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Controlled growth of thin and uniform TS-1 membranes by MW-assisted heating

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ABSTRACT

Thin and uniform Ti-containing silicalite-1 (TS-1) membranes were prepared for the first time by a microwave-assisted secondary growth method. The influence of synthesis temperature (150–200 °C), duration (90–150 min) and Ti concentration in the mother sol (molar ratio Si/Ti = 16–100) on the membrane formation were studied. The quantity of Ti species inserted in the silicalite-1 network was found to vary with these parameters, as well as the membrane quality and performance. TS-1 membranes with a Si/Ti molar ratio in the range 25–40 were successfully prepared from mother sols with compositions in the range Si/Ti = 16–100. An original parabolic evolution of membrane thickness vs. Si/Ti in the mother sol was evidenced, with a minimum thickness for Si/Ti around 50. In all cases Ti species were inserted within the zeolite network as far as no TiO_2 clusters were detected after the thermal treatment at 550 °C. The membranes were typically 0.1–2 μm thick top-layers and crystal preferential orientation varied from *oblique*- to *c*-crystal preferential orientation (CPO) when the temperature was increased from 160 °C to 200 °C. The permeances of He, N_2, O_2, CO_2 were high and lied in the range 1.9–7.48 $\times 10^{-6}$ mol m^{-2} s^{-1} Pa^{-1} when measured between 25 °C and 200 °C. The most selective membrane, prepared at 190 °C during 120 min with a molar ratio Si/Ti = 75 in the mother sol, had an ideal selectivity of 40 for *n*/*i*-C_4H_{10} at 150 °C and 105 for CO_2/SF_6 at 25 °C.

1. Introduction

The performance of zeolites for catalytic applications is related to their molecular pore size and high surface area. Their high thermal and chemical stability is also well adapted to specific niche applications, including by coupling adsorbent and catalytic functions. The catalytic activity of zeolites strongly depends on their elemental composition and may be varied by insertion of active centers like Fe [1–4], V [4–6], Ag [7,8], etc. Many hetero-atom substituted variants of the MFI structure have been reported in the literature, of which the most significant is probably the hydrophobic MFI-type titanosilicate. Ti-silicalite-1 (TS-1) is a very active and versatile oxidation catalyst particularly when using diluted H_2O_2 as the oxidizing agent (e.g. for phenol hydroxylation, for olefin epoxidation, or for ammoximation of cyclohexanone) [9–11]. In these reactions, replacing TS-1 crystals by membranes could potentially increase the product conversion (contactor effect) and the product selectivity (by limiting side reactions).

The direct insertion of the Ti precursor in the mother sol used for the hydrothermal synthesis often leads to both intra- and extra-framework species, the latter being undesirable catalysts (e.g. leading to the decomposition of H_2O_2). Anatase was classically detected by FTIR and Raman spectroscopies below Si/Ti = 40 (i.e. above Ti/(Ti + Si) = 0.024) in the zeolite framework [12]. Hydrophobic TS-1 crystals with a relatively low Si/Ti ratio and attractive properties (homogeneity in size, shape, composition and specific orientation) were successfully prepared by MW-assisted hydrothermal synthesis [13–15]. However equivalent MW-derived TS-1 membranes have never been reported.

A number of publications already reported the classical hydrothermal (CL-HT) *secondary growth* of either TS-1 layers on Si wafers for micro-reactor applications [16], or TS-1 membranes on porous alumina based supports [17]. In these studies, the Ti concentration in the mother sol (Si/Ti = 25–100) was found to influence membrane morphology and slower growth rates were obtained for TS-1 membranes in comparison with pure S-1 ones. However, the durations for CL-HT synthesis being always relatively long (up to 50 h), a constant mean growth rate was measured over the studied range of Ti concentration. Recently, TS-1 membranes prepared by a *direct growth* CL-HT method were also reported by Chen et al. for either pervaporation [18] or selective oxidation reactions [19]. Membranes were obtained on mullite supports after 16–24 h synthesis at 200 °C [18]. The membranes were typically 10–20 μm thick, with randomly oriented crystals and a hardly detectable interface between the membrane and the mullite support [18]. In spite of the attractive characteristics of the membranes prepared by CL-HT *direct growth* method, the insertion of

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support species (e.g. Al) within the zeolite structure in close contact with the support could be suspected in the final membranes. Indeed, when a TS-1 membrane is deposited on a porous alumina based support, support leaching and insertion of Al species within the zeolite framework may strongly impact the zeolite membrane composition and properties. If support leaching occurs, Ti-ZSM-5 hydrophilic membranes with Al Lewis sites are obtained instead of the required Al-free TS-1 membranes. The insertion of Al may cause side reactions in oxidation reactions using TS-1 membrane. This problem was typically pointed out when V-S1 (actually V-ZSM-5) membranes were synthesized on α-Al_2O_3 support by classical synthesis [4]. This problem can be solved either by selecting a chemically stable (usually expensive) support, or by operating very short synthesis durations. The latter option can be typically operated by using both a pre-seeded support and a MW-assisted hydrothermal treatment for the secondary growth with a diluted sol. Indeed the very short synthesis times and intermediate pH required for preparing S-1 membranes by MW-assisted secondary growth [20] are strongly favorable to the synthesis of Al-free silicalite-1 membranes on alumina based supports.

Furthermore, a more homogeneous insertion and specific location of the active species within the zeolite network could be expected when using MW-assisted synthesis. Indeed rapid heating rates and non-equilibrium contributions to equilibration reactions might limit the formation of undesired phases (TiO_2 clusters or Al insertion in the S-1 network) in comparison with conventional heating. A further potential advantage of MW heating is that of selectivity, in cases where some component of the system is selectively sensitive to MW energy input.

The purpose of this work was to synthesize, on α-Al_2O_3 supports, uniform and thin (high flux) Ti-rich TS-1 membranes, free of both Al and extra-framework Ti species, by employing a *MW-assisted secondary growth* hydrothermal method (MW-HT). The influence of important synthesis parameters has been studied in order to control membrane growth and orientation, while maintaining a low number of intercrystalline defects in the membranes.

2. Experimental

The MW oven was a computer controlled Milestone ETHOS 1600, with pressure and temperature sensors in one of the Teflon autoclaves. For each sol composition and autoclave filling rate, the maximum MW power ($0 < P_{max} < 1000$ W), the maximum temperature (T) and the experiment duration (t) were fixed. In this work P_{max}, directly related to the sample heating rate, never over-passed 400 W. The maximum filling rate for the autoclave was 20% for seed synthesis and 55% for membrane secondary growth.

Mother sols were prepared by mixing tetraethylorthosilicate, TEOS (98%, Aldrich), ultrapure water (18.2 MΩ) and tetrapropylamonium hydroxide TPAOH (20% aqueous solution, Sigma). Tetrabutylorthotitanate TBOT (98%, Sigma) was used as Ti precursor.

2.1. TS-1 membrane formation by secondary growth

2.1.1. Seed preparation

Silicalite-1 (S-1) seeds with 50–60 nm size were prepared by a two steps MW-assisted synthesis as reported by Motuzas et al. [21]. The molar composition of the mother sol was SiO_2:0.4TPAOH:19.5H_2O:4C_2H_5OH and the seed synthesis conditions were the followings: $T_1 = 80$ °C, $t_1 = 90$ min, $P_1 = 250$ W for the first step and $T_2 = 125$ °C, $t_2 = 60$ min, $P_2 = 400$ W for the second step. The derived seeds were washed 3 times and dispersed in water by a 40 min ultrasonic treatment. The seed concentration in the final suspension was 0.65 wt%.

2.1.2. Support seeding

The membrane supports were α-Al_2O_3 tubes (ID/OD = 7/10 mm) supplied by *Pall-Exekia* in France. The tubes have a three layer asymmetric structure with mean pore sizes of 10 μm (external layer), 0.8 μm (intermediate layer) and 0.2 μm (internal layer). For gas permeation studies, 5 cm long tubes were used, with 1 cm of enamel at each end. The above mentioned seed suspension was used to deposit a S-1 seed layer by dip-coating inside the α-Al_2O_3 support. The seeded support was dried for 3 h at 150 °C.

2.1.3. Membrane formation by secondary growth

The seeded support was immersed vertically in the autoclave, which contained ~55 g of synthesis sol. The sol used for this secondary growth step was prepared by mixing TEOS, TBOT, ultrapure water, and TPAOH. The molar composition was $y$$TiO_2$:25$SiO_2$:3TPAOH:1500$H_2O$:100$C_2H_5OH$. The TiO_2 concentration in the sol, y, was varied in the range 0.25–1.56. Whatever the Ti concentration, sols were homogeneous after 3 h stirring at room temperature. Because of the hydrolysis/condensation reactions of the Ti precursor, the sol turbidity slightly increased with y. The secondary growth temperature was varied from 160 °C to 200 °C, with synthesis duration in the range 90–150 min, and a MW power of 400 W. Membranes were then washed with distilled water, dried for 6 h at 150 °C, and finally calcined in air using a heating rate of 0.2 °C/min up to 550 °C, where they were dwelled for 4 h.

2.2. TS-1 membrane characterization

Membrane morphology was characterized by FESEM (Hitachi S-4500) and surface chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDX, Quanta 200 FEG Electron Microscopy). FESEM observations (membrane morphology and thickness) and EDX analysis (Ti relative concentration) were made at 3 different locations for three membrane samples on either surfaces or cross-sections. The zeolite phase purity and crystal orientation were checked by X-ray diffraction (PanAnalytical X-Pert Pro). We have to note that recording XRD patterns on the internal surface of a tube is not an obvious task and may generate artifacts. The strategy used to optimize the patterns was described in [20]. The diffraction patterns were recorded at several sample positions (heights) in order to limit the abnormal diffraction doublet sometimes observed for the curved supports.

X-ray diffraction, infra-red (Nicolet NEXUS FT-IR) and Raman (Labran 1B (ISA), $\lambda = 632$ nm) spectroscopies were used for checking the insertion of Ti atoms in the MFI network and the absence of the anatase TiO_2 phase in the calcined samples. Anatase has specific XRD lines at $2\theta = 25.3°$; 37.9°; 48.4° and also Raman absorption bands at 145; 397; 515 cm^{-1}. The insertion of Ti species within the MFI network is generally evidenced by FTIR [22] through the detection of an absorption band at 960 cm^{-1} characteristic of Ti–O–Si bonds.

For studying single gas permeation through the membranes as a function of pressure (for N_2) and up to 200 °C (for He, N_2, O_2, CO_2, n-C_4H_{10}, i-C_4H_{10} and SF_6), membrane supports were equipped with graphite o-rings, sealed in a dead-end stainless steel module and out-gassed at 500 °C for 5 h in N_2 flow. We used the set up described previously in [23] for gas mixtures, except that the in-tube exit and one of the two external tube exits were closed for studying pure gases. The pressure was controlled by a needle valve and a pressure controller on the feed side. The gas permeation through the membrane was measured by a bubble flow meter connected to the atmosphere. The trans-membrane pressure was fixed at either 0.5 bar or 1.5 bar. Single gas permeances were in the range 10^{-5}–10^{-8} mol m^{-2} s^{-1} Pa^{-1} and the estimated permeance error was +2%. The ideal selectivities were calculated as the ratios of single gas permeances.