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Microporous Zirconia–Titania Composite Membranes Derived from Diethanolamine-Modified Precursors

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Inorganic microporous materials show great potential for applications in industrial catalysis, separation technology, membranes, sensors, and optical devices. The most common amorphous, microporous inorganic material is silica. Due to its small pores and straightforward synthesis, amorphous silica has been considered as a promising material for membrane applications. However, its moderate hydrothermal stability limits its extended application in harsh environments.^[1] Of particular interest as alternative materials for stable, high-performance membranes are sol–gel-derived amorphous oxides of transition metals, such as titania and zirconia. These materials show superior stability compared to silica;^[2] however, their synthesis is complicated by the high reactivity of the required precursors.^[3] To date, a few groups have been able to prepare amorphous titania and zirconia membranes for aqueous nanofiltration.^[4]

Herein, we describe the preparation and characterization of microporous zirconia–titania composite membranes. Preparation has been carried out via two different synthesis routes. The first route is based upon using the diethanolamine-stabilized heterometallic precursor $\text{Zr}\{\mu\text{-}\eta^3\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Ti}(\text{O}^i\text{Pr})_3]_2$ (**1**).^[5] The second route involves synthesis using **2**, a mixture of zirconium *n*-propoxide, titanium *n*-propoxide, and diethanolamine in a molar ratio equivalent to that in **1**.

Figure 1a shows thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data for uncalcined powders derived from either **1** or **2**. The data are similar for both powders. A sharp initial weight loss is observed with an onset at 50 °C, corresponding to the removal of adsorbed solvent molecules. A gradual decrease in weight is subsequently

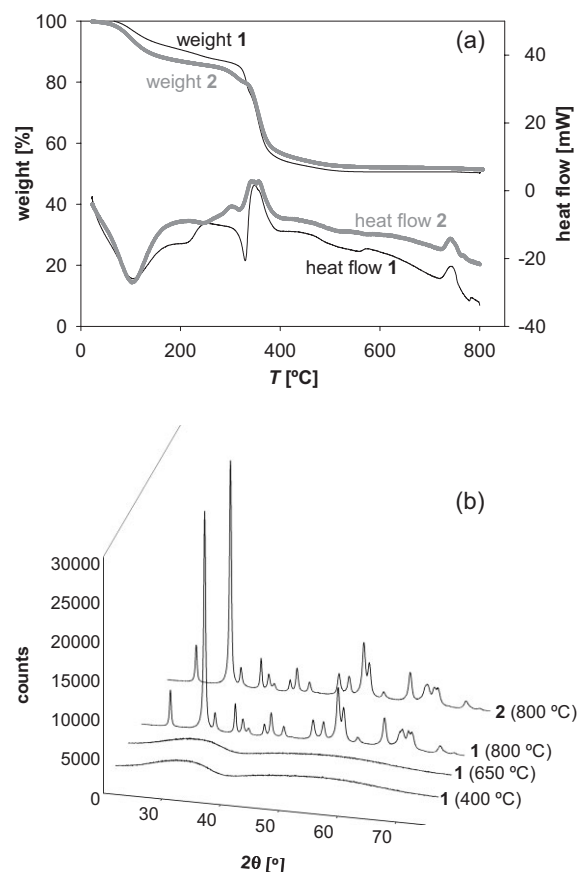


Figure 1. a) TGA and DSC data for powders derived from **1** and **2**. b) X-ray diffraction (XRD) diffractograms for powders derived from **1** and **2**, calcined at either 400, 650, or 800 °C.

observed up to 300 °C. This is attributed to the removal of ligands from the outer surface of the material. Mass spectrometry confirmed the presence of nitrogen in the sweep gas, originating from the amine groups of the ligands. In the range ~300–350 °C, a sharp decrease in weight is observed, which is accompanied by a large change in the heat flow centered at 350 °C. This can be attributed to the removal of ligands located inside the material. Mass spectrometry again confirmed a high concentration of nitrogen in the sweep gas. A further increase of temperature to 450–600 °C causes removal of the remaining alkoxide ligands.

The DSC data suggest that crystallization occurs at ~750 °C, as evidenced by the sharp exothermic peak at this

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temperature. This temperature is considerably higher than that of the crystallization of pure titania^[6,7] and zirconia,^[7,8] which take place in both oxides systems below $\sim 400^\circ\text{C}$. Selected X-ray diffraction (XRD) patterns are displayed in Figure 1b. The data obtained from both precursors **1** and **2** are very similar. The observed broad peaks are indicative of a small particle size. The diffractograms of the powders calcined at 800°C correspond to orthorhombic ZrTi_2O_6 , commonly referred to as srilankite.^[9] Srilankite is of interest for technological application in optics and dielectrics.^[10] Up to now, it could only be prepared at very high pressures and temperatures.^[11]

In Figure 2a, nitrogen sorption isotherms are presented for the powders derived from **1** and **2**, calcined at either 400 or 650°C . The isotherms for the samples calcined at 400°C are

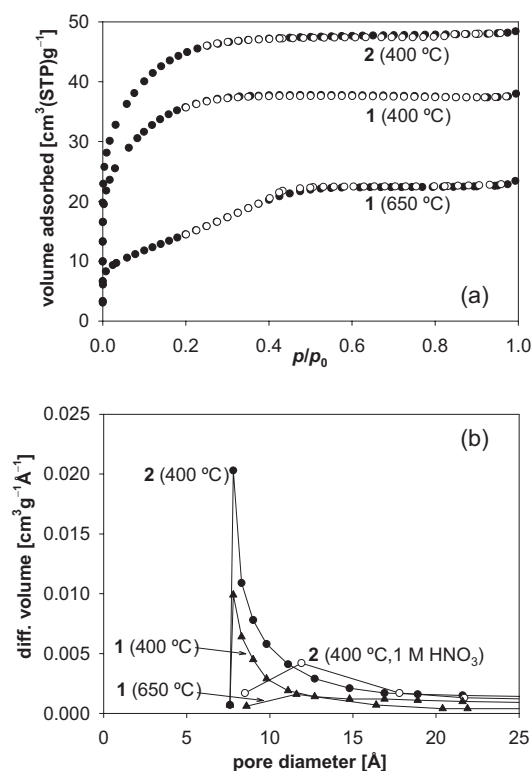


Figure 2. a) Nitrogen sorption isotherms at 77 K for powders derived from **1** and **2**, calcined at 400 and 650°C , and b) the corresponding pore size distribution. 1 M HNO_3 refers to an acidified hydrolysis solution.

type I.^[12] The sorption capacity is of the same order of magnitude as that of microporous silica.^[13] It seems somewhat larger for the material derived from **2**, but it is difficult to conclude whether this is intrinsic or related to differences in the syntheses of both materials (see Experimental). The observed type I sorption behavior is characteristic for microporous materials such as zeolites and amorphous silica. Commonly, sorption isotherms for zirconia- and titania-based materials show a hysteresis loop, indicative for mesoporous materials possibly containing some micropores.^[14] The material sintered at 650°C no longer shows distinctive type I sorption behavior. In accor-

dance with data from XRD, the powder calcined at 800°C has become crystalline and appears to be impervious to nitrogen. Also, for particles from powders calcined at 275°C , no sorption of nitrogen was observed.

Figure 2b displays the pore size distribution for various materials calculated using the Horvath–Kawazoe method, assuming cylindrical pores (Saito–Foley model^[15]). The samples calcined at 400°C show a narrow pore size distribution, with the majority of pores being smaller than 1 nm. For the material calcined at 650°C the average pore size is larger, while the total pore volume has decreased significantly.

Acidification of the hydrolysis solution may have a significant influence on the size and properties of the formed sol particles, and thus on the properties of materials derived from these particles. Acidification causes protonation of amine-based ligands, such as the diethanolamine used in the present study, converting them into better leaving groups. Consequently, more ligand molecules are removed upon acidification of the hydrolysis solution and, hence, densification of the colloidal sol particles will occur. This is confirmed by the results from light-scattering experiments. These indicate the presence of particles in the sol with a size of 50 nm when the hydrolysis solution is acidified, whereas the particle size is only 5 nm when water is used instead. Figure 2b shows the effect of acidification of the hydrolysis solution on pore size distribution of a powder derived from **2** calcined at 400°C . Clearly, acidification results in a substantial decrease in the total micropore volume, combined with a shift of the average pore size to a larger value.

Supported zirconia–titania films were prepared from a sol derived from **2** and characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and single-gas permeance measurements. Figure 3a shows an SEM image of the cross section of a resulting film. Clearly, a distinct layer with a thickness below $0.1\ \mu\text{m}$ is present on top of the support. In agreement with this observation, XPS data indicate the presence of a $\sim 20\ \text{nm}$ layer of zirconium titanium oxide on top of the support, with $\sim 60\ \text{nm}$ infiltration of this material into the support.

Figure 3b shows single-gas permeance data for different gases through the supported zirconia–titania composite film. The permeance for hydrogen is $3.0 \times 10^{-7}\ \text{mol m}^{-2}\ \text{s}^{-1}\ \text{Pa}^{-1}$, which is comparable to that of state-of-the-art silica membranes.^[16] For methane the permeance is a factor of 2.8 lower, corresponding well with the square root of the ratio of molar masses of these molecules, that is, the Knudsen selectivity. The permselectivity of hydrogen with respect to propane is 6.7. This value is larger than the Knudsen selectivity, 4.7, suggesting that mass transport does not only occur via Knudsen diffusion. With respect to butane the observed permselectivity is 54, which is considerably higher than expected for Knudsen diffusion. These results suggest that the pores in the composite film are larger than in typical silica membranes, which show very high hydrogen/methane permselectivity, but are sufficiently small to inhibit the mobility of the larger butane molecules.

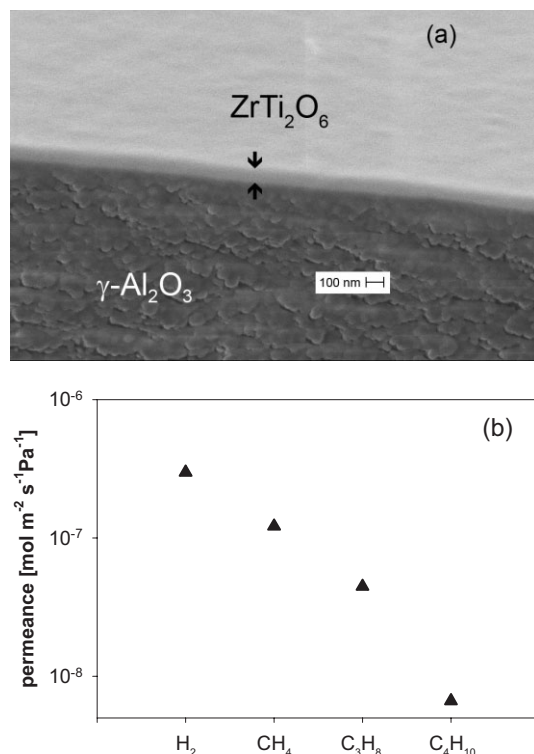


Figure 3. a) SEM image of a membrane cross section, and b) dead-end single-gas permeance at 200 °C.

In conclusion, the heterometallic precursor **1** allows controlled sol–gel chemistry, facilitating the synthesis of homogeneous composite microporous materials. Precursor **1** is formed upon mixing appropriate amounts of the corresponding isopropoxide precursors with diethanolamine, a modifier that acts as both a bridging and a chelating agent. A similar but more practical approach is adopted by using precursor **2**, a mixture of low-cost zirconium and titanium *n*-propoxides modified by diethanolamine. The major difference between both synthesis routes may lie in the nature of the alkoxide ligands. Although formation of a trinuclear heterometallic *n*-propoxide precursor is anticipated, such a compound could not be isolated via crystallization from a solution of zirconium and titanium *n*-propoxide in a molar ratio of 1:2 in *n*-propanol.^[17] The metal–oxygen bond length is expected to be shorter in the case of isopropoxide compared to *n*-propoxide.^[17,18] Hence, the reactivity of the precursors may differ. In spite of possible dissimilarities between both synthesis routes, no significant differences have been observed in the final material properties in this study. The derived materials retain their amorphous morphologies up to very high temperatures, and accommodate pores with a sharp size distribution in the subnanometer range. These properties make the materials interesting candidates to be applied as membranes in demanding molecular separations under harsh conditions. Supported membranes derived from **2** show a high permeance for hydrogen, combined with a low permeance for butane. This differ-

ence is due to the molecular-sieving effect, confirming that the pores in the supported membranes indeed have molecular dimensions.

Experimental

Sol Synthesis: Two different types of sols were prepared, starting with the heterometallic precursor $\text{Zr}\{\mu\text{-}\eta^3\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Ti}(\text{O}^i\text{Pr})_3]_2$ (**1**) or a mixture of zirconium *n*-propoxide, titanium *n*-propoxide, and diethanolamine (**2**). Synthesis of **1** has been described in detail elsewhere [5]. Typical sols derived from **1** were prepared by dissolving 10.0 g of the precursor in a 90 mL mixture of hexane and isopropanol (volume ratio 2:1). Subsequently, 0.1 M HNO_3 and isopropyl alcohol (volume ratio 1:19) were mixed, and the solution rapidly added to the precursor mixture with vigorous stirring. The water/precursor mol ratio was 3:1. Sols derived from **2** were prepared by mixing the zirconium *n*-propoxide and titanium *n*-propoxide together with diethanolamine and *n*-propanol (molar ratio 1:2:3:50). The hydrolysis solution, consisting of 10 mol equivalents (with respect to zirconium *n*-propoxide) of water and *n*-propanol (volume ratio 1:50), was slowly added ($\sim 1 \text{ mL min}^{-1}$) to the precursor solution under vigorous stirring. The effect of acidification on hydrolysis and condensation was investigated by replacing water in the latter hydrolysis solution by a similar amount of 1.0 M HNO_3 . If required, manipulations were carried out in a dry nitrogen atmosphere, using the Schlenk technique or a glovebox. Hexane (Merck, p.a.) was dried by distillation after refluxing with LiAlH_4 , isopropyl alcohol (Merck, p.a.) was dried by distillation after refluxing with $\text{Al}(\text{O}^i\text{Pr})_3$ (for details see the literature [17]). *n*-Propanol (anhydrous, 99.7 %) and diethanolamine were purchased from Aldrich and used as received.

Powder and Membrane Formation: Powders were obtained by drying the sols overnight in a 10 cm Petri dish, followed by calcining in air for 3 h in the range 250–800 °C with heating and cooling rates of $0.5^\circ\text{C min}^{-1}$. Membranes were prepared by dip-coating home-made supported γ -alumina membranes [19] two times with a diluted (ten times) sol derived from **2** under class 100 clean room conditions, followed by drying overnight, and sintering at 400 °C for 3 h in air with heating and cooling rates of $0.3^\circ\text{C min}^{-1}$.

Characterization: The particle size distributions in the sol were measured by dynamic light scattering (ZetaSizer 3000 HSa, Malvern). TGA and DSC were performed using a combined TGA/DSC apparatus (Setsys 16, Setaram). Measurements were performed in a nitrogen flow (20 mL min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ in the temperature interval 25–800 °C. To analyze the burn-out of ligands, experiments were repeated with a 50 mL min^{-1} helium sweep flow and a heating rate of $30^\circ\text{C min}^{-1}$. A mass spectrometer (Omnistar GSD 301-O1, Pfeiffer Vacuum) coupled to the TGA/DSC apparatus was used for detection of nitrogen in the sweep gas. XRD patterns (X'Pert-MPD, PANalytical, Philips) were recorded for the powders calcined at 400, 650 and 800 °C. Pore size distributions were determined from volumetric nitrogen sorption experiments (Micromeritics, ASAP 2000). Prior to sorption measurements, samples were degassed at 250 °C under vacuum for 48 h. Membranes were characterized by SEM (LEO Gemini 1550 FEG-SEM) and XPS (Quantera XPS microprobe, Physical Electronics). Membrane performance was analyzed by dead-end gas permeation (200 °C, $p_{\text{feed}} = 5 \text{ atm}$, $p_{\text{permeate}} = 1 \text{ atm}$, where $1 \text{ atm} = 101.325 \text{ kPa}$).

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