Influence of sol–gel conditioning on the cobalt phase and the hydrothermal stability of cobalt oxide silica membranes

Liang Liu [a,b], David K. Wang [a], Dana. L. Martens [a,b], Simon Smart [a,b], João C. Diniz da Costa [a,b,*]

[a] The University of Queensland, FIMLab – Films and Inorganic Membrane Laboratory, School of Chemical Engineering, Brisbane, Queensland 4072, Australia
[b] Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), Australia

ABSTRACT

This work shows for the first time that the hydrothermal stability of cobalt oxide silica membranes is very dependent upon the cobalt oxide phase. Xerogels with the same cobalt loading (Co/Si=0.1) were characterised by N_2 sorption, CP/MAS ^{29}Si NMR, FTIR, Raman, XPS and DR UV–vis spectroscopy. It was found that the xerogels containing tetrahedrally coordinated cobalt (Co^{2+}) in the silica matrix were hydrothermally unstable leading to a sharp loss of pore volume within 10 h when exposed to 75 mol% water vapour and 550 °C, followed by complete densification after 40 h. However, silica xerogels containing a high content of octahedrally coordinated cobalt (Co^{3+}) in the form of Co_3O_4 were able to oppose structural densification and were consequently much more hydrothermally stable. The Co_3O_4 and Co^{2+} silica membranes were tested for single gas permeation using He, H_2, CO_2 and N_2, delivering similar He permeance (2.48 × 10^{-7} and 2.85 × 10^{-7} mol m^{-2} s^{-1} Pa^{-1}) and a He/N_2 selectivity of 50 and 41 at 500 °C, respectively. Upon exposure to the same harsh hydrothermal conditions as the xerogels, the membranes were tested again for single gas permeation. The high content Co_3O_4 silica membrane saw only a marginal decrease in He/N_2 selectivity to 39 (22% loss) whilst the tetrahedral cobalt coordination silica membrane had a dramatic decline in selectivity to only 11 (73% loss).

Crown Copyright © 2014 Published by Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen is a high quality clean energy carrier and is generally produced from fossil fuel sources such as steam reforming of natural gas and the water gas shift reaction [1,2]. In these processes, there is a need to purify H_2 from streams containing CO_2 and water vapour. Microporous silica membranes have attracted significant interest for H_2 separation with excellent separation performances at high temperature conditions compared to traditional energy consuming separation techniques. The initial development of pure silica membranes was based on sol–gel methods [3–5] and chemical vapour deposition [6,7], which offered great molecular sieving capabilities of silica structures with controlled pore sizes around 3–5 Å. However, high temperature wet gas streams can cause a rapid degradation of the membrane performance due to its poor hydrothermal stability, which remains a major contributing factor to the delay of the commercial applications of microporous silica membranes. Gu et al. [8] reported that H_2 permeance of a silica membrane prepared

from a chemical vapour deposition (CVD) method decreased to less than 10% of its initial value at a steam partial pressure of 16 kPa and at 600 °C. Tsuru et al. [9] also found that the permeance of H_2 and He for a sol–gel derived silica membrane decreased by 65% and 40% after treatment for 9 h at 500 °C and 50 kPa of steam partial pressure (50 mol%).

Amorphous microporous silica membranes are known to be unstable at high temperatures in the presence of water vapour, caused by the densification of the silica network. In general, the densification process occurs via physisorption of water molecules onto the surface of silica due to interactions with the hydrophilic silanol groups (Si–OH), followed by the hydrolysis reaction which enables the cleavage of nearby siloxane groups (Si–O–Si) forming mobile silanol groups [10]. Migration of the mobile silanol groups and subsequent condensation reactions result in the widening of large pores and eventual collapse of small pores, leading to the loss of membrane performance as described by Duke et al. [11].

Several strategies have been employed to improve the hydrothermal stability of silica membranes, including templating [12,13] and hybrid organosilica [14–16]. However, these materials can only be operational at moderate temperatures (< 300–400 °C) because of the degradation of the organic species present in the silica films.

Hence, they are not suitable for high temperature hydrogen separation. Another strategy is to incorporate metals or metal oxides, such as Ni [17], Co [18–20] and Nb [21] into the silica matrix. The metal oxide silica membranes have shown improved gas separation performance under various hydrothermal conditions. In general, the roles of these metal oxide dopants on the structure or hydrothermal stability of the silica matrix are complex and highly dependent on the sol–gel processes and post-synthesis techniques.

There are a limited number of works in the literature regarding the role of composite oxides on the hydrothermal stability of porous silica materials, particularly membranes. Boffa et al. [22] reported that Nb (V), Ti (IV), and Zr (IV) ions acted as network formers in silica-based membranes by stabilising the porous structure and enhancing network connectivity. However, this is not the case for cobalt-doped silica materials. Igi et al. [18] found that 33 mol% cobalt oxide silica membrane calcined in steam showed the best hydrothermal stability. Furthermore, Uhlmann et al. [20] demonstrated that cobalt oxide silica was hydrothermally stable up to 180 °C, indicating that cobalt phases play important roles in the improved hydrothermal stability of silica matrix.

The formation of cobalt oxide in the silica matrix is highly dependent on the cobalt concentration [23,24], the preceding sol–gel method [25] and silica precursor [26]. Nevertheless, Uhlmann et al. [27] carried out a series of hydrothermal cycling up to 500 °C and found that cobalt oxide silica membranes severely lost their performance in terms of separation capabilities. In a further work, Lin et al. [28] showed that cobalt oxide silica xerogel structures immersed in water in temperatures below 100 °C led to significant densification of the matrix within the first day where a structural equilibrium was achieved from thereon. Hence, literature shows that metal oxide silica membranes are hydrostable in some cases and not in other cases.

In this work, we show that the cobalt phase has a significant role in producing silica structures that can oppose hydrolytic attack or not. This is demonstrated by systematically investigating the role played by cobalt oxide in the silica matrices under harsh hydrothermal conditions of 75 mol% vapour at 550 °C as a function of time up to 40 h. We initially developed silica membranes with different cobalt phases by varying the sol–gel parameters (ethanol and water ratio) but the cobalt loading (Co/Si=0.1) for the materials was the kept constant. The physicochemical properties of xerogels were characterised by N_2 sorption, ^{29}Si CP/MAS NMR, FTIR, Raman and XPS, DR UV–vis spectroscopy. Then, single gas testing of the as-synthesised membranes was carried out to investigate the membrane performance before and after harsh hydrothermal exposure.

2. Experimental

2.1. Sol–gel preparation and hydrothermal treatment

Cobalt oxide silica sols were prepared using the specific molar ratios as listed in Table 1. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 98%, Sigma-Aldrich) was initially mixed in double distilled water and ethanol (EtOH, 99%, AR grade) and vigorously stirred until complete dissolution was achieved. Subsequently, the mixture was cooled to

Table 1
Sol composition details (in molar ratios).

	EtOH	H$_2$O	TEOS	Co(NO$_3$)$_2$·6H$_2$O	H$_2$O$_2$
Co^{3+}Si	170	200	4	0.4	9
Co^{2+}Si	255	80	4	0.4	9

0 °C using an ice bath and then hydrogen peroxide (H$_2$O$_2$, 30 wt%) was added. Finally, tetraethoxysilane (TEOS, 99%, Sigma-Aldrich) was added drop-wise and stirred constantly for 3 h to achieve a final sol. The specific molar ratio regimens for the two sols are listed in Table 1. In view of the results obtained in this work, the samples are denominated as Co^{3+}Si and Co^{2+}Si to facilitate the correlations found between structure, gas permeation and hydrothermal investigation. The initial pH of Co^{3+}Si and Co^{2+}Si were 4.4 and 4.1, respectively. After 24 h of drying at 60 °C and prior to gelation, their pHs were measured at 2.5 and 2.1 respectively, indicating very close values for both samples. The sols were dried in an oven at 60 °C for 96 h to form xerogels. These xerogels were ground into fine powders and calcined in an air atmosphere in a temperature controlled furnace at 630 °C for a hold time of 2.5 h with heating/cooling rates of 1 °C min^{-1}.

The hydrothermal exposure of the calcined xerogels was carried out in a custom rig (Fig. 1). The xerogels were placed inside the quartz tube furnace and tested at 75 mol% vapour (5.4 g h^{-1}) and 550 °C up to 40 h to investigate the effect of hydrothermal exposure on the physicochemical properties of the xerogels. Briefly, the temperature of the furnace was controlled by a temperature controller and N_2 was used as carrier gas at a flow rate of 40 ml min^{-1}. The feed water in the reservoir was pressurised by N_2. The water flow rate was controlled by a Bronkhorst flow controller and was heated to 200 °C in the vaporiser prior to entering the furnace.

2.2. Material characterisation

Nitrogen sorption experiments were carried out on a Micromeritics TriStar 3020 analyser after degassing under vacuum on a Micromeritics VacPrep061 at 200 °C for a minimum of 12 h. The specific surface areas were calculated from the adsorption isotherms via the multi-points BET model at relative pressures of P/P_0=0.05–0.3. Pore size distribution (PSD) of the materials were determined by density functional theory (DFT) using the adsorption branch of N_2 sorption with a regularisation factor of 0.40. Solid-state NMR was carried out on the Avance III spectrometer (Bruker), operating at 59.627 MHz for ^{29}Si. The samples were placed in the 4 mm zirconium rotor and rotated at magic angle with 7 kHz frequency and the spectra were recorded using SP-hpdec technique (single pulse with high power proton decoupling). Fourier transform infra-red (FTIR) spectra were recorded with a Shimadzu IRAffinity-1 with a Pike MIRacle diamond attenuated total reflectance (ATR) attachment. Spectra were taken over a wavenumber range of 1400–600 cm^{-1}, which is the range of interest for silica and cobalt oxides Micro-Raman spectra were acquired using a Nicolet Almega XR dispersive Raman spectrometer coupled to an Olympus microscope using a He:Ne laser (633 nm) over 2000–70 cm^{-1}. XPS spectra were conducted using a Kratos Axis ULTRA XPS incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was Al Kα X-rays
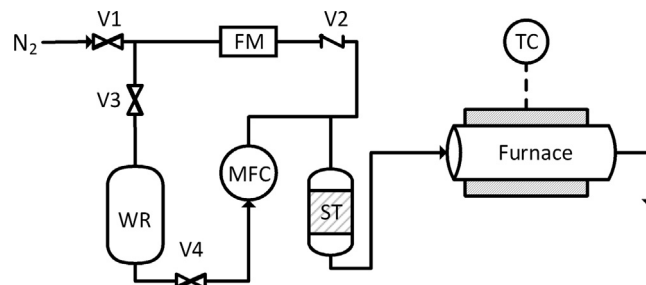
WR: Water Reservoir; FM: Flow Meter; MFC: Mass Flow Controller;
ST: Steam Generator; TC: Temperature Controller; V1-V4: Valves

Fig. 1. Illustration of customised hydrothermal test rig (adapted from [29]).