



## Development of a water-selective zeolite composite membrane by a new pore-plugging technique



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### ABSTRACT

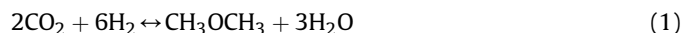
A new membrane preparation method based on mechanical pore-plugging of the supports with appropriate sized seeds followed by secondary zeolite growth by hydrothermal synthesis was optimized for the production of hydroxy-sodalite (hydroxy-SOD) membranes. A series of parameters were investigated during membrane production, including seed loading, presence of Teflon on the coarse side of the support, top-layer orientation in the autoclave, autoclave agitation, synthesis time and temperature, membrane post-synthesis treatment, and nature and pore size of the support (TiO<sub>2</sub>/SS, SS, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>/TiO<sub>2</sub>). Zeolite seeds and synthesized membranes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and gas permeation. The gas permselective separation ability of these membranes was demonstrated from H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O permeation tests at temperature up to 250 °C. The membranes fabricated with the optimized parameters achieved H<sub>2</sub>O/N<sub>2</sub>, H<sub>2</sub>O/CO<sub>2</sub>, and H<sub>2</sub>O/H<sub>2</sub> ideal gas permselectivities of 5.1, 4.8 and 1.4 at 250 °C, while providing a high water permeance ( $J_{H_2O}$  of  $1.26 \times 10^{-7}$  mol Pa<sup>-1</sup> m<sup>-2</sup> s<sup>-1</sup>) at the same temperature.

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### 1. Introduction

The economical production of an efficient, convenient and renewable carbon-neutral fuel is among the most researched field nowadays [1–8]. Many new eco-friendly fuels come with problems ranging from safety (e.g., hydrogen handling and storage) to food crisis [9,10] (e.g., bioethanol production from corn or other edible feedstock), so other fuels and efficient production processes need to be put in place. It is well known that high energy density fuels (biodiesel, gasoline, dimethyl ether (DME), etc. [5,8,11,12]) can be synthesized from syngas and these processes have already proven to be industrially suitable for a large-scale production. On the other hand, the need for syngas' carbon monoxide (CO), which is often produced from hydrocarbon gasification or reforming, makes these processes far from carbon neutral. To achieve carbon neutrality, researchers have instead proposed the use of captured carbon dioxide (CO<sub>2</sub>) as a source of carbon [1,6]. In this manner, captured CO<sub>2</sub>

and hydrogen (H<sub>2</sub>) produced from renewable resources will allow the production of renewable carbon-neutral fuels like DME [13]. DME has the advantages to burn cleanly because of a lack of carbon-carbon bond, to possess good energy density and to be easily implemented to current technologies as compared to other fuel alternatives (hydrogen, methanol, ethanol, etc.) [14]. However, the use of CO<sub>2</sub> instead of CO in DME synthesis has the main drawback of producing relatively large amounts of water (Eq. (1)) thereby thermodynamically braking CO<sub>2</sub> conversion, limiting DME yield and even inducing catalyst deactivation [15–18].



Highly water selective hydrophilic membranes are among the systems that have been proposed for the *in-situ* removal of water from the reaction media [15,16,18]. On the other hand, membrane requirements for the selective water removal in DME synthesis conditions are difficult to achieve. Based on previous works [13,17,19–23], for an economical process the required membrane selectivities for water over the other species present in the reaction ( $S_{H_2O/H_2}$ ,  $S_{H_2O/CO_2}$ ,  $S_{H_2O/CO}$ ,  $S_{H_2O/MeOH}$ ,  $S_{H_2O/DME}$ ) should be around 75 with a target water permeance ( $J_{H_2O}$ ) around

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$10^{-7}$  mol Pa<sup>-1</sup> m<sup>-2</sup> s<sup>-1</sup>. It should be noted, however, that these values have been evaluated from techno-economic studies [13,17,19–23] based on current best available catalysts and projected production price of zeolite membranes over ceramic supports, so they give an estimation of performances that membranes should aim for. The membrane also requires good resistance to harsh reaction conditions of  $\approx 250$  °C, acidic environment and pressure up to 5 MPa. Concerning the membrane type, only supported hydrophilic zeolite membranes seem to offer the potential to fulfill adequately the above-mentioned requirements compared to less temperature resistant polymeric membranes and less selective ceramic membranes [17,18,24–27]. In particular, hydroxy-sodalite (hydroxy-SOD) zeolite could be a promising candidate for this kind of applications as (i) its low Si/Al ratio (Si/Al = 1) makes it highly hydrophilic and (ii) its pore size of around 2.7 Å (ranging between the kinetic diameter of water (2.65 Å) and the other small molecules (H<sub>2</sub>: 2.89 Å, CO<sub>2</sub>: 3.35 Å, CO: 3.76 Å) [22,28]) allow a potential water preferential separation by adsorption and size exclusion. In addition, hydroxy-SOD is remarkably resistant to high temperature (up to 400 °C) and acidic conditions compared to other low Si/Al zeolite like NaA and therefore could possibly be applied in a membrane reactor for the synthesis of DME from CO<sub>2</sub> and H<sub>2</sub> [19].

Based on theoretical calculations, hydroxy-sodalite membranes should demonstrate a near perfect water selectivity over hydrogen [20]. However, no work has been able to produce so far membranes achieving this performance for gas separation. In fact, the best water-hydrogen selectivity ( $S_{\text{H}_2\text{O}/\text{H}_2}$ ) obtained at 200 °C (a lower temperature than required for the reaction of interest) is around 4.6 [23]. It was reported that the low selectivity may arise from hydroxy-sodalite membrane defects like crack, pin hole, bad anchorage of the zeolite to the support or impurities (e.g., formation of other zeolites) [18,23,29]. As these problems are often related to the membrane synthesis technique, we believe that the development of new and more efficient methods could allow to come closer to the theoretical separation performance of hydroxy-sodalite (SOD) membranes.

The primary objective of this work is therefore the development of a new hydroxy-SOD membrane synthesis technique. The major issue with conventional membrane formation as a thin film at the surface of the support is that the film is prone to defects [18,23,29]. In an attempt to prevent defect formation, it has been proposed to synthesize a nanocomposite layer of zeolite in the pores of the support [30–32]. The benefits of pore-plugged membranes are a better mechanical and abrasion resistance from the contact with the reactor catalysts, a better zeolite adhesion to the support, a thinner efficient diffusion layer and a synthesis technique that can be applied to large scale membrane production [31]. Previous syntheses of pore-plugged membranes were done with other zeolites (like ZSM-5 and silicalite) on alumina or stainless steel (SS) and were produced via an interruption during the hydrothermal synthesis to favor reactant diffusion inside the pores of the support [30–32]. To the best of our knowledge, hydroxy-SOD membranes synthesized by a dedicated pore-plugging technique have never been reported in the open literature. In order to achieve the fabrication of this type of membrane, a new seeding technique was developed in this work and multiple hydrothermal synthesis parameters have been analyzed and optimized. Resulting membranes were tested with permeation experiments at temperature up to 250 °C with gases that are present in the reaction of interest (H<sub>2</sub>O, H<sub>2</sub>, and CO<sub>2</sub>).

## 2. Experimental

### 2.1. Materials

For hydroxy-sodalite synthesis, sodium metasilicate non-hydrate ( $\geq 99.5\%$  w/w, Fisher Scientific), LUDOX HS-30 colloidal silica (30% SiO<sub>2</sub> in water, Sigma-Aldrich) and tetraethyl orthosilicate (TEOS) ( $\geq 98\%$  w/w, Sigma-Aldrich) were used as Si sources whereas sodium aluminate (50–56% Al (Al<sub>2</sub>O<sub>3</sub>), 40–45% Na (Na<sub>2</sub>O), Riedel-de Haën) was used as the Al source. Other chemicals used in this work are tetrapropylammonium hydroxide (TPAOH) (1.0 M in water, Sigma-Aldrich), sodium hydroxide ( $\geq 97\%$  w/w, VWR International), nitric acid (70% w/w in water, Fisher Scientific), methanol ( $\geq 99.9\%$  w/w, Fisher Scientific) and deionized water ( $\geq 10$  MΩ cm). All chemicals were used as received without further purification. Various supports were tested for membrane synthesis: stainless steel (SS) disk (Mott Corporation, 19 mm diameter, 1.59 mm thickness, 0.2 μm pore size), TiO<sub>2</sub> on SS tube (Graver Technologies, 12.7 cm porous length, 6/9.1 mm inside/outside diameter, asymmetric 0.5 μm (TiO<sub>2</sub>)/ $\approx 5$  μm (SS) pore size), ZrO<sub>2</sub>/TiO<sub>2</sub> disk (Sterlitech Corporation, 47 mm diameter, 2.5 mm thickness, asymmetric 0.14 μm/ $\approx 1.4$  μm/ $\approx 4$  μm pore size), and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disk (Atech-Innovations, 49 mm in diameter, 2.6 mm in thickness, asymmetric 0.2 μm/ $\approx 2$  μm pore size). Before use, the supports were first cleaned with solutions of NaOH and HNO<sub>3</sub>, following standard recommendations. They were then rinsed with methanol and deionized water until a neutral pH was obtained.

### 2.2. Preparation of hydroxy-SOD seeds

Two alkaline aqueous solutions were first prepared in polypropylene bottles at 50 °C under stirring, one containing the Si source and the other the Al source. When clear solutions were obtained, they were mixed together in order to achieve a clear solution with a molar ratio of 5Si:2Al:100Na:1005H<sub>2</sub>O, which is the optimal one to produce pure hydroxy-sodalite according to Khajavi et al. [29]. The solution was then transferred in a Teflon-lined stainless steel autoclave and put in a pre-heated oven (Mettmert UNE 200) for crystallization. Multiple silicon sources and hydrothermal synthesis conditions were tested (Table 1) to produce pure seeds that also have a particle size appropriate for the newly proposed pore-plugging seeding technique (explained in section 2.4). Synthesis of hydroxy-sodalite by the conversion of silicalite nanocrystals as proposed by Yao et al. [33] was also carried out. After the synthesis, zeolite crystals were washed and centrifuged at 4000 RPM in deionized water multiple times until pH neutrality. The resulting powder was dried overnight at 90 °C, weighed and stored in an air-tight vial for further characterizations. For some samples, 1 g of hydroxy-SOD powder was added to 10 g of water and wet-milled at 400 RPM in an agate planetary ball mill with 18 10-mm agate media for 1000 min to reduce particle size. The resulting suspension was diluted to 50 ml and stored for further characterizations.

### 2.3. Characterization of hydroxy-SOD seeds

The phase purity and crystallinity of the seeds were evaluated by X-ray diffraction (XRD) at room temperature in air using a Bruker D8 Advance A25 system in the 2- $\theta$  range of 4–50°, with a step width of 0.02°, a counting time of 1 s and Cu K <sub>$\alpha$ 1 +  $\alpha$ 2</sub> radiation ( $\lambda = 1.54184$  Å). Morphology, size of particles, as well as purity, were observed by a Hitachi S-800 scanning electron microscope (SEM). Finally, particle size distribution was evaluated by laser granulometry using a Microtrac S3500.

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