MOLECULAR SIEVE SILICA (MSS) MEMBRANES FOR GAS SEPARATION AND REACTION PROCESSES

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Weakly branched silica films formed by the two-step sol-gel process allow for the formation of high selectivity membranes for gas separation. ^{29}Si NMR and gas permeation showed that reduced crosslinking leads to He/CH_4 selectivity improvement from 300 to 1000. Applied in membrane reactor for cyclohexane conversion to benzene, conversions were achieved at 14 fold higher than a conventional reactor at 250°C. Hydrothermal stability studies showed that carbon templating of silica is required for hydrothermally stable membranes. From our work it was shown that with correct application of chemistry, practical membrane systems can be built to suit gas separation (eg hydrogen fuel) and reactor systems.

1 Introduction

The development of silica derived membranes in the last decade has led to major applications in gas separation at high temperature (up to 500°C). Potential applications are also envisaged in membrane reactors to shift the reaction equilibrium to high conversions. MSS membranes have been synthesised by sol-gel processes including a single-step [1-3] and two-step [4, 5] catalysed hydrolysis. The top layer of a MSS membrane provides the molecular sieve properties required to allow a molecule with a small kinetic diameter (d_k) to diffuse whilst hindering the passage of the larger molecule. Controlling the MSS film pore size is fundamental to obtain high separation factors (i.e. permselectivities). Weakly branched fractal sol gel processes has shown promising results in MSS membrane technology [5, 6]. These tend to have a high contribution of silanol groups (Q^2 and Q^3 groups) which allow for a fine pore size control. However, industrial processes for gas separation generally contain a small concentration of water. MSS membranes are hydrophilic and unstable to water reaction with the silanol groups. To address this issue several groups have looked at surface functionalisation [7-10]. This paper addresses MSS film pore size formation and its functionalisation for gas separation and membrane reactor applications.

2 Experimental

MSS layers were synthesised employing a two-step catalysed hydrolysis process using tetraethylorthosilicate (TEOS), absolute ethanol (EtOH), 1M nitric acid (HNO_3) and distilled water (H_2O) as described elsewhere [5, 9, 10]. The mixtures ware refluxed under stirring at 60°C for 180 minutes in a water bath. The final MSS membranes consisted of 4 × silica layers, 2 × γ-alumina layers supported on an α-alumina substrate. The membranes were tested using a dynamic permeation apparatus to check the membrane quality for H_2 permeation for temperatures between 150 to 250°C. The packed bed membrane reactor was assembled with the membrane selective layer and Pt/Al_2O_3 catalyst

facing the feed stream. CP/MAS ^{29}Si NMR was performed using a Bruker MSL 300 spectrometer. Spectra were de-convoluted using a Gauss-Lorentz fit with PeakFit™ (Jandel Scientific) software.

3 Results and Discussion

The two-step samples consistently showed high contribution of silanol groups (Q^2 and Q^3) as depicted in Figure 1a. According to the fractal theory, high concentration of silanols in the sol-gel process leads to the formation of weakly branched dense films with smaller pore size [11]. The gas permselectivities of single-step and two-step membranes are very distinct as depicted in Figure 1b. The translation of the fractal concept into thin film technology resulted in the production of high quality membranes. Using gases of different kinetic diameters as molecular probes, permselectivity ratios close to 1000 for the separation of He and CH_4 were achieved. In agreement with the ^{29}Si NMR findings, the permselectivity results of the two-step membranes showed superior pore size tailorability in the region of 3Å as compared to single-step larger pore size of 3.5 Å.

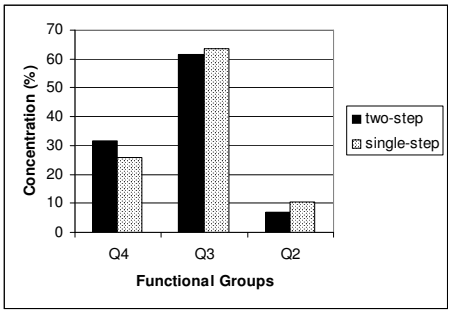

Figure 1a. Concentration of MSS functional groups from CP/MAS ^{29}Si NMR results.

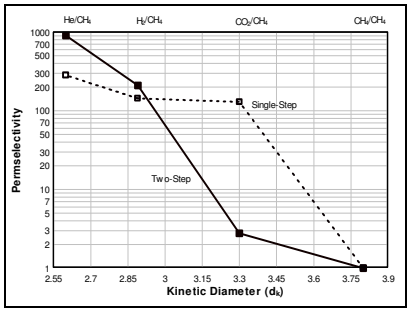

Figure 1b. Permselectivity versus molecular kinetic diameter.

Figure 2a compares the cyclohexane conversion to benzene in the packed bed membrane reactor (MRx) and conventional packed bed reactor (Rx) using membranes with H_2 permeance of 1×10^{-7} mol.m^{-2}.s^{-1}.Pa^{-1}. The conversion over Pt/Al_2O_3 catalyst on the Rx was small and close to equilibrium value. On the other hand, the MRx yielded an 14 fold conversion higher than the Rx at 250°C. These results illustrate the capabilities of the MRx to shift the reaction yield successfully beyond the equilibrium value, by simply removing the H_2 product from the reactor side.

Figure 2b shows how silica membranes are affected by process steam and the improvement offered by carbon functionalisation. Conventional MSS membranes selectivity is reduced by half after exposure to steam. This is largely attributed to the silanol groups which react with water causing pore opening [9, 10]. By the same token, functionalised carbon templated MSS (CTMSS) membrane showed improved selectivity after exposure to steam, clearly indicating that functional groups can maintain and improve selectivities in membrane technology. Functionalised MSS membranes can

therefore find applications for reformate clean up in fuel cell technology and membrane reactors such as the dehydrogenation reactions and the water gas shift reaction.

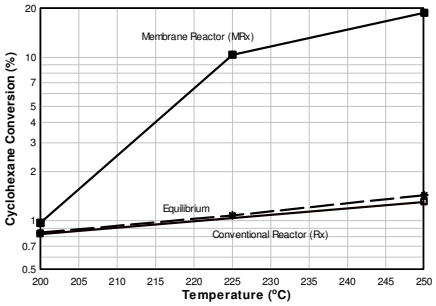

Figure 2a – Conversion of cyclohexane to benzene.

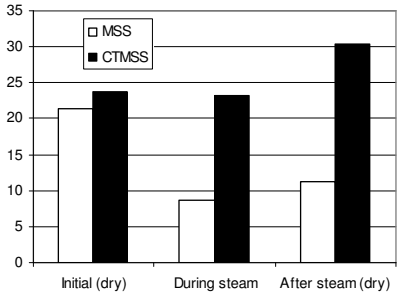

Figure 2b – H_2/CO selectivities for membranes with 34 mol% steam exposure at 200°C

4 Conclusions

Weakly branched silica formed by the two-step sol-gel process was highly selective to gases, which was attributed to a high silanol concentration. Combining the membrane selectivity with reaction in a packed bed membrane reactor, the conversion could be increased over standard packed bed reactor equilibrium. In systems that contain steam, carbon functionalisation of silica surfaces was required for stable operation, as water reacted with silanol groups resulting in pore widening.

Acknowledgments

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