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Synthesis and characterization of MCM-48 tubular membranes

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Abstract

MCM-48 membranes have been prepared on alumina supports of different pore sizes. A battery of characterization techniques has been used to study the physical properties and the quality of the membranes prepared. The highest quality membranes were prepared on supports with pore size of up to 60 nm. The MCM-48 membranes were tested in the separation of gas phase mixtures and a cyclohexane/O_2 selectivity higher than 270 was obtained. The selective separation of organic compounds from inert components is a result of the cooperative effects of capillary condensation in MCM-48 pores and of the specific interactions of the permeating compounds and the membrane material.

Keywords: Mesoporous membranes; MCM-48; zeolite membranes; organic/permanent gas separation

1. Introduction

Microporous inorganic membranes have been extensively studied during the last decade as an alternative to polymeric membranes. Among them, zeolite membranes show great potential for applications as membrane separators, membrane reactors and sensing devices due to their diversity of structures and thermal and chemical stability. Nevertheless, zeolite structures have pores of subnanometric size, which imposes a limit on the size of molecules that can be processed. Therefore, when relatively large molecules are to be separated, other types of porous membranes must be used.

Mesoporous inorganic membranes have also been investigated, mainly consisting of silica, titania, and zirconia, often prepared by the sol–gel method. These membranes are amorphous and do not posses an ordered structure. A different kind of material is the so-called M41S [1,2], whose surfactant-mediated synthesis was first reported in 1992 by researchers from Mobil Oil Corporation. Among M41S are MCM-41 and MCM-48 with uniform pore structures of hexagonal and cubic symmetry, respectively. These materials are interesting for the preparation of membranes as they present narrow pore size distributions that can be tuned from 2 to10 nm.

The preparation of films of these materials has been accomplished primarily over non-porous substrates (e.g., mica [3], glass [4,5], silicon wafers [6,7]), which are not suitable as membrane supports. The first attempt to grow mesostructured silica films on a support was reported in 1996 by Yang et al. [3], who carried out the hydrothermal treatment of a mica support immersed in an aqueous-acid-surfactant mixture. As an alternative synthesis procedure, a classical sol–gel route has been employed for the preparation of the precursor containing the hydrolyzed silica source and the surfactant, followed by deposition of the sol on the support (dip-coating or spin coating) and solvent evaporation. Using this method Ogawa and Masukawa [5] prepared thin films of lamellar, hexagonal and cubic mesoporous silica, over pyrex glass substrates.

While these studies are useful to investigate the conditions leading to the growth of mesostructured films, the application of these films as membranes requires synthesis over porous supports that enable permeation of the target molecules. A further issue to take into account concerns the alignment of the membrane pores with regards to the support surface. While this is not a problem when the three-dimensional structure of MCM-48 is used, alignment of the pore network of MCM-41 parallel to the support surface hinders permeation. This has led to attempts to attain perpendicular alignment of the pores with respect to the

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support surface, often by unusual procedures (e.g. magnetic field alignment [8]).

Nishiyama et al. [9], using a hydrothermal treatment, were able to present the first gas-permeable mesoporous silica membranes made of MCM-48. These membranes were synthesized over flat porous stainless steel supports that were placed horizontally in the autoclave containing the sol precursor during at least two days. The same group [10] presented permeance measurements of different gases and carried out a permeance versus pressure study that confirmed a Knudsen permeation mechanism for these membranes, with nitrogen permeances around $2.5\,10^{-7}$ mol/m^2 s Pa. EDX analysis showed that the membrane consisted of a layer prepared on top of the support, with some siliceous material penetrating the support pores. In a separate study of the same laboratory [11], silylation was carried out using trimethylchlorosilane and triethylclorosilane as silylation reagents, in order to enhance the hydrophobicity and hydrothermal stability of these membranes. The silylated MCM-48 membranes where used for the separation of organic/water mixtures, the organic component being ethanol, methyl-ethyl-ketone or ethyl acetate. They found separation factors and organic permeation fluxes as high as 320 and 5.8 kg/m^2 h, respectively, for a mixture containing 5% of ethyl acetate in water at 300 K.

The synthesis over porous supports, using the sol–gel technique has been less studied. 'Kim and Yang [12] used this method to prepare thin films of mesoporous silica with a cubic structure over α-alumina porous supports whose pores had previously been filled with PVA to prevent sol penetration. This produced 1 μm thick films. However, no permeation measurements were reported.

McCool et al. [13] synthesised mesoporous silica membranes over flat α-alumina supports using both dip-coating and hydrothermal treatment as synthesis methods. While both types of preparation methods yielded membranes that exhibited Knudsen permeation, the fluxes for the dip-coated membrane were nearly three times higher. The maximum separation factor for N_2/Ar mixtures was 1.35 and 1.2 for the hydrothermal-treated and dip-coated membranes, respectively. Mesoporous silica membranes have also been synthesised on flat alumina supports for filtration applications [14] and solvent permeation [15] using the dip-coating and spin-coating techniques.

To our knowledge, the synthesis of MCM-48 membranes over tubular supports has only been reported by Liu et al. [16] but no separation results were presented. The aim of the present work is to contribute to the study of MCM-48 membranes on tubular supports, which are those better suited for industrial use. To this end, we present the preparation of these membranes using hydrothermal synthesis, as well as data obtained from characterization experiments by a battery of techniques: XRD, BET specific surface area, SEM, FTIR, single-gas permeation and permporometry. The MCM-48 membranes were also tested in the gas phase separation of mixtures containing an adsorbable organic compound and an inert component.

2. Experimental

2.1. Synthesis of the membranes

The membranes were prepared on tubular asymmetric supports (Inocermic) of 7 mm i.d., 10 mm o.d. At the innermost part of these ceramic tubes there is either a γ-Al_2O_3 layer, with pores of 5 or 60 nm, or a α-Al_2O_3 layer with 200 nm pores. In order to confine the permeation zone, the supports were subjected to enameling at both ends, defining a permeation length of approximately 5 cm.

The precursor gel for the MCM-48 synthesis had the following molar composition: 1 SiO_2: 61.44 H_2O: 0.62 CTMACl: 0.5 NaOH [17]. In a typical synthesis, TEOS (tetraethylorthosilicate) was added to a sodium hydroxide solution with stirring for 5 min to form a clear solution. Afterwards, surfactant, cetyltrimethylammonium chloride, CTMACl, was added. The mixture was maintained under stirring for 15 min more and the solution turned into a white gel. The gel was then introduced into the pores of the support by immersing the membrane tube into a vessel containing the gel and applying vacuum to its inner side. The gel-containing support was then introduced in a Teflon-lined autoclave containing the synthesis gel, and subjected to hydrothermal treatment in vertical (static) or horizontal (rotatory) position, for 48 h at 363, 376 or 383 K. The synthesis produced MCM-48 on the membrane, and also as a powder which could be collected at the bottom of the autoclave after reaction. The powder product and the membrane were washed with distilled water and dried at room temperature overnight. The material gain of the membrane (see Table 2) was calculated as the weight difference between the membrane after synthesis and the initial support.

The synthesis procedure was repeated until the N_2 permeance became null, usually taken as an indication of good membrane quality. The removal of the surfactant was carried out either by calcination or solvent extraction. A two-step procedure was adopted for the calcinations, with a first stage of heating under N_2 flow (200 N mL/min) at 2 K/min to 813 K, followed by 6 h under air (200 N mL/min) at this temperature. For the chemical extraction, a solution containing EtOH and HCl was used at 328 K for 8 h under reflux. For this procedure, each gram of MCM-48 was refluxed with 7 g of HCl (37 wt.%) and 250 mL of pure ethanol.

2.2. Characterization

The structure of materials obtained after synthesis was characterized by X-ray diffraction (XRD) (Cu Kα radiation on a Philips X'pert MPD). The BET surface area and pore size distribution of the powder were obtained by N_2 adsorption measurements on a Micromeritics ASAP 2020. The morphology of membranes was characterized by scanning electron microscopy (SEM, JEOL JSM-6400 operating at 20 kV). Infrared spectroscopy was used for the examination of MCM-48 samples after removal of the surfactant by different methods. The FTIR spectra were collected with a Mattson Research Series II instrument, equipped with a MCT detector (DRIFT