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Development of rapid thermal processing of tubular cobalt oxide silica membranes for gas separations

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ABSTRACT

This work shows for the first time that sol–gel derived cobalt oxide silica membranes can be produced on large scale, tubular supports through successful implementation of the rapid thermal processing (RTP) techniques. The combination of fast sol–gel methods and RTP techniques reduced the overall membrane fabrication time from a minimum of 7 days to approximately 12 h. The successful RTP technique was developed by changing the silica precursor from tetraethyl orthosilicate to ethyl silicate 40 and adjusting the nitric acid and water ratios in the sol–gel process. The optimized sol–gel conditions for the best membranes were found to deliver average He permeances of 3×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and He/N_2 permselectivities of 69 at 450 °C. This work has enormous potential for transforming the traditional processing pathways associated with sol–gel derived membranes for both research and commercial separation applications.

1. Introduction

Industrial processing of gases and liquids using membrane technologies is an attractive and viable alternative to traditional separation processes because of the improved process intensification [1], particularly at high temperatures. Polymer membranes have become a well-established separation technology for a number of industrial applications using various operational modes, such as reverse osmosis, membrane distillation and dialysis [2]. Nevertheless, their applications are restricted to low temperature and non-caustic environments due to the degradability of their organic constituents. On the other hand, inorganic membranes are well suited to these harsh industrial conditions because of their superior chemical and thermal stability relating to their physicochemical and thermodynamic properties, such as mechanical strength, non-swellable rigid framework, high melting temperature, crystallinity and pore size [3]. While these advantages of inorganic membranes are generally well-regarded and demonstrated, their industrial deployment has been slow and they are under-utilized because of several limiting factors associated with production, quality and reproducibility.

The production of an inorganic membrane varies significantly between the material types, geometry and applications. The main considerations are membrane performance and stability, quality assurance, chemical precursors, synthesis methods and fabrication time. Collectively, these factors are intrinsically tied to the overall cost analysis of the membrane and the profitability of its applications. Membrane performance is defined by the permselectivity or separation factor and molecular fluxes which directly translate to purity and performance requirements [4]. Hence, membranes must be very thin and relatively free of surface defects with a microstructure that is capable of separating important industrial commodities of interest. Moreover, membrane stability relates to the extent of temporal variation in performance under different industrial processing conditions such as wet and/or sour gas streams.

The performance and stability of inorganic membranes, particularly metal-modified silica membranes, have been investigated for the application of high temperature gas processing under steam and/or caustic conditions. The research of metal modified-silica membranes has been gaining momentum in the last decade, where metal oxides such as alumina [5–8], titania [9], zirconia [10], nickel [11–13], niobia [14] and cobalt oxide [15–20] have been systematically incorporated to enhance both membrane performance and stability. Igi et al. [16] showed that the cobalt oxide in the silica matrix reduced the extent of densification that is typically associated with the pure silica membranes under hydrothermal conditions. The performance of cobalt oxide silica membranes was also reported to be stable in the presence of hydrogen sulphide containing gas streams [18] which are detrimental to the functioning of other inorganic membranes such as those based on palladium [21]. The industrial potential of cobalt oxide silica membranes for H_2 separation has been recently demonstrated by both their performance at temperatures up to 600 °C with mixed gas feeds [19] and their stability during a long term (> 2000 h) study using a scaled up, multi-tube membrane module [20].

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Despite these concerted efforts, one major drawback of silica based membranes lies in the time-consuming and complex preparation techniques. Two of the most common preparation techniques for silica based membranes involve (1) sol–gel processing that requires simple, low cost chemicals but a long fabrication time or (2) a costly and complicated chemical vapour deposition processing that is offset by its excellent gas selectivity. Indeed, membrane production that is cheap, simple and fast with scale up potential will determine the industrial acceptance and future deployment of the membranes for separation technology. In order to accelerate the membrane fabrication times, research groups are now focusing on a rapid thermal processing (RTP) technique which utilizes a fast heating rate in the order of 100 °C s^{-1}. Recent RTP reports have demonstrated the application of RTP for small scale silica [22] and alumina [23] membranes on flat substrates and hybrid-RTP techniques for cobalt oxide silica membranes on tubular substrates [24].

In this work, we show for the first time the preparation of larger scale, tubular geometry membranes by a true RTP technique. Our RTP involves the rapid calcination of each membrane layers for only 1 h at 600 °C without a temperature ramping step. This allows silica-derived membranes, with multiple sol–gel coats, to be prepared in a single day rather than taking a week or more as per our previous thin film coating procedures. This processing strategy goes against conventional wisdom that it is practically impossible to produce defect-free, thin film silica membranes capable of separation via RTP, as fast heating rates lead to thermal stresses and eventual cracking [25]. Our previous work showed that a hybrid-RTP process was successful but still required conventional (i.e. slow) thermal calcination steps for two of the six thin-film layers per membrane [24]. In essence, all the membranes prepared in this current study consisted of six thin-film layers and were fabricated in their entirety in less than 12 h by the RTP techniques only. Here we present a comparison of the membrane performance and physicochemical properties of bulk xerogels prepared via RTP techniques from two different silica precursors tetraethyl orthosilicate (TEOS) and ethyl silicate 40 (ES40). In addition, we report the effect of acid addition and water ratio variation in the sol–gel processing on the final properties of the membranes. The RTP membranes were tested for single gas permeation and permselectivity for helium, hydrogen, carbon dioxide and nitrogen at temperatures ranging from 200 °C to 450 °C. Finally the membranes were examined by scanning electron microscopy to characterize their morphology and determine the effect of RTP on defect formation.

2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$; 98%, Alfa Aesar), tetraethyl orthosilicate (TEOS; Sigma Alrich) and ethyl silicate 40 (ES40; Colcoat Co.) were used without further purification. Absolute ethanol (EtOH; AR grade) and nitric acid (HNO_3; 70% AR grade, RCI Labscan) were used. Tubular alumina support (10 mm i.d., 14 mm o.d., 100 mm length) consisting of α-alumina substrate and γ-alumina interlayer was purchased from the Energy Research Centre of the Netherlands (ECN).

2.2. Sol–gel processing of xerogels and membrane fabrication

The membrane coating solution was prepared using a modified sol–gel method reported in our previous works [24,26]. Briefly, Co $(NO_3)_2 \cdot 6H_2O$ was dissolved in a mixture of double distilled water, nitric acid and ethanol followed by a drop-wise addition of TEOS or ES40 under stirring to achieve a final molar ratio of the Si:Co $(NO_3)_2.6H_2O$:EtOH:H_2O:HNO_3 sol as displayed in Table 1. For sol–gel processing of the CoTEOS and CoES40 xerogels and membranes, the sols were prepared with a fixed effective water ratio of 46 in the absence of nitric acid, whereas the CoES40_A, B and C samples employed different water ratios while keeping the nitric acid ratio constant at 0.15. In each sample, 6 mol of water is an indirect contribution from the hexahydrate of the cobalt salt and the water contribution from the 70% nitric acid is calculated to be 0.064 mol which is a very small contribution and is therefore rounded down in the H_2O_{eff} column in Table 1. After 10 min of mixing at room temperature, all the sols were dried on Petri dishes in an oven at 80 °C for 30 min. The dried samples were transferred into quartz boats then directly calcined in an air atmosphere in a pre-heated furnace at 600 °C for 1 h to simulate the RTP conditions experienced by the membranes.

Table 1
Feed ratios of the reagents used in sol–gel processing of the RTP membranes.

Membrane	Si (TEOS)	Si (ES40)	$Co(NO_3)_2 \cdot 6H_2O$	EtOH	H_2O_{eff}	HNO_3
CoTEOS	4	–	1	255	46	–
CoES40	–	4	1	255	46	–
CoES40_A	–	4	1	255	46	0.15
CoES40_B	–	4	1	255	26	0.15
CoES40_C	–	4	1	255	6	0.15

Thin membrane films were coated on ECN support using a dip-coater with a dwell time of 1 min and a withdrawal rate of 10 cm min^{-1}. After the deposition of each layer, the membrane layer were dried in an oven and then calcined in a furnace according to the same treatment described above for the xerogels, hence the temperature ramping rate experienced by the membrane was on the order of >100 °C s^{-1}. After each calcination step, the membrane was immediately removed from the hot furnace and allowed to cool on the bench top of a laminar flow cabinet to prevent dust contamination. This cycle of dip-coating, drying and calcination was repeated six times for a total of six membrane layers.

2.3. Xerogel characterization and membrane testing

All the xerogel samples were synthesized according to the methodology described above, and exposed to the same fast thermal calcination process at 600 °C in an air atmosphere. The xerogels were ground into powders for nitrogen adsorption and FTIR measurement. Nitrogen gas adsorption measurements were carried out in triplicate samples degassed for a minimum of 6 h to a pressure of 2 Pa at 200 °C in a Micromeritics VacPrep061 prior to analysis by a Micromeritics Tristar 3020 analyzer. Specific surface area and micropore volume measurements were determined by the Brunner–Emmett–Teller (BET) method. The analysis of pore size distribution was obtained using the density functional theory (DFT) method for pore sizes between 1 and 60 nm [5,27–29]. The DFT method was applied to the whole adsorption branch of the isotherms using cylindrical pores in oxide surfaces with a low regularization. Fourier transform infra-red-attenuated total reflectance (FTIR-ATR) characterization was performed on a Shimadzu IRAffinity-1 with a PIKE MIRacle single-bounce diamond crystal plate accessory. FTIR spectra were collected at a resolution of 4 cm^{-1} in the range of 4000–600 cm^{-1} for a total of 32 scans. IR spectra were normalized to the maximum intensity of the band at $\sim$1030 cm^{-1}, which was assigned to the anti-symmetric Si–O–Si stretching vibrations [30]. This peak appears to be very stable without any change in its shape or its relative intensity to that of the 796 cm^{-1} band which is associated with the symmetric Si–O–Si stretching vibration. Peak deconvolution of the absorption