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Mesostructure Design via Poly(acrylic acid)−C$_n$TAB Complexes: A New Route for SBA-1 Mesoporous Silica

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A wide variety of highly ordered silica-based mesostructures have been synthesized in the past by employing one of the well-known pathways, (S^+I^-), (S^-I^+), ($S^+X^-I^+$), and ($S^-M^+I^-$), where S, X, M, and I correspond to surfactant, halide, cation, and inorganic species, respectively.[1−3] The cubic SBA-1 phase is generated by the ($S^+X^-I^+$) pathway by implementation of strongly acidic conditions and surfactants with large headgroups. The 3d cage-type mesoporous SBA-1, much less studied than MCM-48, has been attracting much attention as a catalyst support.[4−6] A serious drawback though to one-step synthesis of metal-incorporated SBA-1 is the highly acidic synthesis enviroment. This fact does not favor the incorporation of high metal content on the mesostructure (1−4%)—which could even be affected by washing of the samples—because of the weak bonding of the metal species onto the silicious framework.

The present new concept for the synthesis of similar mesostructures is based on poly(acrylic acid)−surfactant organic complexes, first introduced by Antonietti and Conrad, which possess a high degree of ordering as liquid-crystalline phases.[7,8]

A typical synthesis is as follows: at ambient temperature 0.5 g of poly(acrylic acid) (Aldrich) of MW = 2000 au (Pac2) (or other as Pac15 and Pac250) is dissolved in 100 g of water under stirring. The pH of the solution measured online is typically 3.2. HCL acid is then used to set the pH at 1.5, so as to avoid complexation of the polyelectrolyte with the surfactant added next. Then the trimethyl derivatives of C_{14}TAB or C_{16}TAB (Merck) are added at a stoichiometric amount with respect to polyelectrolyte functional groups (2.5 g for C_{16}TAB) and a clear solution is obtained. Finally, 5 mL of TEOS (Merck) is introduced. The molar composition of the mixture was TEOS/C_nTAB/Pac2/H_2O 1/0.32/0.01/253. Then dropwise addition of NH_3 takes place within 2 h. Intermediate samples are isolated at any desired pH and/or time during the process. Precipitates first appear at pH 3.2−3.3 and are left for 24 h in the final mixture of pH 5.5, unless stated otherwise. The samples are then subject to filtration, washing with water, drying at 90 °C (T_g = 106 °C for poly(acrylic acid)), and calcination at 600 °C for 6 h with a heating rate of 2 °C min^{-1} under atmospheric conditions.

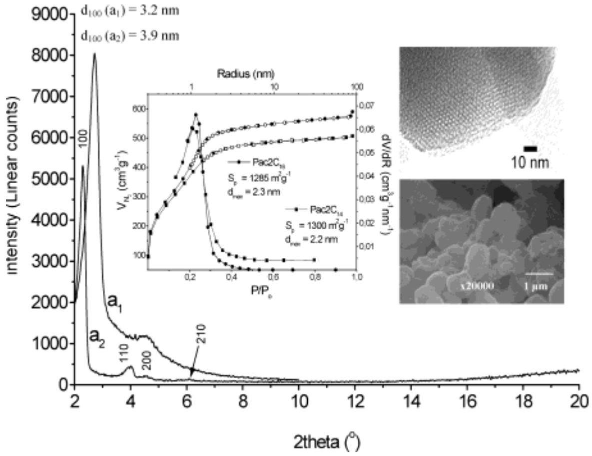

Figure 1. (a) X-ray diffractograms of the corresponding (a_2) uncalcined and (a_1) calcined samples Pac2C_{16}. The SEM and TEM micrographs correspond to a_2 and a_1, respectively. Nitrogen adsorption−desorption isotherms at 77 K and pore size distribution according to the Horvath−Kawazoe (H.K.) method of the calcined Pac2C_{16} and Pac2C_{14} samples.

Nitrogen adsorption measurements were performed at 77 K on a Sorptomatic 9000 by Fisons Instruments after outgassing for 12 h at 473 K and P = 0.005 Torr. X-ray diffraction measurements were acquired on a Bruker Advance D8 system using Cu Kα radiation (λ = 1.5418 Å) with a resolution of 0.01°. Scanning electron microscopy was performed on a JEOL JSM 5600 at 20 kV. TEM photos were recordered in a JEOL 120CX instrument equipped with CeB6 fillament. pH was monitored on a PH82M standard pH meter by Radiometer Copenhagen.

X-ray diffractograms of Pac2C_{16}, a sample developed by poly(acrylic acid) of MW = 2000 g mol^{-1} and C_{16}-TAB (pH 5.5, 24 h), show four Bragg peaks in the low-angle region 2° < 2θ < 7° fully indexed according to a hexagonal unit cell, indicating a long-range order of the uncalcined sample (Figure 1a$_2$). After 24 h in the final mixture of pH 5.5 and calcination at 600 °C a thermally stable structure (Figure 1a$_1$)—as implied by higher intensity—is formed, which possesses high surface area, 1285 m^2 g^{-1}, and an adsorption−desorption isotherm typical of ordered mesostructures (inset Figure 1). The broadening though of the second-order peaks indicates some loss of ordering.The TEM image shows clearly the hexagonal arrangement of pores for the calcined material. SEM also reveals an interesting preference of the 1-μm uniform uncalcined particles toward hexagonally shaped morphology.

If C_{14}TAB instead of C_{16}TAB is used (Pac2C_{14}), a different mesophase is obtained. The uncalcined samples (Figure 2) show three low-angle Bragg peaks that are fully indexed to a cubic unit cell. These XRD patterns

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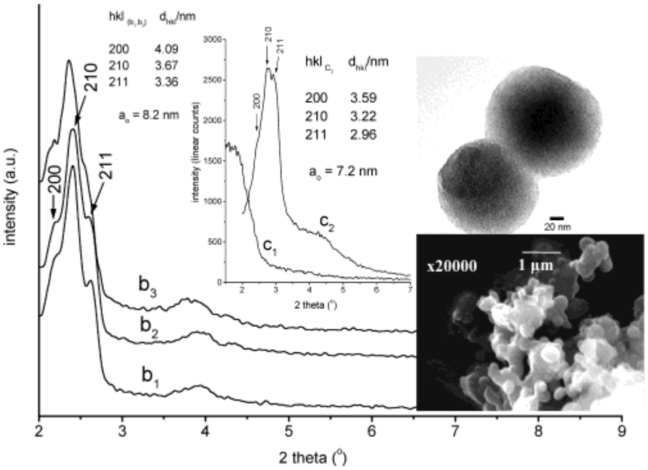

Figure 2. X-ray diffractograms of Pac2C$_{14}$ corresponding intermediate samples isolated from the same mixture. The SEM and TEM micrographs correspond to c$_2$.

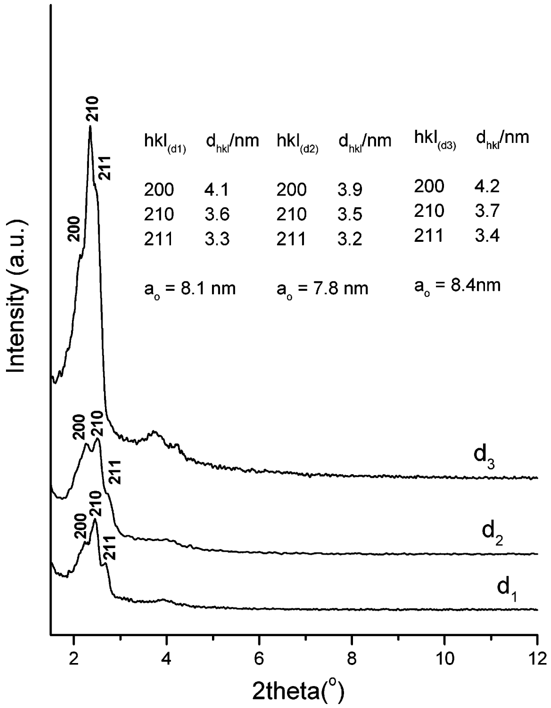

Figure 3. X-ray diffractograms of uncalcined Pac250C$_{14}$ (d$_1$) at pH = 4.5, Pac15C$_{14}$ (d$_2$) at pH = 4.5, and Pac15C$_{14}$ (d$_3$) at pH = 5.5.

are typical of cubic SBA-1-type mesostructured materials.[9] Several samples were isolated at various pH values covering a pH range 4.0−7.0. The samples isolated at pH 4.0 (Figure 2b$_1$) and 5.5 (Figure 2b$_2$) have the same cell parameter $a_o = 82$ Å, while the sample isolated at pH 7.0 exhibits slightly increased value $a_o = 83$ Å (Figure 2b$_3$). The XRD pattern of the calcined material (the one isolated at pH 5.5) shows that the cubic pore order is retained; however, the coherence length is smaller, as indicated by the broader Bragg reflections (Figure 2c$_2$). The XRD pattern c$_1$ (Figure 2c$_1$) corresponds to the uncalcined material synthesized according to the synthesis protocol described above, using C$_{14}$TAB, but no Pac2. It is clearly observed that no ordered phase is obtained, which indicates the role of Pac2 as the main structural component. If instead of Pac2, Pac250 (MW = 250000 a.u.) or Pac15 (MW = 15000 a.u.) is used in combination with C$_{14}$TAB, we also obtain the SBA-1 mesophase, with higher cell parameters, depending also on the pH (Figure 3): 84 Å for Pac15C$_{14}$ (d$_3$) at pH = 5.5, but 82 Å for Pac2C$_{14}$ at the same pH and 81 Å for Pac250C$_{14}$ (d$_1$), but 78 Å for Pac15C$_{14}$ (d$_2$) at pH = 4.5. So Pac also finely controls the cell parameter, a fact that we believe implies the presence of Pac in the globular micelle, if also seen in combination with the fact that without Pac no ordered phase is observed. The calcined material isolated at pH 5.5 (c$_2$) exhibits a typical adsorption−desorption isotherm and high surface area, 1300 m^{2}g^{-1} (inset Figure 1). Typical SEM and TEM images of this sample (inset in Figure 2) show the formation of spherical agglomerated particles.

Phase transformations similar to the above-presented phase transformations by varying the surfactant chain length have been reported by Kim and Ryoo.[10] It was established that use of triethylalkylammonium (CTEABr) surfactants with chains varied between C$_{12}$ and C$_{18}$ favor the $Pm3n$ phase, while C$_{20}$ leads to the $P6mm$ phase under highly acidic conditions. It was also stated that high acidity favors the cubic phase due to an increase of I$^+$ species concentration, resulting thus in higher curvature of the (S$^+$X$^-$I$^+$) micelle. Moreover, Che et al. have reported the occurrence of similar transformations due to the co-anion introduced by the acid.[11] The fact was explained in terms of different adsorption strengths of these anions on the CTEAX surfactants headgroup, resulting in different curvature of the micelles. But as also stated the mesophase formation is mainly controlled by the condensation of silica, which is known to cause a decrease of the positive charge density of the framework.[3] To maintain interfacial charge matching, surfactants pack according to a higher curvature pattern, favoring the transformation from $P6mm$ to $Pm3n$ phase under highly acidic conditions, as observed by Che et al.[12] In our case with the use of trimethyl instead of triethyl derivatives of the alkylammonium surfactants, pH conditions in the range 4−7, while the concentration of Cl$^-$ and Br$^-$ anions remains constant, the curvature needed for spherical micelle formation cannot be achieved according to these references and as is also shown in Figure 2c$_1$. It seems that complexation of surfactant with the carboxylate groups of Pac, as pH rises, leads to the formation of complexated Pac-C$_n$ chains with adequate curvature to form the necessary spherical micelles for the $Pm3n$ phase. It seems that Pac is able to stabilize these micelles in a wide range of pH, even up to the neutral region. In-depth research is under way to clarify the mechanistic pathway of this complex system.

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