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A novel malonamide bridged silsesquioxane precursor for enhanced dispersion of transition metal ions in hybrid silica membranes

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ABSTRACT

Microporous hybrid silica membranes are known to have superior (hydro)thermal and chemical stability. By incorporating metal ions, such as Ce^{4+} and Ni^{2+} into these membranes, their affinity and selectivity towards particular gases may be altered. To promote the dispersion of metal ions within the hybrid silica matrix, the sol–gel precursor *N,N,N′,N′*-tetrakis-(3-(triethoxysilyl)-propyl)-malonamide (TTPMA) was synthesized. The malonamide ligands clearly coordinated the Ce^{4+} and Ni^{2+} metal centers and enhanced their dispersion. During annealing these metal centers redistributed into small nanosized grains of CeO_2 (<5 nm) and Ni_2O_3 (<15 nm). These Ce-TTPMA and Ni-TTPMA membranes showed higher H_2/N_2 permselectivities as compared to previously reported hybrid silica membranes based on the 1,2-bis-(triethoxysilyl)ethane precursor. The TTPMA-precursor was found suitable for membrane separation and can be a promising and versatile precursor for the incorporation of metal ions within hybrid silica matrices.

1. Introduction

At present over 85% of the global energy is provided by burning fossil fuels [1]. This leads to increasing amounts of CO_2 into the atmosphere [1,2], so we need to reduce CO_2 emission. CO_2 can be separated from the fuel gas in a pre-combustion setup or from the flue gas (N_2) in a post-combustion setup, which stresses the need for separation membranes [1]. The implementation of a post-combustion is most straightforward within the current infrastructure, but requires a high CO_2/N_2 selectivity [1]. Membrane separation of CO_2 and N_2 is difficult, since these gases have similar kinetic diameters of 3.30 and 3.64 Å, respectively [2]. Most membranes that have been developed so far do not reach the required CO_2/N_2 selectivity of 200 to make them economically feasible [3]. Membranes that meet these requirements are based on affinity with CO_2, such as glycine-sodium glycerol, where performance relies on the presence of moisture [4]. Therefore, hybrid silica membranes offer a more robust alternative given their applicability at elevated temperatures ($T > 100$ °C) [5–9]. As alternative to post-combustion schemes, CO_2 can also be separated from H_2 after gasification in a pre-combustion setup [1,10]. The difference in kinetic diameter between H_2 and CO_2 is slightly larger (2.89 versus 3.30 Å) and these gases can be separated by size exclusion in silica membranes with a permselectivity of 70 [11].

The selectivity of silica membranes towards H_2 was increased with one order of magnitude by doping them with cobalt or nickel oxide [12,13]. These metal centers increased the surface adsorption and thereby the surface diffusion rate of H_2 on the pore walls. The CO_2/N_2 permselectivity of sol–gel derived silica membranes can be altered by increasing their affinity towards CO_2 [8,9,13–15]. CO_2 is known to bind irreversibly with a large variety of metal oxides [16,17]. The carbonyl moiety has a particularly strong affinity towards nucleophilic, electron donating species due to its electron-deficient carbonyl moiety, and chemisorbs irreversibly onto basic sites of alkaline earth metal oxides [18,19]. This affinity explains the poor mobility of CO_2 in mesoporous magnesia doped γ-alumina [20]. By doping γ-alumina with magnesia the amount of CO_2 adsorbed on the surface did not increase, but the mobility of adsorbed CO_2 species decreased. The authors attributed this to increased basicity of the active sites upon doping alumina with magnesia. On the other hand, the amphoteric character of CO_2 allows chemisorption on

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acidic sites as well [21], which explains the low permeance of CO_2 in microporous niobia doped silica [14]. Ceria may be a good alternative, since it is a weaker nucleophile as compared to earth alkaline oxides [22], while Fourier Transform Infrared (FTIR) experiments revealed substantial affinity of CO_2 on a ceria surface [23,24].

Dispersion of metal centers on atomic scale into a microporous silica or hybrid silica network is not straightforward: the metal oxide that is introduced tends to phase separate while the silica matrix forms. Metal salts, e.g. metal nitrates, have limited solubility within the alcoholic environments in which the silica sol is formed and these salts tend to precipitate while the sol is drying [13]. Metal alkoxides dissolve well in apolar silicates, but they are much more reactive towards hydrolysis and condensation than silica precursors, generally resulting in the formation of dense metal oxide clusters within the silica sol [25–27]. The reactivity of the alkoxides can be tempered by chelating ligands such as acetylacetone, which retard the gelation in the presence of water [28–31]. It has been debated whether the reactivity is due to a reduced nucleophilic character of the metal center, or an increased shielding of coordination sites by the chelating ligands, i.e. a steric hindrance effect [26,30]. In the latter case, the introduction of chelating ligands would not help to increase the degree of dispersion of the metal oxide in a silica matrix, since they would be shielding the metal center from silicon species as well.

Rupp et al. [32–34] synthesized a triethoxysilylpropyl adduct to acetylacetone and subsequently coupled this molecule to a titanium, zirconium or aluminum alkoxide. The approach solved two problems: (1) it connects the metal alkoxide precursors to the silica precursors prior to the sol–gel process, thereby increasing the dispersion of the metal alkoxides within the glassy silica matrix; (2) it tempers and shields the reactive metal center in the metal alkoxide precursor, thereby reducing its tendency to form a condensed metal oxide phase [32]. The latter possibility was supported by XRD data that revealed a strong reduction of the anatase and rutile grain sizes [32], and SAXS data that revealed a limited metal oxide size cluster size with aluminum alkoxides [34].

In the present work we describe a bridged silsesquioxane precursor with four triethoxysilyl-propyl groups attached to a single malonamide chelating group. As compared to pendant silsesquioxanes, bridged silsesquioxanes exhibit much higher mechanical strength and fracture resistance due to enhanced connectivity and the absence of dangling carbon substituents [35–38]. The presence of dangling carbon substituents resulted in microporous structures with larger pore sizes, but lower permeances and selectivities in comparison to bridged silsesquioxane glasses [7]. In comparison to microporous silica, bridged silsesquioxanes exhibits higher solvolytical and acid stability, which allows these materials to work under harsher conditions [5–7]. The bridged silsesquioxane precursor that consists of a malonamide chelating group was formed through the formation of amide bonds between malonyl chloride and two bis-(3-(triethoxysilyl)-propyl)-amine molecules. Malonamides are strong chelating units. Through formation of enolic bidentate ligands they can easily form complex bonds with a large variety of metals cations, including lanthanides and actinides [39–46]. Since a large variety of metal cations can thus be incorporated into a hybrid silica matrix, the approach is versatile and its affinity towards certain probe molecules may be controlled by the choice of metal(s). In this study, we doped the TTPMA matrix with cerium (IV) isopropoxide isopropanol adduct and nickel nitrate hexahydrate to enhance the affinity towards carbon dioxide and H_2, respectively.

2. Experimental

2.1. Synthesis of N,N,N′,N′-tetrakis-(3-(triethoxysilyl)-propyl)-malonamide (TTPMA)

The synthesis was performed via a base catalyzed (by using a tertiary amine) N-acylation of malonyl chloride on N-substituted amines in dichloromethane at temperatures below $T = 5$ °C as reported elsewhere [47,48]. See Scheme 1. The synthesis was performed inside a glove box under nitrogen atmosphere. Dichloromethane (BOOM, 99%) triethylamine (Sigma–Aldrich, 99%), and dimethylsulfoxide (Sigma Aldrich, 99%) were dried over anhydrous sodium sulfate (Sigma Aldrich, 99%) and dichloromethane was cooled to $T = -5$ °C. Then, 30 mmol of bis-(3-(triethoxysilyl)-propyl)-amine (ABCR chemicals, 97%) was dissolved in 183 mL of the cooled dichloromethane inside a 250 mL Erlenmeyer flask. Then, 30 mmol of triethylamine was added. In a dropping funnel, a 10% excess (16.5 mmol) of malonyl chloride (Sigma Aldrich, 97%) was dissolved in 48.4 mL of dichloromethane, which was added dropwise to the solution in the Erlenmeyer flask in 30 min. Please note: malonyl chloride is reactive and may decompose with formation of hydrochloric acid upon temperature increase; after use the bottle was immediately returned to the fridge.

After addition, the Erlenmeyer flask was stirred for 7 days in an oil bath at 20 °C. Dichloromethane was distilled using a Vacuumbrand vacuum pump that automatically adapts its pressure to the solvent pressure. TTPMA was extracted from the remnant slurry with 150 mL hexane and triethylammonium chloride was removed by filtration using a 2.7 μm filter (Whatman, grade 50). The Erlenmeyer flask and Büchner funnel were washed twice with 50 mL hexane. The filtered hexane solution was washed once with dimethylsulfoxide to remove remnant ammonium byproducts. Hexane was then removed by vacuum distillation at room temperature. Remnant dimethylsulfoxide was removed by vacuum distillation at 80 °C. An orange colored, viscous liquid remained present in the flask which contained 87% TTPMA: (yield 70%); ^1H NMR results: $\delta_H = 3.74$ (m, $4 \times CH_2$), 3.38 (s, CH_2), 3.24 (m, $4 \times CH_2$), 1.58 (m, $4 \times CH_2$), 1.14 (m, $4 \times CH_3$), 0.51 (m, $4 \times CH_2$); ^{13}C NMR: $\delta_C = 166.8$ (C=O), 58.4 ($4 \times CH_2$), 50.9 ($2 \times CH_2$), 48.6 ($2 \times CH_2$), 41.0 ($2 \times CH_2$), 22.3 ($2 \times CH_2$), 20.8 ($2 \times CH_2$), 18.3 ($4 \times CH_3$), 7.57 ($4 \times CH_2$). Additional resonance peaks were explained by the presence of 13% 2-chloro-3-oxo-N,N,N′,N′-tetrakis-(3-(triethoxysilyl)-propyl)-pentanediamide) that was formed as a byproduct: ^1H NMR: $\delta_H = 5.13$ (s, CHCl) 3.62 (s, CH_2), 3.30 (m, $2 \times CH_2$); ^{13}C NMR $\delta_C = 196.6$ (C=O), 165.2 (C=O), 62.7 (CHCl), 50 ($2 \times CH_2$), 48.4 ($2 \times CH_2$). All measurements were done on a Bruker Ascend-400 spectrometer operating at 400.13 MHz for ^1H- and 100.61 MHz for ^{13}C, using a 5 mm gradient-probe. The assignments of these shifts were clarified with additional 2D-NMR measurements, as discussed in more detail in the electronic supporting information. Given the similarity between the byproduct and TTPMA, we were not able to separate the byproduct from TTPMA. On the other hand, since the byproduct contains both chelating carbonyl moieties and condensable triethoxysilyl groups, it was expected to be condensed simultaneously with TTPMA, yielding a similar capability of dispersing metal ions within the network that was being formed.

2.2. Sol preparation and particle size analysis

A stock-solution was prepared: approximately 3 mmol $Ce(O^iPr)_4 \cdot {}^iPrOH$ (CeTiP; ABCR Chemicals, 31.5–32.4% Ce weight) was weighed accurately in a 50 mL polypropylene vessel. A stoichiometric amount of TTPMA was added to yield a [Ce]/[Si] ratio of 1:9, which corresponds to [Ce]/[TTPMA] = 1/2.25. The mixture was diluted in 15 mL of isopropanol, yielding a solution with a density of