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HYDROTHERMAL STABILITY ANALYSIS OF CARBONISED TEMPLATE MOLECULAR SIEVE SILICA MEMBRANES

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ABSTRACT

For fuel cell CO clean up application, the presence of water with silica membranes greatly reduces their selectivity to CO. We show results of a new functional carbonised template membrane of around 13nm thickness which offered hydrothermal stability with no compromise to the membrane's H₂/CO permselectivity of 16. Lost permeance was also regenerated.

INTRODUCTION

Worldwide, our consumption of energy is growing at an unsustainable rate, which is driving researchers to develop technologies for renewable sources as well as utilise our current sources more efficiently. Fuel cells are fast becoming a viable solution to sustainable energy supply due to their use of fuels such as H₂. One technique to supply H₂ gas to a fuel cell is to reform hydrocarbons. Byproducts of the reforming process such as CO however must be removed to at most 100 ppmv or fuel cell effectiveness will be reduced due to anode poisoning.

Water gas shift is generally used post reforming, but only reduces CO levels to 1% (1). The final clean-up can be performed using catalytic process such as selective oxidation, but this is highly dependant on catalyst efficiency and cost. Membranes on the other hand are simple in operation, requiring only a pressure drop to drive the separation mechanisms. Palladium composite membranes are effective to achieving high H₂ purities, but materials are expensive and must operate above 400°C for effective performance. Palladium films also suffer from poor thermo-mechanical stability. Silica membranes on the other hand are cost effective and thermo-mechanically stable while offering separation of H₂ from CO at most practical temperatures. The mechanism of separation is by molecular sieving whereby small molecules (e.g. H₂: $d_k = 0.289$ nm) selectively permeate through the membrane, while the larger molecules (e.g. CO: $d_k = 0.376$ nm) pass over, exiting in the retentate stream as depicted in Figure 1. This process is activated with temperature as the molecule of gas obtains more energy to diffuse through the pore.

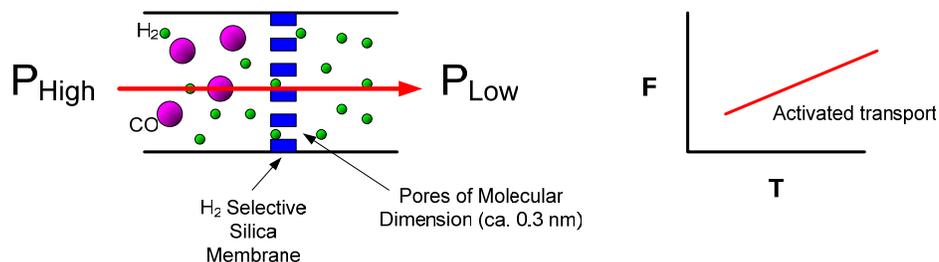


Figure 1: Diagram showing idealised activated molecular sieve transport mechanism

The mechanism is accommodated as a membrane system whereby the rejected molecules pass out via the retentate stream shown in Figure 2.

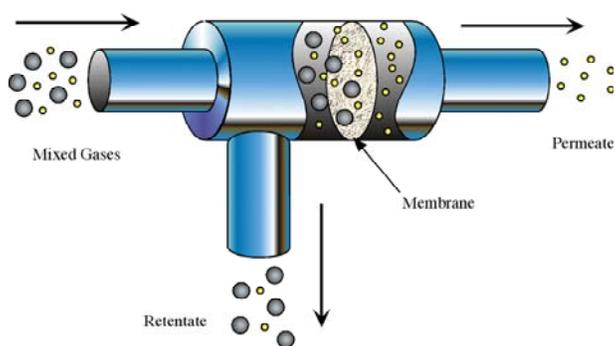


Figure 2: Membrane operation showing separation of small gas, H₂, from larger gases in mixture (eg. CO)

Silica membranes have however, only been developed in laboratories in the last 15 years for the separation of dry gases (2). More recently, the poor hydrothermal stability of standard silica membranes has been addressed by incorporation of hydrophobic methyl ligands (3, 4). Although effective for separations of water from large molecule organics, the tight pore cut-off of around 0.3 nm necessary for separation of H₂ from CO is lost because of these ligands. We have on the other hand, achieved hydrothermal stability without the use of covalent ligands. Instead, we incorporated carbonised surfactant templates into the silica which do not compromise selectivity of H₂ from CO (5). In this work we present characterisation of our carbonised template molecular sieve silica (CTMSS) membranes including film formation and permeation effects from hydrothermal treatment.

EXPERIMENTAL

Silica membranes were prepared following our standard procedure described in more detail elsewhere (5). The supported membranes are synthesised by dip-coating porous alumina substrates with sol gel layers, graduating to the top selective silica layer. The order of coating on the substrate was first α -alumina, then the intermediate methyl templated silica, then finally the acid catalysed sol-gel films. The silica sol was made using the acid catalysed two-step sol gel process to control pore size after calcination to around the 0.3 nm necessary for selective gas transport. The hydrothermally stable CTMSS material was synthesised by including a short chained cationic surfactant in the sol-gel process at a composition below the CMC to prevent

assembly of ordered silica structures. The surfactant was then carbonised *in situ* by calcination of the membrane in vacuum conditions.

Characterisation of the CTMSS membrane film was performed using TEM. Cross sectional TEM samples were prepared from membrane slices of approximately one millimetre thickness, cut from the alumina-supported membrane with a diamond saw. These were mounted in a tripod polisher, and ground with silicon carbide grinding paper and polycrystalline diamond films (3 and 1 μm films) until the surface of interest was only several μm thick. The final thinning to electron transparency was carried out in a Precision Ion Polishing System (Gatan). The samples were examined in a 200 kV Field Emission TEM (FEI Tecnai-20) in bright field imaging mode in order to enhance contrast between the phases present.

Permeation measurement was performed using a dead-end dynamic setup allowing for accurate measurement of small fluxes. Standard (MSS) and CTMSS membranes were tested individually by loading the membrane into the test cell and sealing with Viton o-rings. This limited tests to 200°C. All permeation tests were performed with a feed pressure of 2 bar (absolute) and vacuum on the permeate side. During the test, the vacuum was shut off and the pressure build-up was recorded using MKS Baratron transducer and Pico data logger, then converted to membrane permeance. Hydrothermal treatment of the membrane involved continuous exposure of the membrane to 34 mol% steam at 200°C in a synthetic reformat mixture (42% H₂, 36% N₂, 13% CO₂ and 9% CO - molar). The performance of the membrane around this exposure was measured by He permeance and H₂/CO selectivity (ratio of H₂ to CO permeance).

RESULTS AND DISCUSSION

The TEM image of the membrane cross section is shown in Figure 3. A film is clearly evident on the surface and is in the order of 13 nm thick. This is less than the thicknesses reported in previous studies (6), but different substrates and coating schedules can easily lead to different film morphologies.



Figure 3: TEM micrograph of CTMSS membrane cross section

Thinner films can lead to increased chance of defects in the film not thick enough to substantially cover the sublayer roughness. However our membranes still showed good selectivity of smaller molecule gases like He and H₂ to larger molecule gases like CO₂, N₂ and CO, as shown in

Figure 4.

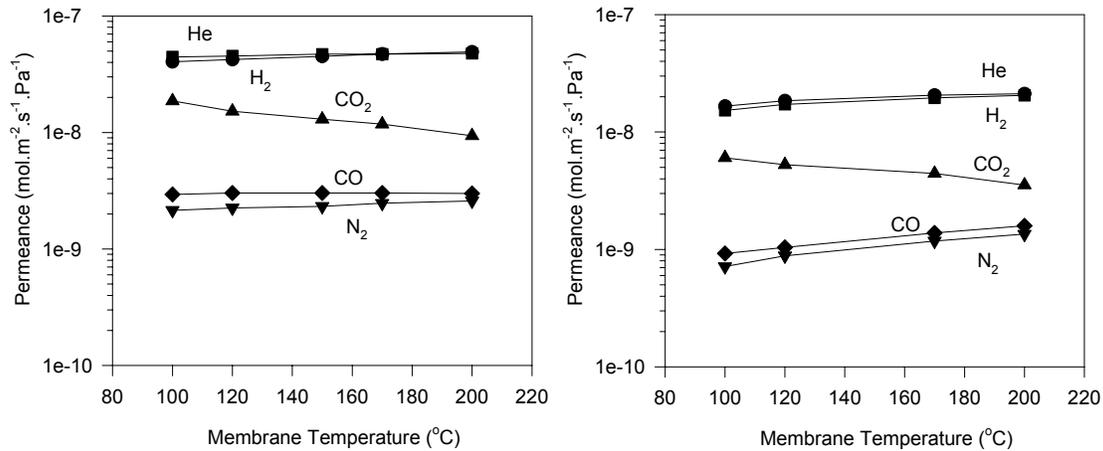


Figure 4: Permeance as a function of temperature for standard MSS membrane (left) and hydrothermally stable CTMSS membrane (right).

Following the activated transport model, permeation of gases increased with the membrane's temperature. The only exception to this was CO₂ which can be explained by its higher heat of adsorption, also observed by other silica membrane researchers (6). The interesting feature of the CTMSS membrane is that it showed very similar performance to the MSS membrane in terms of permselectivity, both being around 15-16. The reduced overall permeation was possibly attributed to a more compacted silica structure due to the calcination in vacuum. The inclusion of the carbonised surfactant therefore did not reduce the permselectivity quality of the membrane and is therefore suitable for separation of H₂ from CO.

Hydrothermal test results revealed the effectiveness of the CTMSS membrane over the standard MSS membrane. Figure 5 shows the He permeance change over several days of testing. Permeance decayed constantly for both membranes, showing a small amount of pore blockage. This blockage occurred for even the smallest pores for which He can access.

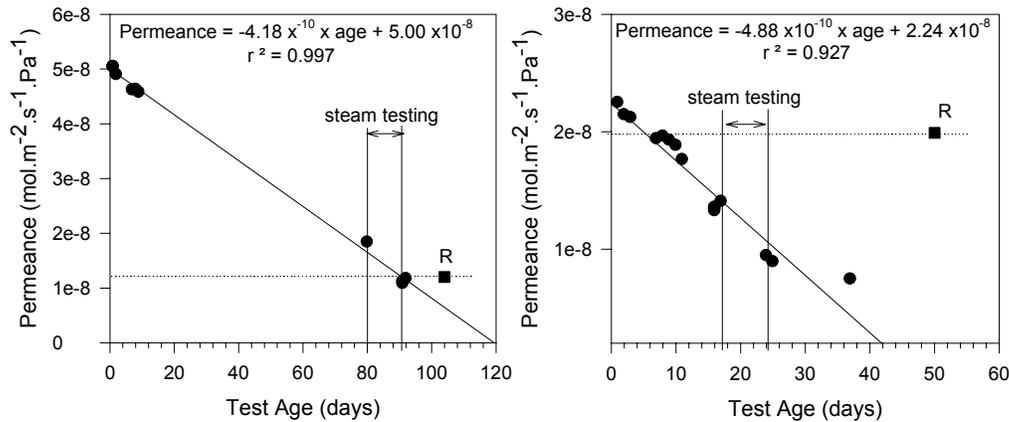


Figure 5: Helium permeance over time after ambient storage and steam testing for MSS (left) and CTMSS (right) membranes.

The exposure to steam did not appear to affect this normal decay rate of either membrane, but the major difference between the MSS and CTMSS first became clear after regeneration of the membrane in vacuum to 500°C. The MSS membrane showed little return in He permeance, while the CTMSS membrane showed a significant return to near original permeance. The actual selective performance of the membrane in terms of H₂ permeance over CO is shown in Table 1. The standard silica membrane showed a permselectivity loss of around half its original value. Recent studies by Yoshino's group also reported major reductions to membrane permselectivity as a result of high temperature steam exposure (Z). Our CTMSS material didn't show any selectivity losses, and actually increased slightly. The carbonised template technology provided the necessary hydrothermal stability to the membrane at 200°C over the 140 continuous hours of hydrothermal exposure.

Table 1: Ideal H₂/CO permselectivity measured to indicate change to performance after steam testing and regeneration

Test status	MSS	CTMSS
Before steam	16	15
After steam	8.2	18
Regeneration	8.9	23

The permstructure is the porous structure of the silica which gives it its selective permeation characteristics. The steam fed to the membrane unit at high temperatures obviously affected the permstructure leading to a drop in the ratio of small to large pores needed for preferred transport of H₂. The CTMSS material resisted this change to the permstructure. Knowing that CTMSS contained small carbon templates, from these results we can conclude the carbon prevented the loss of the small pores relative to the larger ones and from this, gave the material its hydrothermally stable property.

CONCLUSIONS

Silica membranes are a suitable candidate for fuel cell CO clean up stages as they selectively purify H₂ from CO. A new carbonised template molecular sieve silica (CTMSS) method was proposed which produced carbon groups *in situ* to improve hydrothermal stability. Thin CTMSS membrane films were formed over the ceramic substrate in the order of 13 nm thick and showed a H₂/CO permselectivity of around 15-16 for both membranes. A simple regeneration procedure which could be performed *in situ* led to restored permeance of the CTMSS membrane only. The 140 hour hydrothermal exposure period reduced MSS membrane permselectivity by around 50%, while the hydrothermally stable CTMSS membrane resisted structural changes and thus showed a slight increase in permselectivity. The CTMSS material is therefore suitable for clean energy systems which purify H₂ in the presence of steam.

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KEY WORDS

Inorganic membrane, silica membrane, hydrothermal stability, hydrogen separation, fuel cell, CO clean up, clean energy, activated transport, microporous silica