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One-Pot Synthesis of a New High-Aluminium-Content Super-Microporous Aluminosilicate

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A new super-microporous aluminosilicate having a high aluminium content (Si/Al ca. 1) has been prepared through a surfactant-assisted procedure with the use of a commercially available binary precursor (di-*sec*-butoxyaluminooxytriethoxysilane) as a single source of both Al and Si. The formation of super-micropores is a result of a significant network shrinkage associated with the thermal elimination of the surfactant. This solid has been studied by X-ray powder diffraction, electron microscopy, nuclear magnetic resonance spectroscopy and porosimetry. A preliminary analysis of the acidity and the catalytic activity of the super-microporous solid for the selective catalytic reduction of NO_x is also presented.

Introduction

The discovery of the M41S family of mesoporous silicas by Mobil's researchers was a major step towards the expansion of the typical sizes of uniform micropores in zeotypes.[1] Since then, considerable effort has been devoted to the systematization of processing routes for the manufacture of silica-based mesoporous derivatives that contain pore sizes in the 2–10 nm range. The use of surfactants with alkyl chains of different lengths is the typical procedure employed for this endeavour.[2] While many investigations have been aimed at establishing the most suitable strategies to achieve large mesopores, the number of publications dealing with porous solids in which the pore sizes range between micropores and small-mesopores is limited.[3] The scarcity of results, however, is not an indication of the lack of interest in super-microporous solids since they are in high demand for their potential use in a large variety of applications, such as molecular recognition, adsorption, drug delivery and catalysis.[4] In fact, materials with uniform pore sizes in the 1–2 nm range (i.e. super-microporous) are expected to exhibit interesting shape- and size selectivity in the conversion of large organic substrates.

As mentioned above, there are few reports on super-microporous materials. Sung et al.[5] described the synthesis of porous niobium oxide with pore diameters below 2 nm. Shpeizer et al.[6] have recently reported on a general non-surfactant-assisted procedure to prepare super-microporous mixed oxides. With the exception of these two contributions, all of the remaining publications on super-microporous materials are centred on silica-based compositions. Super-microporous pure silicas have been prepared by different one-pot procedures, which implies the use of "structure-directing agents" or "templates". These templates vary greatly and range from micellar aggregates of surfactants (e.g. ω-hydroxy-bolaform[7] or long chain alkyl amines[8]) to simple, but bulky, organic molecules (e.g. adamantanamine[9]). Besides surfactant-assistance strategies, some strategies are based on the use of a single Si source (α-sodium disilicate[4]) or on a more complex multistep process (pore-entrance size decreases after post-synthetic treatment[10]). In some cases, mesoporous materials can be progressively altered to microporous materials through the incorporation of heteroelements such as Al or Zr.

Porous aluminosilicate compositions have traditionally attracted great interest owing to their capability to act as acid catalysts for bulky hydrocarbon conversion.[11] In practice, a solid acid material in the super-microporous domain could bridge the gap between zeolites and mesoporous aluminosilicates. Incorporation of Al centres in the framework of mesoporous silicas usually leads to a certain pore size decrease. Hence, aluminosilicates with pore sizes at the lower end of the mesoporous range have been obtained with high Al content materials.[12] However, pores in the super-microporous range usually cannot be achieved even with Si/Al ratios as low as 7.[13] In this case, the preparation of super-microporous aluminosilicates requires the combined effects of short-tail surfactants and high Al content in the starting solution[14] or, alternatively, the use of post-syn-

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thetic strategies of Al-grafting.[15] Following these synthetic procedures, super-microporous silicas with a maximum Al content in the Si/Al = 2.5–7 range have been described.[16]

We report here on a new, direct and reproducible procedure that has allowed us to prepare a new porous silica with a very high Al content and with pore sizes in the super-microporous range.

Results and Discussion

Synthesis Strategy

Our surfactant-assisted strategy is based on the use of a "single-source molecular precursor" (i.e. a molecular precursor that simultaneously contains all the required oxide forming elements, Al and Si in this case). Under the synthetic conditions selected, and working in a water/triethanolamine medium, the use of such a precursor leads to poorly condensed mesostructured solids. Subsequently, the thermal treatment required to eliminate the surfactant also induces a significant network shrinkage, which leads to the formation of the super-micropores. The final material shows a high proportion of tetrahedral Al, and consequently a high acidity, and reasonable catalytic properties in the selective catalytic reduction (SCR) of nitrogen oxides (NO_x).

The use of bimetallic complexes, employed extensively by the Tilley group,[17,18] as inorganic precursors constitutes a polished approach towards the synthesis of a variety of mesoporous oxides. Although the composition of the final mixed oxide depends on that of the precursor, this approach is advantageous as it ensures an intimate mixture of the reactive elements from the initial preparative steps. In our case, we have additionally benefited from the complexing ability of triethanolamine (leading to atrane complexes), which in turn plays an essential role as the cosolvent.[19] The first step in our strategy involves the transesterification of commercially-available alkoxy derivatives (primary source of the oxide forming elements) through their treatment with dried triethanolamine at moderate temperatures (130–170 °C). This reaction leads to the formation of atrane complexes (real hydrolytic precursors). In fact, the use of atranes as precursors has allowed us to successfully prepare a diverse range of mesoporous single- and mixed oxides.[19–25] The additional use of triethanolamine as the cosolvent[19] is also supported by its use in the preparation of mesoporous materials in water/alcohol media;[26] however, atrane complex formation does not occur in water-rich media. The atrane alkoxy complexes are, in general, unstable but they are relatively inert towards hydrolysis. In many cases, this resistance towards hydrolysis (induced by the triethanolamine-like ligands) aids in the orchestration of the self-assembling processes (between the inorganic moieties and the surfactant aggregates) that lead to stable mesostructured phases.[19] In fact, the nucleophilic displacement of triethanolamine-related ligands, which occurs as a result of the attack of water on the silicon or aluminium centres, becomes more difficult than for monodentate alkoxo groups. In short, the combined effects of: (1) the use of a rigid binary "single-source molecular precursor", (2) the intrinsic "hydrolysis retarding effect" associated with the formation of atrane complexes, and (3) the buffered water/alcohol medium generated by the triethanolamine favours the formation of a low-condensed mesostructured material. The subsequent thermal evolution of the surfactant (to open the pore system) occurs together with a significant network shrinkage because of the completion of the condensation reactions, which leads to pores in the super-micropore domain.

Characterization

As expected, the Si/Al molar ratio in the final material [1.2 ± 0.2 from electron probe microanalysis (EPMA)] is very close to that present in the mother liquor. This fact indicates that there is no degradation of the bimetallic precursor under the working conditions. EPMA shows that the samples are chemically homogeneous at the micrometer level (spot area ca. 1 µm) with a regular distribution of Al and Si atoms throughout the inorganic walls. We can conclude that there is no preferential incorporation of Al or Si into the final net.

The mesophasic nature of both the as-synthesized and the super-microporous materials is illustrated by their X-ray powder diffraction (XRD) patterns and TEM images (Figure 1 and Figure 2). Both solids show low-angle XRD patterns with only one strong and relatively broad diffraction peak, which is typical of mesostructured/mesoporous materials prepared through surfactant-assisted procedures (Figure 1). This signal is usually associated with the (100) reflection if a MCM-41-like lattice is assumed. The observation of only one broad signal is characteristic of highly disordered pore systems. The absence of additional signals in the XRD pattern of the as-synthesized material could be due to the incorporation of Al into the walls. In fact, similar XRD patterns were recorded for Al-containing silica materials prepared from independent Si and Al molecular precursors under similar conditions.[12] In general, the incorporation of heteroelements into silica-based hexagonal porous frameworks implies a progressive lowering of the order in the pore array. After calcination, the intensity of the signal decreases, while it also appears significantly broadened. Moreover, calcination also results in a significant shift in the maximum towards high 2θ values.

Hence, the value of the a_0 parameter (cell parameter assuming an MCM-41-like hexagonal array; $a_0 = 2{\cdot}d_{100}/3^{1/2}$) pronouncedly decreases after calcination (from 5.77 to 5.05 nm). This behaviour indicates that surfactant elimination results in a significant reorganization of the porous walls. A relative loss of order together with a significant network shrinkage occur as a consequence of the calcination process.

While the TEM images (Figure 2) fully correlate to the XRD observations, the N_2 adsorption–desorption isotherms confirm the shrinkage of the framework (Figure 3).

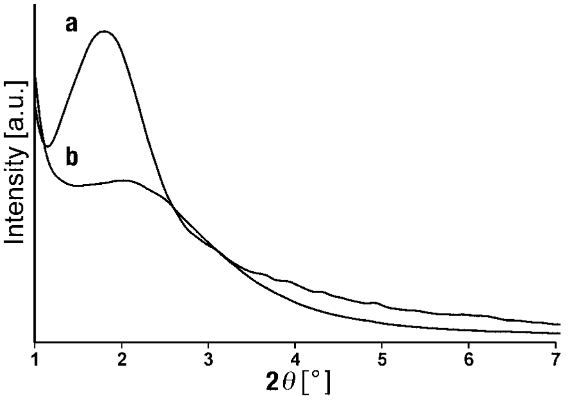

Figure 1. XRD patterns of (a) as-synthesized and (b) super-microporous materials.

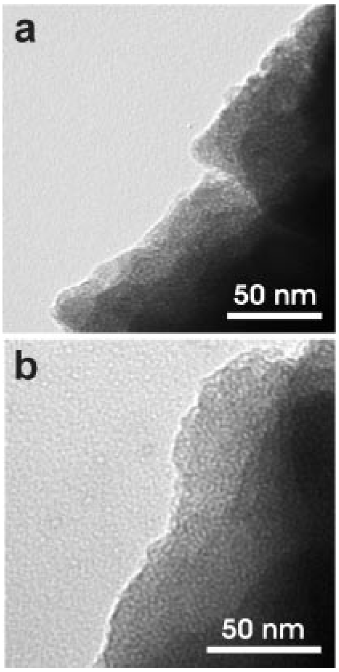

Figure 2. Representative TEM images of (a) as-synthesized and (b) super-microporous materials.

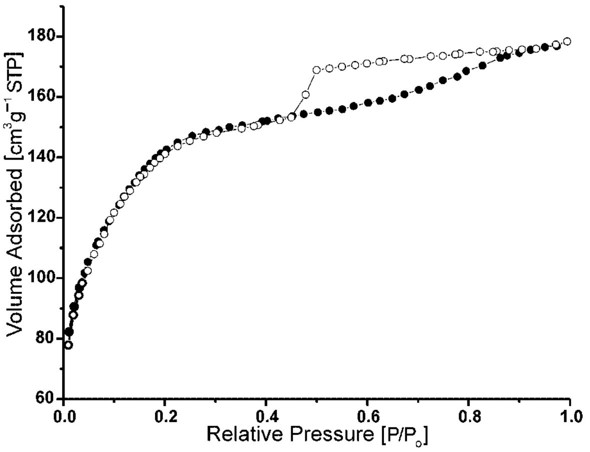

Figure 3. N_2 adsorption–desorption isotherms of the super-microporous aluminosilicate.

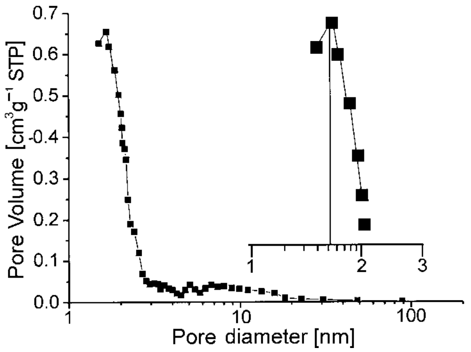

Figure 4. BJH pore size distribution on the adsorption branch of the isotherm.

Thus, although the surfactant used (CTMABr) usually leads to the formation of mesopores (i.e. pores usually in the 2–3 nm range), the pore size estimated in this case falls in the microporous domain. In fact, the mean pore size resulting from the $D = 4V/S$ equation (which maintains a certain validity for super-micropores)[16] indicates a pore dimension of 1.3 nm, i.e. in the super-micropore range [pore volume (V) = 0.18 $cm^3 g^{-1}$, BET surface area (S) = 519 $m^2 g^{-1}$]. Application of the BJH method also indicates pore sizes in the super-micropore range, although these are slightly out of the optimum working range of the instrument. Indeed, we can observe a small maximum in the BJH pore size distribution at ca. 1.45 nm (see Figure 4). Also, the high value of the thickness of the average pore wall (3.8 nm, defined as wall thickness = a_0 – pore size) suggests a certain tendency to increase the wall condensation by calcination.

Besides the above observations, the NMR results provide further evidence and confirm the theory that the condensation occurs in the inorganic walls as a consequence of the thermal treatment. Thus, in the case of the as-synthesized solid, the ^{27}Al MAS NMR spectrum shows essentially only one resonance signal at ca. δ = 57.0 ppm (Figure 5a), which is characteristic of tetrahedral Al sites. On the other hand, its ^{29}Si MAS NMR spectrum shows a very strong and broad signal whose centre appears to be shifted downfield (δ = –80.9 ppm, Figure 5c) when compared to that of a pure siliceous MCM-41. This signal displacement is in accordance with the resonance of Q^4 (4Al) environments. The broadness of the signal might be a consequence of other resonances that result from additional minority Si environments [such as Q^4 (3Al) and other Q^3 sites]. Thus, the MAS NMR results are consistent with the Si/Al = 1.2 ± 0.2 molar ratio determined from EPMA. The evolution of the NMR spectra indicates the occurrence of a significant conversion from a tetrahedral Al to an octahedral Al, which is a consequence of the surfactant removal (Figure 5b). This process also affects the Si sites. In fact, the ^{29}Si MAS NMR signal shifts from δ = –80.9 ppm to δ = –89.4 ppm (Figure 5d). This is consistent with an increase in Q^4 (3Al) centres. In short, the thermal surfactant removal also induces a reorganization, by way of a condensation reaction, of the inorganic walls, and this shrinkage is responsible for the formation of the super-micropores. A similar behaviour (evolution from meso to micropores through calcination) has been recently reported in the preparation of pure porous silicas from hydrated α-sodium disilicate as a Si source.[4] In our case, we propose that the geometrical constraints imposed by the use of a single Si–Al molecular source lead to the framework in the as-synthesized material. In fact, when independent Si and Al precursors were used under similar working conditions, the final pore contraction was significantly lower, which resulted in solids with pore sizes that fall within the low limit of the mesoporous range.[12]

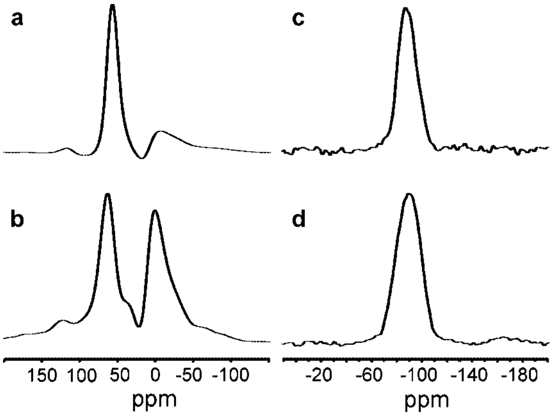

Figure 5. ^{27}Al MAS NMR spectra of (a) as-synthesized and (b) super-microporous sample. ^{29}Si MAS NMR spectra of (c) as-synthesized and (d) super-microporous sample.

Although ca. 50% of the Al centres have evolved from tetrahedral to octahedral sites after calcination, the final super-microporous material shows significant acidity, with a total number of acid sites of $800\ \mathrm{mmol\,g^{-1}}$ (determined by nonselective NH_3 adsorption), – $375\ \mathrm{mmol\,g^{-1}}$ corresponding to Lewis acid sites (estimated from Lewis selective acetonitrile adsorption) and the remaining $425\ \mathrm{mmol\,g^{-1}}$ to Brønsted acid sites. This result is consistent with the ^{27}Al MAS NMR spectrum, which shows both tetrahedral Al (responsible for Brønsted acidity) and octahedral Al (responsible for Lewis acidity) after calcination. A preliminary study on the use of this super-microporous aluminosilicate as a catalyst for the low-temperature (433 K) SCR of NO_x with NH_3 gives a reasonable conversion level (ca. 72%) with little ammonia leakage. Comparatively, under the same temperature and flow conditions, the use of NH_4Y (Si/Al = 5.7), whose Brønsted acidic strength is higher than that of our super micro-porous aluminosilicate, leads to 100% NO_x conversion without NH_3 leakage; this result is in accordance with the acidity values.

Conclusions

We report here on a simple and reproducible one-pot surfactant-assisted procedure for obtaining a new high-Al-content super-microporous aluminosilicate with well-dispersed Al and Si centres throughout the inorganic walls. Our strategy to diminish the pore size is based on the intermediate formation of a low-condensed framework starting from a binary (Al and Si) rigid precursor. Super-micropores are then formed as a consequence of the structure shrinkage induced by calcination. The final material presents with a high acidity and a reasonable catalytic activity in the SCR of NO_x. This strategy can be extended to the preparation of other bimetallic super-microporous oxides.

Experimental Section

Chemicals: All the synthetic reagents were analytically pure and were used as received from Aldrich and Gelest. The Si and Al primary source used was di-*sec*-butoxyaluminooxytriethoxysilane (from Gelest). 2,2′,2′′-Nitrilotriethanol or triethanolamine [$N(CH_2–CH_2–OH)_3$] was used for obtaining the binary (Si and Al) atrane precursor. The templating agent used was cetyltrimethylammonium bromide (CTMABr).

Synthesis: The method was a modification of the so-called "atrane route", a simple preparative technique whose main points have been described previously in detail.[19] In a typical synthesis di-*sec*-butoxyaluminooxytriethoxysilane (13.20 g, 0.0375 mol) was slowly added to liquid triethanolamine (33.5 mL, 0.255 mol), and heated at 150 °C for 5 min. After the solution was cooled to 90 °C, CTMABr surfactant (6.84 g, 0.0187 mol) was added. The solution containing the binary (Si and Al) atrane complex (with the triethanolamine-related species as ligands) and the templating agent (CTMABr) was cooled to 60 °C and mixed with water (120 mL, 6.66 mol). After a few seconds, a white powder appeared. The resulting suspension was kept at room temperature for 12 h. The final (mesostructured) powder was filtered off, washed with water and ethanol, and air dried. In order to open the pore system (by surfactant removal), both calcination and chemical extraction procedures were tested. Typical extraction protocols, such as the suspension of the mesostructured solid in an HCl/ethanol solution (about 1 g of powder, 15 mL of 35% HCl and 150 mL of 96% ethanol), were unsuccessful. In practice, this process results in a significant mesostructure degradation or collapse that is provoked by the leaching of a large proportion of the Al atoms in the form of chloride complexes. This result indicates a high accessibility of the Al centres in the mesostructure, which provides evidence for a relatively low condensation in its inorganic walls. Removal of the surfactant was carried out by calcination. The as-synthesized solid was heated at 50 °C under static air for 5 h, thus yielding the final super-microporous material.

Physical Measurements: Both the as-synthesized and the super-microporous solids were analyzed for Si and Al content by electron probe microanalysis (EPMA, Philips SEM-515 instrument). X-ray powder diffraction (XRD) data were recorded with a Seifert 3000TT θ-θ diffractometer with Cu-K_α radiation. TEM images were obtained with a Philips CM10 microscope operated at 120 kV. N_2 adsorption–desorption isotherms were recorded with a Micromeritics ASAP2010 automated sorption analyzer. ^{29}Si- and ^{27}Al MAS NMR spectra were recorded with a Varian Unity 300 spectrometer operating at 79.5 MHz, and with a magic angle spinning speed of at least 4.0 KHz. Acidity was estimated from in situ FTIR experiments with a Nicolet Nexus FTIR instrument equipped with a quartz cell for the NH_3 or acetonitrile adsorption. Activity for the SCR of NO_x with NH_3 was determined from operando FTIR experiments with a homemade infrared reactor cell.[27] More procedural details about both in situ and operando experiments are given in ref.[28]

Acknowledgments

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