Ultra-Microporous Membrane Separation Using Toluene to Simulate Tar-Containing Gases

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Abstract

This study investigates the performance of ultra-microporous cobalt oxide silica membranes for processing simulated gas streams containing toluene as a model tar compound in gasification. The performance of the membranes was initially investigated for He (simulating H₂), CO₂, N₂ and Ar in a range of temperatures. Subsequently, toluene was added to a gas mixture containing He and tested to

simulate the effect of toluene as a tar compound in gasification. The membranes delivered molecular sieving features, showing activated transport as the permeation of the smaller molecular gas He increased with temperature whilst the permeation decreased for the other larger molecular gases. Prior to toluene exposure, He permeance increased by almost twofold from 3.6×10^{-8} to $7.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ as the temperature was raised from 50 to 200 °C. Under a feed gas containing 0.24 mol% toluene, He permeance decreased by an average value of 17%. Upon regeneration of the membrane by heat, He permeance was not fully recovered, a clear indication of tar fouling. A toluene balance calculation showed toluene being retained by the membrane.

Keywords: Gas separation; membranes; ultra-micropores; tars.

1. Introduction

The impact of fossil-fuel use on climate change has led to the development of carbon capture and storage (CCS) technologies and a rapid increase in the use of renewables for power generation. Electricity can be produced using biomass by direct combustion in a thermal power plant, or by gasification to produce a secondary fuel (or energy carrier) which may then be fed to a power plant for the generation of electricity [1] or used as feedstock for fuel production [2, 3]. Hence, biomass is an attractive option in the energy mix, as CO₂ emissions during the conversion of biomass to electricity are roughly matched by that sequestered during biomass growth. Therefore, biomass can be considered carbon neutral in its lifecycle [4].

Biomass gasification results in the production of syngas, containing mainly CO and H₂ plus some contaminants. The CO can be further reacted with water to produce more H₂ and CO₂ via the water gas shift reaction (WGSR). Biomass gasification processes also produce tars as contaminants which pose a

major technical obstacle in implementing this technology. Tars are a complex mixture of condensable hydrocarbons, which includes single ring to complex polynuclear aromatic hydrocarbons along with other oxygen-containing compounds [5]. Tars present a problem to downstream use of the gas, as they can condense to cause fouling [6] and coke formation in equipment [7] and upgrading catalysts. Tar generation is also common in coal gasification processes [8, 9]. The raw syngas from a circulating bed gasifier can be expected to contain around 15 g Nm^{-3} of tar [10], and with downstream processing and wet scrubbing such as absorption/adsorption [11] or catalytic decomposition [12, 13], this may be reduced to around 1 g Nm^{-3} .

H_2 is a gas of major industrial interest due to its high energy content for power production, with an added benefit as a feedstock for fuel production or as fuel in fuel cell systems. In principle, H_2 can be separated after the water gas shift reactors using conventional gas separation technologies such as solvent stripping or adsorption. However, these technologies require gas streams preferably closer to ambient temperatures to operate efficiently. As the water gas shift reaction is exothermic with reactors operating between 200 and 600 °C, cooling down large volume of gases for cold wet scrubbing for the final CO_2/H_2 separation is energy intensive [14].

To address this problem, several groups have developed metal/alloys [15-18] or microporous ceramic membranes based on silica [19-22] and zeolites [23-25] for H_2 separation at high temperatures. In addition, membrane reactor configurations have been investigated, where WGSR catalysts and membranes are integrated into a single process unit for H_2 separation and the subsequent WGSR shifting, overcoming equilibrium limitations at the same time [25-29]. In general terms, metal oxide silica membranes have shown to be thermally stable [30] and deliver high H_2 purities of $> 98 \text{ mol\%}$ for processing syngas downstream from the water gas shift reactors [31].

Whilst the bulk of the work published in literature has been confined to the use of pure gases only, further research is warranted to understand the effects of tars on gas mixture separation. To this end, this work investigates the transport of gases through microporous cobalt oxide silica membranes in gas streams containing pure gases as well as a condensable hydrocarbon (toluene) as the major component of tars from biomass or coal gasification. The membrane was exposed to a gas mixture at a range of temperatures, and gas permeation was investigated prior, during and after exposure to toluene, to simulate tar-gas mixtures.

2. Experimental

2.1 Membrane preparation and characterisation

Cobalt oxide silica sols were prepared according to an adapted sol-gel procedure published elsewhere [32]. In this procedure, cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in a hydrogen peroxide solution (30 wt% H_2O_2 in water) and placed in an ice-cooled bath. Ethanol (EtOH) and tetraethyl orthosilicate (TEOS) were then added to the sol and stirred for 3 hours to reach a final molar ratio of $\text{TEOS} : \text{EtOH} : \text{H}_2\text{O}_2 = 4 : 255 : 5$ and $\text{Si} : \text{Co} = 5 : 1$. The resultant sol was used to coat the outer shell of commercial tubular alumina tubes (supplied by Energy Research Centre of the Netherlands) in a custom dip-coater. The alumina tubes consisted of α -alumina substrate (inner shell) and γ -alumina interlayer, 20 cm in length and 1.4 cm in diameter. The tubes were immersed in the sol for 1 min with an immersion/withdrawal speed of 10 cm min^{-1} . Subsequently, the coated tubes were calcined in air at 630°C for 2 hours with a heating/cooling rate of 1°C min^{-1} . This process was repeated for each sequential membrane layer. The final membrane had 4 coated layers. The membrane morphology was examined under a FESEM Jeol 7001F scanning electron microscope with a hot (Schottky) electron gun at an acceleration voltage of 10kV.

The inner shells of the membranes were then pressurized to 0.2 MPa and the membranes were immersed in a water bath at room temperature to verify if there were any defects. Defect-free membranes were tested for single gas permeation (He, CO₂, Ar and N₂) from 100 to 500 °C in a dead-end volume experimental rig as described elsewhere [32]. The membranes were tested at the University of Queensland in Australia using a steel pressurised vessel. Special graphite seals [33] were used to seal the membrane tubes, thus allowing high temperature permeation tests at a feed pressure of 300 kPa. Additional defect-free membranes were tested in a simulated syngas atmosphere.

2.2 Simulated syngas testing

The simulated syngas separation experimental work was carried out at Imperial College London in the United Kingdom. He (an inert gas) was chosen instead of H₂, as it has a similar kinetic diameter (0.26 versus 0.29 nm). He is a non-explosive gas, thus conforming with safe experimental procedures. Further, both He and H₂ gases have been reported to exhibit permeances of the same order of magnitude through micro-porous silica membranes [34, 35]. With respect to tar compounds, benzene, toluene and naphthalene have been used as tar models for catalytic studies [36] and for elucidating the interactions between tars and solid oxide fuel cell anodes [37]. In this work, toluene was chosen as the model tar compound as single ring aromatic compounds may account for approximately two thirds of the percentage weight of tars in the product gas [38]. Therefore, toluene should prove to be a good approximation to the interactions between membranes and an actual tar mixture produced from biomass gasification [39, 40]. A point of interest here is that the effect of single-ring aromatics tars on solid oxide fuel cell anodes were found to represent an even more challenging problem than the actual tars [41]. Moreover, the choice of toluene avoids the handling and safety issues associated with naphthalene and benzene. The investigation was conducted using He and toluene as model compounds to simulate the system of interest.

A schematic of the membrane test rig is shown in Fig. 1. He gas was continuously supplied to the feed line. Liquid toluene (C_7H_8) was injected at a constant rate into the feed line by a syringe pump injection system, where it evaporated and mixed with the He feed to create a nominal toluene concentration of 10 g Nm^{-3} (0.24 mol%). The toluene/He mixture was then directed to the membrane module containing a microporous cobalt oxide silica membrane, which was housed in a vertical tubular electric furnace heated to the selected operating temperature. Gas permeation tests were limited to 200°C by the maximum working temperature of the membrane Viton seals. Toluene was sampled from both permeate and retentate streams by batch condensation and scrubbing in chilled heptane, and the amount collected determined from the intensity of fluorescence at 285 nm using a Perkin Elmer LS55 luminescence spectrometer.

Fig. 1. Schematic of membrane test rig

The experimental procedure consisted of five phases. In Phase 1, the membrane was activated at 150°C in He for one hour; this was carried out to clean the membrane from any adsorbed atmospheric gases and moisture. Phase 2 consisted mainly of single gas permeation experiments prior to exposure to

the simulated gas mixture. The permeation of He was measured by a bubble flowmeter. He feed flowrate of 30 mL min^{-1} was constantly maintained and the membranes were tested at temperatures of 50, 100, 150 and 200 °C and a total feed pressure of 130 kPa. In Phase 3, toluene was injected in the feed line containing He at a concentration of 10 g Nm^{-3} . Subsequently, gas permeation was carried out at the same conditions of Phase 2. Membrane regeneration was conducted in Phase 4, where the membrane was heated to 150 °C in pure He for one hour; the moderate regeneration temperature was necessary to minimize the risk of prematurely damaging the polymer O ring seals used to seal the experimental rig. Finally, a repeat of the single gas permeation measurements at the same temperatures was conducted in Phase 5 in a similar fashion as in Phase 2.

3. Results and discussions

A cross section SEM micrograph of a cobalt oxide silica membrane is shown in Fig. 2. The cobalt oxide silica top layer contains a very thin cobalt oxide silica layer $\sim 250 \text{ }\mu\text{m}$ thick as reported elsewhere [42]. The top layer was coated on two γ -alumina interlayers of total $\sim 3 \text{ }\mu\text{m}$ depth, with the required smooth surface for thin film deposition. Subsequently, there are two further interlayers $\sim 30 \text{ }\mu\text{m}$ thick each coated on a substrate of α -alumina particles. In this system, the pore size on the top layer is generally well below the resolution capability of SEM equipment, whilst the pore size of the interlayers increased towards the substrate, thus forming an asymmetric structure.

Fig. 2. SEM micrograph of a cross section profile of a cobalt oxide silica membrane.

Fig. 3 shows single gas permeation results up to 500 °C, for membrane samples retained and examined at the University of Queensland. The permeance of the gas with the smaller kinetic diameter He (2.6 Å) increased with temperature while that of the larger molecular gases, CO₂ (3.3 Å), N₂ (3.7 Å) and Ar (3.4 Å), decreased. These results are features of ultra-microporous membranes with average pore diameters between 3 and 5 Å. Hence, these membranes are characterised by molecular sieving structures, delivering a temperature dependent gas transport, also known as activated transport and described by the following equation derived from Barrer's diffusion model [43] through porous structures:

$$J_x = -D_0 K_0 \exp\left(\frac{Q_{st} - E_m}{RT}\right) \frac{dp}{dx} \quad (\text{Eq. 1})$$

where J is the gas flux ($\text{mol m}^{-2} \text{s}^{-1}$), D_0 and K_0 are temperature independent proportionality constants, E_m is the mobility energy or the activation energy for diffusion (J mol^{-1}), Q_{st} the isosteric heat of adsorption (J mol^{-1}), R the gas constant ($\text{J.mol}^{-1} \text{K}^{-1}$), T the absolute temperature (K) for a dp/dx of pressure p (Pa) over a membrane thickness x (m). Gas adsorption on silica films is generally constant as a function of pressure, thus in the low coverage of Henry's regime except that CO₂ shows minor

non-linearity [44]. Due to the stronger adsorption of CO₂ on porous silica based materials than N₂ and other gases [45, 46], the permeance of CO₂ tend to be lower than those gases with slightly larger kinetic diameters such as N₂ and Ar. This has been demonstrated for a number of metal oxide silica membranes such as in this work, including niobia silica [47], cobalt oxide silica [33], hydrothermally treated cobalt oxide silica [21], and iron cobalt oxide silica [48] membranes. As He is essentially a non-adsorbing gas at the tested conditions [49], He gave a positive apparent energy of activation whilst this apparent energy was negative for the other gases due to stronger adsorption effect. This classical behaviour of molecular sieving membranes favours gas separation at high temperatures. For instance, He/CO₂ permselectivity from the data shown in Fig. 3 was 56.3 at 500 °C, though a much lower value of 6.7 at 100 °C.

Fig. 3. Permeance ($\pm 10\%$) of He, N₂, Ar and CO₂ as a function of temperature from 100 to 500 °C in single gas permeation experiments.

Fig. 4a shows the permeance of He at a temperature range of 50 °C to 200 °C before toluene exposure, during toluene exposure and after the regeneration of the membrane by heat treatment,

determined for membrane samples tested at Imperial College London. Prior to toluene exposure, the permeance of He at 50 °C of $3.6 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ increased almost twofold at 200 °C reaching $7.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, also following an activated transport mechanism. This molecular sieving feature can be further verified against the permeance of toluene, which is almost two orders of magnitude below that of He. Fig. 4a shows the substantially lower value of the permeance to toluene, which was almost constant at $1.0 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, slightly decreasing as the temperature increased in excess of 150 °C. It is important to note that the He permeance of the membrane tube tested at Imperial College London in the United Kingdom was threefold larger than the membrane tube tested at The University of Queensland in Australia. This type of permeance variation is common in silica derived membranes from the same batch, and is attributed to variations in the porous substrate morphology which tends to affect the morphology of the top silica, together with minor variations during membrane dip coating and calcination. Nevertheless, the molecular sieving structure of the different membranes are evidenced by He/CO₂ and He/toluene permselectivities at 200 °C of 20.1 and 57.57, respectively.

For temperatures of 50, 100, 150 and 200 °C in Fig. 4a, the percentage mole fraction of toluene in the permeate stream was 0.0210, 0.0174, 0.0169 and 0.014%, respectively. This reduction in toluene content with temperature is due to the fact that as the temperature increased, the permeation of He likewise increased. As a result, the toluene concentration in the permeate stream decreased. It is interesting to observe that as the toluene feed composition was maintained constant at 0.24 mol%, the decrease in the concentration of toluene in the permeate stream as a function of temperature can be translated into a reduction of the partial pressure of toluene. Hence, the driving force, which is the toluene partial pressure difference between the feed and permeate streams, also increased with temperature.

Fig. 4 (a) He and toluene permeance ($\pm 10\%$) and (b) He permeance as a function of temperature for before toluene exposure ($\bullet$), during toluene exposure ($\blacksquare$) and after membrane regeneration ($\blacktriangle$).

In order to provide a more meaningful visualization of the effect of toluene on He permeance as the simulated syngas in this study, the He permeances in Fig. 4a are displayed in Fig. 4b on a smaller y-axis scale. The exposure to toluene resulted in a He permeance reduction between 10 and 25%, with an average value of 17%, whilst the larger decrease occurred at higher temperatures. Upon regeneration, the membrane was tested again in pure He. The permeance to He increased, almost regaining the values obtained prior to toluene exposure at 50 and 100 °C, though lower by 10-15% for the higher temperatures, 150 and 200 °C. The gas stream containing toluene seems to have fouled the performance of the membrane, even after regeneration. To further understand the fouling effect of toluene, a mass balance was performed by considering the total amount of toluene injected in the feed stream, and the total amount measured in both exit lines, the permeate and retentate streams. The difference was the amount of toluene retained in the membrane.

Table 1. Toluene Loss and apparent adsorption as a function of temperature

Temperature (°C)	50	100	150	200
Loss of Toluene ^a (%)	26.0	23.9	20.0	18.6
Apparent Adsorption by membrane ^b (mg m ⁻²)	313	289	242	225

Notes: a Loss of toluene by difference, as a percentage of permeate + retentate

b Loss of toluene per unit of active membrane area

Table 1 shows the results of such a toluene balance, expressed as a percentage loss and as a mass per unit area, as a function of temperature. The loss of toluene and the apparent adsorption by the membrane decreased with temperature in a manner consistent with adsorption principles, as the physical adsorption of molecules onto a solid surface reduces with increasing temperature [50]. This effect can possibly be explained by the equilibrium adsorption/condensation of toluene onto the membrane outer surface as well as within the membrane pores. In other words, as the temperature increased, the equilibrium amount of toluene adsorbed onto membrane surface or within the pore structure decreased. Even after regeneration, He permeance was not totally recovered as shown in Fig. 4b, thus suggesting that toluene was not totally desorbed during the regeneration process, possibly requiring higher temperatures for its removal from the membrane matrix.

Due to the morphological features of silica film structures, silica derived membranes have a pore size distribution (PSD) that can be better described by molecular probing tests, as shown in Fig. 5. The molecular probing PSD was normalized based on relative ratio of gas/vapour permeance over the permeance of He. The idealized PSD of the first membrane tested at The University of Queensland (Australia) shows that there is an abrupt reduction of the relative ratio of He/He from 1 to He/CO₂=0.049, equivalent to a He/CO₂ permselectivity of 20.1. Small variations in Ar and N₂ occurred, also attributed to sorption effects of these gases. The second membrane tested at Imperial

College London (United Kingdom) shows further reduction of the relative ratio C_7H_8/He to 0.017, a permselectivity of 57.7. These results clearly indicate that the majority of the pore sizes which control permeation have dimensions below 3.2 Å. The number of pores reduced by over one order of magnitude for the diffusion of CO_2 , N_2 and Ar, and almost two orders of magnitude for the diffusion of toluene. For toluene to permeate through the membrane there might be micro-defects or percolation pathways with pore sizes larger than 6.1 Å. Micro-defects tend to cause parallel transport of gases, greatly reducing the permselectivity of the membranes, and leading to either Knudsen or bulk diffusion flows which reduce with temperature. This is not the case in these membranes as He permeance increases with temperature for all tests carried out. Due to the amorphous nature of ultra-microporous silica, pore sizes tend to have a tri-modal distribution peaking at 3, 8 and 12 Å [51]. As the cobalt oxide silica film is very thin in the region of 0.25 µm, there is always a probability of the larger pores being connected, thus forming a percolation pathway. Hence, it was concluded that the cobalt oxide silica matrix has a small percentage of constrictions in excess of 6.1 Å which are linked together, thus allowing for the diffusion of toluene.

Fig. 5. Molecular probing pore size distribution based on the relative permeance of gases/vapour over the permeance of He at 200 °C as a function of the kinetic diameters (the broken line is a guide for eyes only).

He is essentially a non-adsorbing gas [49]. In the case of the separation of gas mixtures, the performance of gas permeation is significantly different from single gas permeation as reported by Yacou and co-workers [33]. Apart from fluid dynamic effects [52], competitive adsorption plays an important role in the gas transport through microporous membranes [53-55]. In other words, the stronger adsorbing gas or vapour (toluene in this work) preferentially adsorbs on surfaces and/or within the pore of the membranes. To further explain the transport of gas/vapours in this work, an idealized schematic is provided in Fig. 6. The percolation pathway shows He diffusing through the membrane. In pathway 2, toluene diffuses through the amorphous cobalt oxide silica membrane, though it cannot pass the constrictions below 6.1 Å. Due to its strong adsorption, toluene may block some of the pore constrictions, thus impeding the diffusion of He. This is the reason for the observed fouling, leading to the decrease in He permeance under toluene exposure shown in Fig. 4a, and also after regeneration of the membrane, as toluene remained adsorbed on the membrane matrix. Pathway 3 allowed for the passage of both He and toluene, whilst the latter stayed adsorbed on the silica matrix. However, the aperture between the toluene molecule and the silica structure is still large enough to allow for He diffusion. The last pathway 4 shows a series of connected pores larger than 6.1 Å, thus forming a percolative pathway for the permeation of toluene.

Fig. 6. Idealised schematic of gas pathways for the cobalt oxide silica film coated on alumina substrate.

4. Conclusions

The effect of toluene, as one of the components in gasification tars, on gas separation membranes was assessed in this study. Cobalt oxide silica membranes exhibiting molecular sieving features for single gas separation also delivered the same activated transport trend for simulated gas containing He and toluene. In other words, the permeation of the smaller atomic size gas He increased with temperature under the presence of the larger molecular size toluene vapour, whilst the permeance of the latter was essentially constant, with only a slight decrease at higher temperature. Toluene was able to diffuse through the membrane, though its permeance values were very low resulting in reasonably high He/toluene permselectivities of 57.7. Based on the permeation of several gases with different kinetic diameters, it was ascertained that the majority of the constrictions which control gas diffusion were below 3.2 Å. The cobalt oxide silica matrix resulted in a pore size distribution with a number of percolation pathways which allowed for very low permeance values of larger atomic or molecular gases such as CO₂, N₂, Ar and toluene vapour. A fraction of toluene was retained by the membrane, and its adsorption on the cobalt oxide silica matrix fouled the permeation of He. Toluene still remained partially adsorbed in the membrane even upon regeneration by heat treatment, which led to He permeance partially regaining its original values prior to toluene exposure. The stronger adsorbed

toluene may have blocked some of the pores which would otherwise be accessible for He permeation, thus explaining the fouling effect. Therefore, the design of gas separation units and operations for biomass or coal derived syngas must consider the effect of toluene and other condensable gases in tars.

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