Input the number that correspond
s"
2060   INPUT "to the retention time of the reactant",
RTR%
2070 UNTIL RTR%>=0 AND RTR%<=(peaknum-1)
2080 RT=peak(RTR%)
2090 PROCret_time
2100 PRINT
2110 VDU2

```

```

2120 PROCdata
2130 PROCzero
2140 FOR I=0 TO num-1
2150   conv=mean(det,I):deltaconv=error(det,I)
2160   PRINT "*****"
2170   PRINT "**CALCULATION NUMBER ";I+1;"**"
2180   PRINT "*****"
2190   @X=&030A
2200   PRINT
2210   PRINT
2220   PRINT "OUTPUT DATA IS:"
2230   T=T(I)+273
2240   mol_flow=WHSV(I)*MZ/(60*92)
2250   max=(WHSV(I)+DELTAWHSV(I))*(MZ+.0002)/(92*60)
2260   min=(WHSV(I)-DELTAWHSV(I))*(MZ-.0002)/(92*60)
2270   PRINT TAB(4) "MOLECULAR FLOW IS ";mol_flow;" m
ol/min"
2280   PRINT TAB(17) "(MAX ";max;" mol/min)"
2290   PRINT TAB(17) "(MIN ";min;" mol/min)"
2300   press=760
2310   max_press=760
2320   min_press=760
2330   old_press=760
2340   max_old_press=760
2350   min_old_press=760
2360   vol_flow=mol_flow*22.4*T*1000/273
2370   max=max*22.4*(T+2)*1000/273
2380   min=min*22.4*(T-2)*1000/273
2390   REPEAT
2400     vol_flow=vol_flow*old_press/press
2410     max=max*max_old_press/max_press
2420     min=min*min_old_press/min_press
2430     old_press=press
2440     max_old_press=max_press
2450     min_old_press=min_press
2460     press=760+12.69*vol_flow
2470     max_press=760+12.69*max
2480     min_press=760+12.69*min
2490   UNTIL (press-old_press)<.05 AND (press-old_pre
ss)>-.05
2500   PRINT TAB(4) "VOLUMETRIC FLOW IS ";vol_flow;"
ml/min"
2510   PRINT TAB(18) "(MAX ";max;" ml/min)"
2520   PRINT TAB(18) "(MIN ";min;" ml/min)"
2530   PRINT TAB(4) "INLET PRESSURE IS ";press;" mm H
g"
2540   PRINT TAB(17) "(MAX ";max_press;" mm/Hg)"
2550   PRINT TAB(17) "(MIN ";min_press;" mm/Hg)"
2560   c_time=MZ*60/vol_flow
2570   max_c_time=(MZ+.0002)*60/max
2580   min_c_time=(MZ-.0002)*60/min
2590   PRINT TAB(4) "CONTACT TIME IS ";c_time;" sec"
2600   PRINT TAB(15) "(MAX ";max_c_time;" sec)"
2610   PRINT TAB(15) "(MIN ";min_c_time;" sec)"
2620   init_conc=press*273/(22.4*T*760)
2630   max_init_conc=max_press*273/(22.4*(T-2)*760)
2640   min_init_conc=min_press*273/(22.4*(T+2)*760)

```

```

2650 PRINT TAB(4) "INITIAL CONC IS ";init_conc;" mo
1/litre"
2660 PRINT TAB(15) "(MAX ";max_init_conc;" mol/litr
e)"
2670 PRINT TAB(15) "(MIN ";min_init_conc;" mol/litr
e)"
2680 final_conc=press*273*conv/(T*22.4*100*760)
2690 max_final_conc=max_press*273*(conv+deltacnv)/
((T+2)*22.4*100*760)
2700 min_final_conc=min_press*273*(conv-deltacnv)/
((T-2)*22.4*100*760)
2710 PRINT TAB(4) "FINAL CONC IS ";final_conc;" mo
1/litre"
2720 PRINT TAB(13) "(MAX ";max_final_conc;" mol/lit
re)"
2730 PRINT TAB(13) "(MIN ";min_final_conc;" mol/lit
re)"
2740 PRINT
2750 PRINT "***KINETIC DATA FOR FIRST ORDER KINETICS
**"
2760 PRINT
2770 rate=LOG(final_conc/init_conc)
2780 max_rate=LOG(max_final_conc/max_init_conc)
2790 min_rate=LOG(min_final_conc/min_init_conc)
2800 PRINT TAB(4) "INTEGRATED RATE IS ";rate
2810 PRINT TAB(18) "(MAX ";max_rate;")"
2820 PRINT TAB(18) "(MIN ";min_rate;")"
2830 PROCtable
2840 PROCstore
2850 PRINT
2860 PRINT "***KINETIC DATA FOR SECOND ORDER KINETIC
S**"
2870 PRINT
2880 rate=(1/init_conc)-(1/final_conc)
2890 max_rate=(1/min_init_conc)-(1/min_final_conc)

2900 min_rate=(1/max_init_conc)-(1/max_final_conc)
2910 PRINT TAB(4) "INTEGRATED RATE IS ";rate
2920 PRINT TAB(18)"(MAX ";max_rate;")"
2930 PRINT TAB(18)"(MIN ";min_rate;")"
2940 PROCtable
2950 PRINT:PRINT
2960 @X=10
2970 NEXT I
2980 VDU3
2990 PRINT "      Do you want to calculate the"
3000 PRINT "      Arrhenius parameters? (Y/N)"
3010 fit$=GET$
3020 IF fit$="Y" THEN PROClinefit
3030 ENDPROC
3040
3050 DEF PROCdata
3060
3070 REM Reads in the variables for each
3080 REM set of experimental conditions.
3090

```

```

3100 LOCAL I
3110 INPUT TAB(4) "Mass of zeolite (g)",MZ
3120 PRINT:PRINT
3130 FOR I=0 TO num-1
3140   INPUT TAB(4)"WHSV is (/Hr)",WHSV(I)
3150   INPUT TAB(4) "Error in WHSV is (/HR)",DELTAWHS
V(I)
3160   INPUT TAB(4) "Temperature is (Cent)",T(I)
3170   PRINT:PRINT
3180 NEXT I
3190 ENDPROC
3200
3210 DEF PROCcalc(initial,final)
3220
3230 REM Calculates the mean and S.D. for each
3240 REM peak in the runnumber range. If
3250 REM any of the peaks are 0 then stop
3260 REM is set to 0 and the data from that
3270 REM particular runnumber is discarded.
3280
3290 LOCAL I
3300 FOR I=0 TO range
3310   stop=1
3320   FOR K=0 TO peaknum-1
3330     IF store(K,I)=0 THEN stop=0
3340   NEXT K
3350   IF stop<>0 THEN FOR M=0 TO peaknum-1:mean(M,co
unt)=mean(M,count)+store(M,I):NEXT M:div=div+1
3360 NEXT I
3370 FOR N=0 TO peaknum-1
3380   mean(N,count)=(mean(N,count))/div
3390 NEXT N
3400 FOR I=0 TO final-initial
3410   stop=1
3420   FOR K=0 TO peaknum-1
3430     IF store(K,I)=0 THEN stop=0
3440   NEXT K
3450   IF stop<>0 THEN FOR M=0 TO peaknum-1:error(M,c
ount)=error(M,count)+((store(M,I)-mean(M,count))*(sto
re(M,I)-mean(M,count))):NEXT M
3460 NEXT I
3470 FOR I=0 TO peaknum-1
3480   error(I,count)=SQR(error(I,count)/div)
3490 NEXT I
3500 ENDPROC
3510
3520 DEF PROCtable
3530
3540 REM Calculates and prints the rate
3550 REM data for activation energy plots.
3560
3570 PRINT
3580 k=-rate/c_time
3590 max_k=-max_rate/min_c_time
3600 min_k=-min_rate/max_c_time
3610 IF k>0 THEN nat_log_k=LN(k) ELSE nat_log_k=0

```

```

3620 IF max_k>0 THEN max_nat_log_k=LN(max_k) ELSE ma
x_nat_log_k=0
3630 IF min_k>0 THEN min_nat_log_k=LN(min_k) ELSE mi
n_nat_log_k=0
3640 max_RT=1/(T-2)
3650 min_RT=1/(T+2)
3660 PRINT TAB(14),"VALUE"," ","MAX"," ","MIN"
3670 PRINT"*****"
*****
3680 PRINT TAB(4);"TEMP(K)";TAB(20);T;TAB(40);T+2;TA
B(60);T-2
3690 PRINT TAB(4);"k(/sec)";TAB(20);k;TAB(40);max_k;
TAB(60);min_k
3700 PRINT TAB(4);"LN(k) ",TAB(20);nat_log_k;TAB(40
);max_nat_log_k;TAB(60);min_nat_log_k
3710 PRINT TAB(4);"1/TEMP ";TAB(20);1/T;TAB(40);max
_RT;TAB(60)min_RT
3720 PRINT"*****"
*****
3730 ENDPROC
3740
3750 DEF PROCzero
3760
3770 REM Sets the variables used in the
3780 REM linear regression to zero
3790
3800 SX=0
3810 SY=0
3820 SXX=0
3830 SYX=0
3840 SXY=0
3850 ENDPROC
3860
3870 DEF PROCstore
3880
3890 REM Accumulates the data required
3900 REM for the linear regression
3910
3920 X=1/T
3930 Y=nat_log_k
3940 XX=X^2
3950 YY=Y^2
3960 XY=X*Y
3970 SX=SX+X
3980 SY=SY+Y
3990 SXY=SXY+XY
4000 SXX=SXX+XX
4010 SYX=SYX+XY
4020 ENDPROC
4030
4040 DEF PROClinefit
4050
4060 REM Calculates the linear regression
4070 REM parameters for the activation
4080 REM energy plots.
4090

```

```

4100 div=(num*SXX)-(SX^2)
4110 grad=((num*SXY)-(SX*SY))/div
4120 con=(SY*SXX-SX*SXY)/div
4130 dev=(SQR(num*SY*SY-SY^2-((num*SXY-SX*SY)^2/div)))
/num
4140 sdgrad=num*dev/(SQR((num-2)*div))
4150 sdcon=num*dev*(SQR(SXX))/(SQR(num*(num-2)*div))
4200 corr=((grad^2)*div)/((num*SY*SY)-(SY^2))
4210 VDU2
4220 @%=&02010A
4230 PRINT "ACTIVATION ENERGY IS ";(-grad*8.314/1000
);" KJ/mol"
4240 PRINT "PRE-EXPONENTIAL FACTOR IS ";con
4250 @%=&02030A
4260 PRINT "CORRELATION COEFFICIENT IS ";corr
4270 @%=&02010A
4280 PRINT "DEVIATION IN PRE-EXPONENTIAL FACTOR IS "
;sdcon
4290 PRINT "DEVIATION IN ACTIVATION ENERGY IS ";-sdg
rad*8.314/1000;" KJ/mol"
4300 ENDPROC

```

REFERENCES

1. R.M. Barrer
Zeolites and Clay Minerals as Sorbents and Molecular Sieves
Academic Press, (1978)
2. R.J. Argauer and G.R. Landolt
U.S. Patent, 3,702,886 (1972)
3. D.W. Breck; W.G. Eversole; R.M. Milton; T.B. Reed and T.L. Thomas
J. Amer. Chem. Soc.
78, 5963, (1956)
4. G.T. Kokotailo; S.L. Lawton; D.H. Olson and W.H. Meier
Nature
272, 437 (1978)
5. R.W. Grose and E.M. Flanigen
U.S. Patent, 4,061,724 (1979)
6. D.G. Hay; H. Jaeger and G.W. West
J. Phys. Chem
89, 1070, (1985)
7. J. Klinowski; T.A. Carpenter and L.F. Gladden
Zeolites
7, 73, (1987)
8. C.A. Fyfe; G.J. Kennedy; C.T. De Schutter and G.T. Kokotailo
J. Chem. Soc., Chem. Comm.
8, 541, (1984)
9. H. Lerner; M. Draeger; J. Steffen and K.K. Unger
Zeolites
5, 131, (1985)
10. G.T. Kokotailo and W.M. Meier
Chem. Soc. Spec. Pub.
33, 133, (1979), Ed. R.P. Townsend
11. D.H. Olson; G.T. Kokotailo and S.L. Lawton
J. Phys. Chem.
85, 2238, (1981)
12. G.T. Kokotailo; P. Chu; S.L. Lawton and W.M. Meier
Nature
275, 119, (1978)
13. S.M. Meier and D.H. Olson
Atlas of Zeolite Structure Types
Juris Druck und Verlag AG, (1978)

14. S.L. Suib; G.D. Stucky and R.J. Blattner
J. Catal
65, 174, (1980)
15. C.E. Lyman; P.W. Betteridge and E.F. Mason
ACS Symp. Ser. (Intrazeolite Chemistry)
218, 275 (1983)
16. E.G. Derouane; S. Detremmerie; Z. Gabelica and N. Blom
Appl. Catal.
1, 201, (1981)
17. R. Von Ballmoos and W.M. Meier
Nature
289, 782, (1981)
18. J.G. Fripart; F. Berger-Andre; J.M. Andre and E.G. Derouane
Zeolites
3, 306, (1983)
19. E.G. Derouane and J.G. Fripart
Zeolites
5, 165, (1985)
20. L. Zenyi; Z. Nangjin; Y. Qin; L. Guanglie; L. Wangwong; W. Shuju; Z. Youshi and L. Bingxiong
Proc. 7th. Int. Zeolite Conf.
Butterworths, 415, (1986)
21. A.W. Chester; Y.F. Chu; R.M. Dessau; G.T. Kerr and C.T. Kresge
J. Chem. Soc., Chem. Comm.
289, (1985)
22. M. Hunger; J. Karger; H. Pfeifer; J. Caro; B. Zibrowius; M. Bulow and R. Mostowicz
J. Chem. Soc., Faraday Trans. I
83(11), 3459, (1987)
23. J. Datka and E. Tuznik
Zeolites
5, 230, (1985)
24. G.L. Woolery; L.B. Alemany; R.M. Dessau and A.W. Chester
Zeolites
6, 14, (1986)
25. R.M. Dessau; K.D. Schmitt; G.T. Kerr; G.L. Woolery and L.B. Alemany
J. Catal.
104, 484, (1987)
26. A. Araya and B.M. Lowe
Zeolites
6, 111, (1986)

27. J. Dwyer; F.R. Fitch; G. Qin and J.C. Vickerman
J. Phys. Chem.
86, 4574, (1982)
28. G. Debras; A. Gource; J.B. Nagy and G. De Clippeleir
Zeolites
6, 241, (1986)
29. P.A. Jacobs and R. von Ballmoos
J. Phys. Chem.
86, 3050, (1982)
30. N.Y. Topsoe; K. Pederson and E.G. Derouane
J. Catal.
70(1), 41, (1981)
31. P.A. Jacobs and H.K. Beyer
J. Phys. Chem.
83, 1174, (1979)
32. S. Beran; P. Jiru and B. Wichterlova
J. Phys. Chem.
85, 1951, (1981)
33. R.D. Shannon; K.H. Gardner; R.H. Staley; G. Bergeret, P.
Gallezot and A. Auroux
J. Phys. Chem.
89(22), 4778, (1985)
34. P.A. Jacobs; H.E. Leeman and J.B. Utterhoeven
J. Catal.
33, 17, (1974)
35. D.E. Blackmond and J.G. Goodwin Jr.
J. Catal.
78, 34, (1982)
36. V.R. Choudhary and S.G. Pataskar
Zeolites
6(4), 307, (1986)
37. A. Auroux; V. Bolis; P. Wierzchowski; P.C. Gravelle and J.C.
Verdine
J. Chem. Soc., Faraday Trans. I
75, 2544, (1979)
38. J. Dakta and E. Tuznik
J. Catal.
102, 43, (1986)
39. V.R. Choudhary and V.S. Nayak
Zeolites
5, 15, (1985)

40. J. Dwyer
Chem. and Ind.
April 1984
41. E.G. Derouane
Intercalation Chemistry
Academic Press, 101, (1982)
42. P.B. Weisz
Chem. Technol.
3, 498, (1973)
43. D.M. Ruthven
ACS Symp. Ser
218, 345, (1983)
44. P. Wu; A. Debebe and Y.H. Ma
Zeolites
3, 118, (1983)
45. D.H. Olson and W.O. Haag
ACS Symp. Ser.
248, 275, (1983)
46. R. Le Van Mao; V. Ragaini; G. Leofanti and R. Fais
J. Catal.
81, 418, (1983)
47. P. Wu and Y.H. Ma
Proc. 6th. Int. Zeolite Conf.
Butterworths, (1983)
48. P.B. Weisz and V.J. Frelette
J. Phys. Chem.
64, 382, (1960)
49. J.F. Tempere and B. Imelik
Bull. Soc. Chim. Fr.
4227, (1970)
50. S.M. Csicsery
Zeolites
4, 202, (1984)
51. E.G. Derouane and Z. Gabelica
J. Catal.
65, 486, (1980)
52. E.G. Derouane; P.A. Jacobs and Z. Gabelica
J. Catal.
70, 238, (1981)
53. C.G. Pope
J. Catal.
72, 174, (1981)

54. E.G. Derouane
J. Catal.
72, 177, (1981)
55. F.A. Lowenheim and M.K. Moran
Industrial Chemicals, 4th. Edition
John Wiley, 874, (1975)
56. L.B. Young; S.A. Butter and W.W. Kaeding
J. Catal.
76, 418, (1982)
57. L.B. Young; S.A. Butter and W.W. Kaeding
J. Catal.
69, 392, (1981)
58. N.Y. Chen; W.W. Kaeding and F.G. Dwyer
J. Amer. Chem. Soc.
101, 6783, (1979)
59. P. Ratnasamy; G.P. Babu; A.J. Chandwadkar and S.B. Kulkarni
Zeolites
6(2), 98, (1986)
60. P. Dejaifve; A. Auroux; P.C. Gravelle; J.C. Vedrine; Z. Gabelica and E.G. Derouane
J. Catal.
70, 123, (1981)
61. V. Mavrodinova; C. Minchev; V. Penchev and H. Lechert
Zeolites
5, 217, (1985)
62. W.W. Kaedling; C. Chu; L.B. Young; B. Weinstein and S.A. Butler
J. Catal.
67, 159, (1981)
63. M. Niwa; S. Kato; T. Hattori and Y. Murakami
J. Chem. Soc., Faraday Trans. I
80, 3135, (1984)
64. Handbook of Chemistry and Physics, 52nd. Edition
Chemical Rubber Company
(1971-1972)
65. M. Guisnet; F.X. Cormerais, Y.S. Chen; G. Perot and E. Freund
Zeolites
4, 108, (1984)
66. V.R. Choudhary and V.S. Nayak
Zeolites
5, 325, (1985)

67. F.X. Cormerais; Y.S. Chen; M. Kern; N.S. Griep; G. Perot and M. Guisnet
J. Chem. Research
5, 290, (1981)
68. A. Vogel
A Textbook of Quantitative Inorganic Analysis: Theory and Practice, 2nd. Edition
Longmans, (1953)
69. J. Klinowski; J.M. Thomas; S. Ramdas; G.C. Gobbi; M.W. Anderson and C.A. Fyfe
ACS Symp. Ser. (Intrazeolite Chemistry)
218, 159, (1983)
70. A. Dyer; H. Enamy and R.P. Townsend
Sep. Sci. & Technol.
16(12), 173, (1981)
71. E. Glueckauf
Nature
163, 414, (1949)
72. G.L. Gaines and H.G. Thomas
J. Chem. Phys.
21, 4, (1953)
73. R.M. Barrer and J. Klinowski
J. Chem. Soc. Faraday Trans. I
70, 2080, (1974)
74. P. Chu and F.G. Dyer
ACS Symp. Ser. (Intrazeolite chem.)
218, (1983)
75. B.M. Munday
Ph.D. Thesis
University of London, (1969)
76. M.O. Tarhan
Catalytic Reactor Design
McGraw-Hill, (1983)
77. G.F. Froment
Chemical Reactor Analysis and Design
Wiley, (1979)
78. J.B. Butt
Reaction Kinetics and Reactor Design
Prentice-Hall, (1980)
79. Satterfield and Sherwood
The Role of Diffusion in Catalysis
Addison Welsey, (1963)

80. J. Scherzer
ACS Symp. Ser.
248, (1984)
81. D.J. Collins; R.J. Medina and B.H. Davies
Can. J. Chem. Eng.
61, 29, (1983)
82. V. Sreedharan and S. Bhatia
Chem. Eng. J.
36, 101, (1987)
83. J.R. Hopper and D.S. Shigemura
AIChE. J.
19(5), 1025, (1973)
84. J. Wei
J. Catal.
1, 538, (1962)
85. J. Wei
J. Catal.
1, 526, (1962)
86. W.O. Haag and H. Pines
J. Amer. Chem. Soc.
82, 2488, (1960)
87. W.O. Haag and H. Pines
J. Amer. Chem. Soc.
82, 387, (1960)
88. Data book of Chemical and Thermodynamic Constants
Nuffield Science
89. R.T. Sanderson
Chemical Bonds and Bond Energy, 2nd. Edition
Academic Press, (1976)
90. W.J. Mortier
J. Catal.
55, 138, (1978)
91. D.M. Ruthven
Can. J. Chem
52, 3523, (1974)
92. D. Theodorou and J. Wei
J. Catal.
83, 205, (1983)
93. R.M. Barrer and L.V.C. Rees
Trans. Faraday Soc.
50, 989, (1954)

94. N.G. Parsonage and L.A.K. Staveley
Disorder in Crystals
Oxford University Press, (1978)
95. D.M. Bibby; L.P. Aldrige and N.E. Mileston
J. Catal.
72, 373, (1981)
96. J.M. Newsan and D.E.W. Vaughan
Proc. 7th. Int. Zeolite Conf.
Elsevier, 457, (1986)
97. S.T. Wilson; B.M. Lok and E.M. Flanigen
US Patent 4,310,440 (1982)
98. E.M. Flanigen; B.M. Lok and S.T. Wilson
Pure and Appl. Chem.
58, 1351, (1986)
99. C.D. Chang and J.N. Miale
US Patent 4,435,516 (1984)
100. J.N. Miale and C.D. Chang
US Patent 4,427,788 (1984)
101. E.G. Derouane; J.B. Nagy; Z. Gabelica and N. Blom
Zeolites
2, 299, (1982)
102. R.M. Dessau and G.T. Kerr
Zeolites
4, 315, (1984)
103. X. Liu; J. Klinowski and J.M. Thomas
J.Chem. Soc., Chem. Comm.
8, 582, (1986)