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Structure, stability and permeation properties of NaA zeolite membranes for H_2O/H_2 and CH_3OH/H_2 separations

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ABSTRACT

NaA zeolite membranes were synthesised in the secondary growth hydrothermal method based on the seeding of the inner surface of a ceramic α-alumina tube. The impacts of crystallisation time and zeolite precursor concentration (in H_2O) were investigated. The structure and stability of the prepared NaA zeolite membranes were also investigated with operating temperatures, times and pressures. The results indicate that the optimal synthesis gel molar composition was $3Na_2O$: $2SiO_2$: Al_2O_3: $200H_2O$. This led to cubic-shaped NaA zeolite which showed good stability. The optimal NaA zeolite membrane had H_2O and CH_3OH fluxes of 2.77 and 0.19 kg/m^{2}h, with H_2O/H_2 and CH_3OH/H_2 separation factors of ∞ and 0.09 at a temperature of 30 °C. The NaA zeolite membrane had high thermal stability, but poor separation performance at high temperature (240 °C). The results suggested that the H_2 permeation flux is significantly influenced by preferential adsorption of vapour in the NaA zeolite membrane.

1. Introduction

Methanol (CH_3OH) is a key commodity for the production of industrial chemicals such as formaldehyde, acetic acid, methyl tertiary-butyl ether (MTBE) and dimethyl ether (DME). The CH_3OH market is estimated to have a world capacity of *ca.* 100 million tonnes per year, with production of 70 million tonnes in 2013 [1]. The current industry is one of the world's most dynamic and vibrant, with CH_3OH typically produced when pressurised synthesis gas (syngas, a mixture of mainly H_2, CO and CO_2), reacts in the presence of a catalyst (e.g. Cu/ZnO-based systems) [2] at between 200 and 250 °C and 5–10 MPa [3]. The product CH_3OH can be continuously removed from the gas phase based on selective adsorption over a solid or in a liquid. Also, the product stream may contain up to 18vol% H_2O, and also CH_3CH_2OH, higher alcohols, ketones and ethers and fed to a distillation plant which removes the volatiles, while another unit removes H_2O and higher alcohols [4]. In the case of H_2O-washing followed by distillation, the H_2O is introduced into a previously H_2O-free mixture and cannot be removed completely afterwards. In addition, this process requires three distillation columns, and thus a relatively large amount of space. Furthermore, it consumes a large amount of energy and generates waste H_2O that in turn has to be treated.

Pervaporation, a membrane separation process, is often used to remove H_2O from organic components (e.g. solvents). The process is simple and avoids the problems associated with traditional technologies [5]. Continuous *in situ* extraction of CH_3OH and H_2O from the synthesis reactor would enhance the desired product yield by shifting the equilibrium [6]. To apply membranes in the industrial synthesis of CH_3OH, both membrane selectivity and thermal stability are important considerations. However, studies concerning membrane application in vapour/gas separation at high temperatures are limited. Struis et al. first applied a membrane reactor to methanol synthesis using a Li-Nafion® membrane, but Nafion® membranes cannot be applied above 478 K due to lack of thermal stability [7–9]. Chen et al. also investigated silicon ceramic membranes for separation of CH_3OH and H_2O from H_2, with these membranes presenting high thermal stability, but poor separation performance [10].

In recent years, zeolite membranes have acted as potential separators in the chemical industry because of their unique physicochemical properties, including molecular sieving and preferential adsorption, as

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well as high thermal and chemical stabilities [6,11]. Various membranes based on MFI, DDR, LTA, FAU, and CHA zeolites have been successfully synthesised and applied in the separation of H_2O from gas-liquid mixtures [12–23]. Sawamura et al. investigated the separation properties of CH_3OH and H_2O from H_2 on mordenite membrane at 523 K [19]. This zeolite membrane provided excellent selective permeation of H_2O; however, the thermal stability was poor at high temperatures. A silicalite-1 membrane has also been investigated for the separation of CH_3OH and H_2 at 100 °C and a total pressure of 1–10 bar [20]. It was found that the separation factor was 3 and adsorbed CH_3OH blocked the pores responsible for H_2 permeation. Sato et al. [6] evaluated the separation of H_2O-CH_3OH-H_2 mixtures using FAU-based membranes. The separation factor for CH_3OH/H_2 was 35 at 180 °C. Sandström et al. [21] used MFI membranes for methanol/hydrogen separation with operating temperatures of 175 °C. It was found that the separation factor for CH_3OH/H_2 was 32 at room temperature, but nearly 0 above 100 °C.

Among the various zeolite membranes, NaA zeolite membranes have been widely studied for dehydration of organics by pervaporation or vapour permeation [22]. In terms of porosity, NaA zeolite has a pore size of 0.41 nm, larger than the kinetic diameters of H_2O (0.265 nm) and CH_3OH (0.380 nm) respectively, with large adsorption capacities for these molecules [23]. NaA zeolite membranes have mostly been applied in the dehydration of alcohols in pervaporation, as NaA is known to be one of the hydrophilic zeolites and perhaps one of the easiest to synthesise [18]. To our knowledge, there have been few reports on vapour/gas separation using NaA zeolite membrane. Shirazian et al. [24] evaluated the permeation of H_2O vapour and CH_4 gas mixtures through NaA membranes. It was found that the permeation fluxes of H_2O vapour and CH_4 were 5.7×10^{-6} and 5.0×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, whereas the ideal selectivity was 11 at room temperature. Aoki et al. [25] reported that the NaA zeolite membrane had high separation factors, but its stability at $T > 200$ °C is currently unknown. Cho et al. [26] sought to improve the thermal stability of NaA zeolite membrane. It was suggested that control of the intermediate layer is an effective tool to improve the thermal stability of NaA zeolite membranes, but its thermal stability at temperatures above 130 °C has not been reported thus far.

There has been no previous study on the effect of structure stability and H_2O or CH_3OH/H_2 (or indeed syngas) separation performance of NaA zeolite membranes. Thus, the purpose of this study was to synthesise an optimal NaA zeolite membrane, and examine its structure stability and permeance of H_2O, CH_3OH and H_2. Therefore, NaA zeolite membranes were prepared based on secondary growth hydrothermal method, with the impact of zeolite crystallisation time and precursor concentration investigated, with particular regard to structuration, morphology and stability. Finally, the separation of H_2O/H_2 and CH_3OH/H_2 mixture over an optimised NaA zeolite membrane has also been investigated.

2. Experimental

2.1. Synthesis of NaA zeolite membranes

Ceramic α-alumina based tubes with 0.2 μm pore size (10 mm O.D., 7 mm I.D., 113 mm length, supplied by Philips Ceramics Uden, Netherlands) served as membrane substrates in this study. For the preparation of NaA zeolite membranes, sodium hydroxide, aluminium hydroxide and sodium metasilicate were used without further purification (Sigma Aldrich, Canada).

NaA zeolite membranes were synthesised based on seeding of the inner surface of the ceramic α-alumina tubes, followed by deposition of the zeolite phase from the aqueous phase. For zeolite seeding, the commercially available zeolite powder (Molecular sieves, 4 Å, Sigma Aldrich) was used as the seed crystal. Powder was first crushed in an agate mortar. Then crushed zeolite powder was mixed with deionised H_2O, and the seeding solution was treated in an ultrasonic bath. at room temperature. The whole outer surface of the substrate was wrapped with teflon tape to prevent any deposition of zeolitic material. After the seeding and synthesis, the teflon wrap was removed. The alumina tubes were immersed vertically into a 3.0% (by mass) seed suspension. The seeded support tubes were then dried at 70 °C for 2 h before membrane synthesis. For the aqueous phase zeolite deposition, a synthesis hydrogel of a molar composition $3Na_2O{:}xSiO_2{:}Al_2O_3{:}yH_2O$ was prepared by mixing the aluminate and silicate precursor solutions, where $x = 0.5$, 1.0, 2.0, 2.5 and 3.0, and $y = 80$, 120, 200, 500 and 1000, respectively. The aluminate solution was prepared by dissolving sodium hydroxide and aluminium hydroxide in deionised H_2O (90 g), under stirring at 70 °C, for 1 h. The silicate solution was prepared by dissolving a sodium metasilicate solution in deionised H_2O (210 g), again with stirring at 70 °C for 1 h. These two solutions were then mixed and stirred at 70 °C for a further 30 min. The resulting synthesis gel was then poured into a Teflon-lined stainless steel vessel, followed by transfer of the seeded support tubes to this vessel. Synthesis was carried out in a H_2O bath at 70 °C for 1–24 h. The products were next washed and then dried in an oven at 70 °C for 3 h.

2.2. Characterisation

Scanning Electron Microscope (SEM) images were acquired using an Hitachi S3000N VP device equipped with an Energy-Dispersive X-ray (EDX) detector, enabling characterisation of the surface and cross-section of the as-synthesised membranes. In order to determine the crystal structure of the membranes, X-ray diffraction analysis (XRD) was performed using an Rigaku MultiFlex instrument equipped with a 2 kW X-ray generator and a monochromator and scintillation counter detector. XRD patterns were acquired in the range of $2\theta = 5$–$50°$ at a scanning rate of 4°/min.

2.3. Permeation tests

CH_3OH or H_2O and gas permeance tests were performed using a tubular membrane module set-up (Scheme 1). The NaA zeolite membrane was sealed in a membrane module by double O-rings to prevent leakage. The tubular membrane module was placed in a temperature-controlled electric furnace. H_2O or CH_3OH at a flow rate of 0.33 ~ 0.42 cc/min was fed to the inside of a membrane tube by a syringe pump with H_2. Methanol vapour supply pipe was made of stainless steel (1/8‘ sus) and wrapped with a heating band for 200 °C to prevent condensation.

The flow rate on the permeate side was measured by bubble flow meters. The H_2 feed flow rate was 500 cc/min, and the sweep gas (He) flow rate was 100 cc/min. The pressure on the retentate side of the membrane was controlled by a back-pressure regulator. Permeated vapour was condensed by a cold trap.

The permeation flux was obtained from the weight of the condensate collected over 1 h. The separation factor (α) and permeance flux (J) are defined as:

$$a = \frac{y_i/y_j}{x_i/x_j} \tag{1}$$

$$J = \frac{W}{A \cdot \Delta t} \tag{2}$$

where y_i/y_j is the molar ratio of CH_3OH or H_2O to H_2 in the permeate, and x_i/x_j is that in the feed. W is the total mass gained by the permeate in kg. A is the separation area of the inner membrane, m^2, and Δt is the time of collection, h.