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Titanosilicate AM-3 membrane: A new potential candidate for H_2 separation

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ABSTRACT

Small pore titanosilicate AM-3 has been prepared as a continuous layer on α-alumina and stainless-steel porous tubes by seeded hydrothermal synthesis. The influence of the synthesis conditions has been studied, and pure AM-3 membranes about 12 μm thick have been obtained, exhibiting a good intergrowth of crystals. The samples have been characterised by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectrometry and X-ray mapping. The membranes have also been evaluated by measuring the permeances of single gases at programmed temperature, and their trends have been discussed. The available evidence shows that the titanosilicate AM-3 membrane is a potential candidate for H_2 separation.

1. Introduction

It is well known that petroleum and coal fuels generate green house gases while hydrogen only produces water. The development of advanced hydrogen technologies requires high efficient processes and materials for purification, separation and storage. Several techniques for hydrogen separation are already available or under study, such as pressure swing adsorption [1], cryogenic separation [2], catalytic purification [3], and membrane separation [4]. Palladium membrane is used in many applications due to its high hydrogen permeability and catalytic surface, as well as good mechanical characteristics [5,6]. However, palladium and its alloys are: (i) extremely expensive although thin metal layers supported on ceramic or metallic substrates may be used to reduce the cost; (ii) highly sensitive to chemicals, such as sulphur, chlorine and carbon monoxide in most applications. Therefore, the search for new membrane materials is an active field of research.

Inorganic porous membranes usually have good thermal and chemical stability, and high mechanical strength, which make them promising materials for gas separation applications. They generally consist of a separation layer, with micro- or nanopores, and a thicker mesoporous support. Microporous materials exhibiting molecular sieving ability, such as zeolites, have already been used as the separation layer of porous membranes [7]. Microporous titanosilicates may broaden the scope of application of classical zeolites. Their structures consist of interlinked octahedra (sometimes pentahedra) and tetrahedra, forming frameworks with channels of molecular dimensions [8]. The few studies available on microporous titanosilicate membranes encompass ETS-10 [9–12], ETS-4 [12–16] and AM-2 [17–19]. AM-3 [20] is a synthetic microporous titanosilicate with the structure of the mineral penkvilksite-2*O* and has the ideal formula $Na_2TiSi_4O_{11}{\cdot}2H_2O$. Like titanosilicate AM-2, the structure of AM-3 consists of chains of SiO_4 tetrahedra connected by individual TiO_6 octahedra, forming a three-dimensional framework with six-membered ring channels [20], which are partially occupied by Na^+ cations and water molecules. AM-3 is a poor nitrogen adsorbent but adsorbs copious amounts of water. It may be reversibly dehydrated and has cation exchange capacity [20]. Furthermore, the synthesis of AM-3 is environmentally friendly, in the sense that no templates are used and the pH is moderate.

Our previous work [17–19] indicates that the small pore AM-2 membranes have potential for the separation of H_2 containing mixtures. This prompted further research on the synthesis of new small pore membranes with potential for H_2 separation. In this work we will report the synthesis, structural characterisation and single-gas permeation results for the first AM-3 membrane ever prepared. The results showed that small pore AM-3 membranes are good candidates for the separation of H_2 containing mixtures.

2. Experimental

2.1. Materials preparation

AM-3 membranes have been prepared on commercial tubular symmetric α-alumina (Inopor) and stainless-steel (Mott) supports, by subjecting the seeded supports to a secondary growth step, which was performed in Teflon-lined autoclaves at 230 °C under autogenous pressure without rotation. The molar compositions used for the preparation of AM-3 membranes were in following

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ranges: 5.3–5.4 Na_2O:0.6 K_2O:5.0–5.1 SiO_2:1.0 TiO_2:113–274 H_2O. The α-alumina supports have an average pore size of 3.0 μm and thickness of ca. 1.5 mm, while the stainless-steel ones have pore size of 500 nm. Before the hydrothermal synthesis, the supports were seeded by rubbing AM-3 seeds. The inner side of the 8 cm long tubes was not seeded, reducing the crystal growth in this region. The AM-3 seeds were firstly synthesised using the procedure published elsewhere [20] and then ground using a planetary ball mill. The seeded support was placed vertically in the bottom of a Teflon-lined autoclave with Teflon holder where the growth (synthesis) gel was poured. Sodium silicate solution (27 wt.% SiO_2, 8 wt.% Na_2O, Merck) and titanium trichloride solution (15 wt.% $TiCl_3$, 10 wt.% HCl, Merck) were used as Si and Ti sources. A typical precursor for AM-3 membrane synthesis was prepared as follows. 16.25 g of sodium silicate solution were diluted in 7.80 g of distilled water. Then, 3.69 g of sodium hydroxide (Merck), 1.20 g of sodium chloride (Panreac) and 1.41 g of potassium chloride (Merck) were added. Finally, 14.98 g of titanium trichloride solution were added with thoroughly stirring and homogenited for more than 30 min. This process resulted in a viscous mixture which was then treated at 230 °C for 48 h. The autoclaves were cooled down with flowing water and the samples were washed with distilled water. In order to increase the thickness and/or crystallinity, or decrease the existent meso- and microdefects, AM-3 membranes were also prepared through a two-step synthesis, i.e., after synthesis at 230 °C the sample was well washed by distilled water and then immersed into a fresh gel and treated at the same temperature for another period of time.

2.2. Materials characterisation

The phase formation was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectrometry (EDS). The X-ray map technique through the cross-section was used to analyse the composition homogeneity of the membranes. XRD was performed between 5° and 50° 2θ on a Philips X'pert MPD diffractometer using CuKα radiation. SEM images, EDS and X-ray mapping were recorded on a Hitachi S-4100 or SU-70 microscopes equipped with Rontec EDS system. The samples for X-ray mapping were prepared by inserting the fractured membrane into an epoxy matrix and polishing in the direction perpendicular to membrane surface.

2.3. Temperature programmed permeation of single gases (TPP)

In order to get valuable information about gas permeation, a temperature programmed permeation (TPP) system was employed to measure single-gas permeances of H_2, N_2, O_2 and CO_2 through the membranes. They were placed in a stainless-steel module and sealed with viton o-rings. Before running TPP, heating and cooling cycles were always carried out up to ca. 200 °C under continuous He flow (20 cm^3 (PTN)/min) through the membrane in order to remove any adsorbed species. The membrane module containing each sample was placed in an oven and the experiments were conducted between 25 and 120 °C, at a fixed heating rate of 1 °C/min. The feed flow rate was fixed by a mass flow controller, the permeate side was kept at atmospheric pressure, and the transmembrane pressure drop was controlled by a back pressure regulator located at retentate outlet. Permeances were computed by using the measured permeation fluxes and ΔP.

3. Results and discussion

The first description of the synthetic analogue of the small pore sodium titanosilicate mineral penkvilksite-2*O* powders (AM-3) has been published over 10 years ago [20]. To date, no details about the synthesis behaviour have been reported. The first pure AM-3 sample was obtained after 17 days of synthesis at 230 °C. At shorter times, the samples contained ETS-10, ETS-4 and AM-1 phases. This synthesis condition is clearly not convenient for the preparation of membrane samples. Therefore, the effect of the experimental conditions on the crystallisation of AM-3, such as seeding, alkaline content of the starting mixture and synthesis time, as well as the possibility of leaching of the support under the synthesis conditions, must be studied. Although a higher alkaline content may decrease the synthesis time and the amounts of undesired phases, it is not suitable for membrane synthesis since it will result in the leaching of the support. SEM image of AM-3 [20] showed a flower-like intergrowth with a size of ca. 75 μm, implying that the crystals grew from a few nuclei in the "flower" centre. With this consideration in mind, the seeding effect was studied as a first step

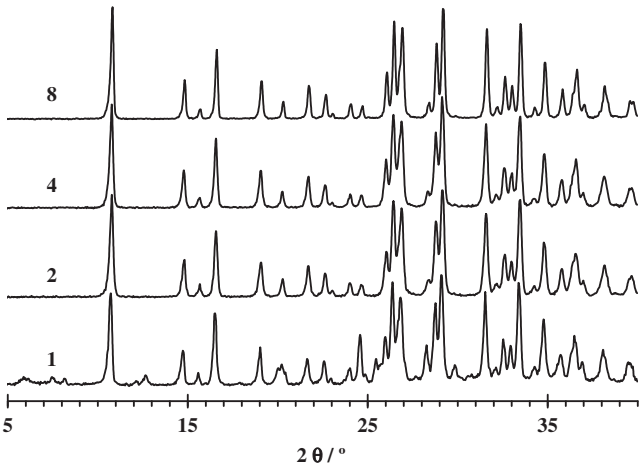

Fig. 1. Seeding effect on the formation of AM-3 phase. The samples were synthesised at 230 °C for the number of days depicted. The peaks at ca. 6.0°, 7.5° and 8.1° 2θ are from ETS-10, ETS-4 and AM-1, respectively.

Table 1
Some synthesis conditions of selected samples prepared on α-alumina support for characterisation by XRD, SEM, EDS and X-ray mapping.

Sample	M1	M2	M3	M4	M5	M6
Time (day)	2 + 2	2	4	2	1 + 1	2 + 1
H_2O/Ti	113 + 274	113	113	274	4500	113 + 4500

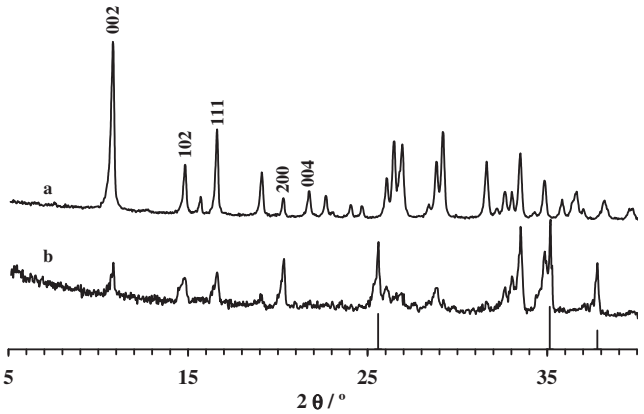

Fig. 2. XRD patterns of pure AM-3 powder (a) and AM-3 membrane M1 (b) synthesised via two-step process. The bars depict reflections from the α-alumina support.