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Cationic templating with organic counterion for superstable mesoporous silica

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Superstable mesoporous silicas LUS-1 templated using cationic surfactants of various chain lengths were synthesized in the presence of tosylate anions in basic media with low surfactant to silicium ratios. The highly structured hexagonal silica mesophases are stable in boiling water for several days and, after calcination up to 1093 K. A stabilizing hydrothermal treatment before calcination further improves the stability up to 1273 K. It is believed that the outstanding stability of the LUS-1 is related to the hydrophobic control obtained using an organic surfactant counterion in the surfactant-silicate interface during polycondensation.

1. INTRODUCTION

Mesostructured porous materials are very attracting for industrial applications as, for instance, specific absorbents, molecular sieves, catalyst supports and, for metal remediation. They are indeed characterized by very narrow pore size distribution in the range 2-30 nm and high surface area of about 1000 m²/g. Nonetheless, these materials are not very stable [1]. This is particularly true for the {S⁻, X⁻, I⁺} or {S⁻, I⁺} synthesis routes implying interfaces with either cationic or anionic surfactant S⁺ or S⁻, respectively and, a positively charged inorganic phases I⁺. The inorganic anions X⁻ or the sulfonates or phosphonates S⁻ surfactants generate more hydrophilic interfaces than quaternary ammonium surfactants in the {S⁺, I⁺} route. The latter route is known to generate more stable materials in which the surfactant counterion plays an important role on the long-range order, the nature of the phase and on the hydrophobicity of the organic-inorganic interface [2]. Besides, non-ionic route using amines in HMS materials or block copolymers such as polyethers leads to more hydrophobic interface, larger pore wall and better-condensed inorganic matter. The latter are indeed very stable materials however their structures are quite disordered [3]. To go further with the idea that counterion may control the interface, TMS were prepared according to the {S⁺, I⁺} route in the presence of hydrophobic tosylate (Tos) and tested for their both thermal stability and hydrothermal stability [4].

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2. EXPERIMENTAL

The mesoporous templated silicas were prepared from clear sodium silicate solutions, alkyltrimethylammonium (RTMA) and tosylate (Tos⁻, paratoluenesulfonate) as counterion for LUS-1. To compare counterions, MCM-41 were prepared in the same conditions than that of the LUS-1 using various halogenides, X⁻ = Cl⁻, Br⁻ and I⁻. However, for stability tests, the comparison was made with a MCM-41 made according the optimized recipe of Song et al. [5]. Typical gel compositions for a LUS-1 were: 1 SiO₂; 0.266 Na₂O; m RTMAX, 79.9 H₂O where R = C10 to C22 n-alkyl and, the surfactant to silica ration m = 0,01 0,1 [4]. The silica source may be commercial water silica or Ludox solution. The hydrothermal treatment was performed at 403 K for 24 h followed by calcination at 823 K. Further stabilization consisted in a second hydrothermal treatment of the solid immersed in pure water for 24 h at 403K. The XRD data were measured on the stabilized and calcined sample exposed to ambient air using a Siemens D5005 diffractometer. The SEM pictures were taken using a Hitachi S800 FEG. For ²⁹Si Solid State NMR, the samples were loaded under pure oxygen into 4 mm rotor. The rotation frequency was about 8 KHz and the data were collected using a 400 MHz Bruker solid state NMR spectrometer. The hydrothermal stability was performed in boiling water for several days using the appropriate vessel equipped with a cooling column. The samples were calcined in ambient air ramping the temperature at 1 K/min up to the desired temperature, the latter maintained for 1 hour before cooling.

3. RESULTS AND DISCUSSION

Four well-distinguishable XRD peaks (100, 110, 200 and 210) typical of the hexagonal mesophase, were obtained for C12 to C18 surfactants (the narrowest peaks for C12 and C14). A single broad XRD peak was observed for C10 and C22. For the materials prepared using the C16-surfactant, 20% up to 70% structure losses were measured after exposure to boiling water for 48 and 72 hours respectively, according the XRD peak intensity. MCM-41 prepared with bromide as counterion reaches these levels of degradation in less than 6 and 12 hours, respectively. Calcination in air shows clearly that the stability is improved when the anion is changed from Cl⁻ to I⁻, with a structure collapse at 1093 up to 1273 K, respectively. The mesophases obtained with tosylate, which leads to slightly less stable structure upon calcination than iodine, are further improved, as shown on Figure 1, by post-synthesis hydrothermal stabilization according to the procedure describe in the literature [5].

Up to 1173 K, there is a progressive decrease of the silanol concentration measured from FT-IR and H-NMR with minor morphology changes (d_{100} and pore diameter kept constant at about 4 nm and 2.9 nm, respectively) and loss of surface area (from 1100 to 935 m²/g) (see table 1). At 1273K, the structure shrinks by 15 %, the surface drops down to 635 m²/g accompanied with wall thickening bringing the solid to the limit of the microporosity. For higher temperature, the structure begins to collapse as illustrated by the decrease of the intensity on the diffractograms (figure 1d, e). However, at 1373K a well ordered hexagonal structure (illustrated by a narrow half-width) is kept and according to the d_{100} equal to 2.9 nm corresponds to pores, which are probably microporous.

The surface area of 33 m²/g measured for non-calcined stabilized LUS-1 is consistent with the external surface of fibers of 40 nm diameter. On figure 2, the fibers are much larger than 40 nm. However, on Transmission Electron Microscopy, the well-ordered domains are indeed of 30 to 60 nm wide. A detailed observation of the SEM pictures reveals that the fibrous material

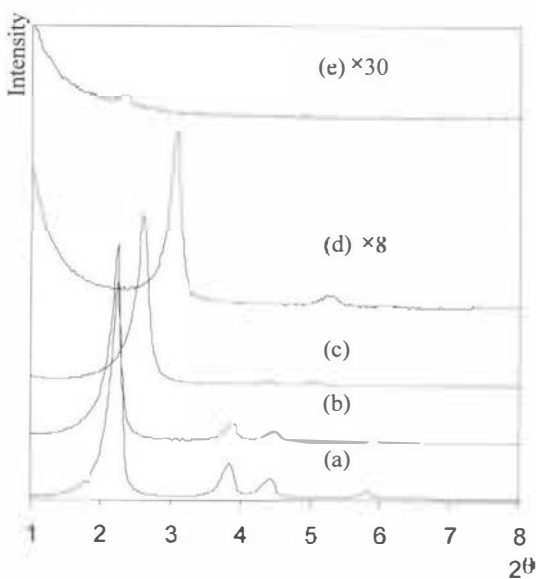


Fig. 1. XRD of stabilized LUS-1 calcined at a) 873, b) 1173 c) 1273, d) 1373, e) 1473 K

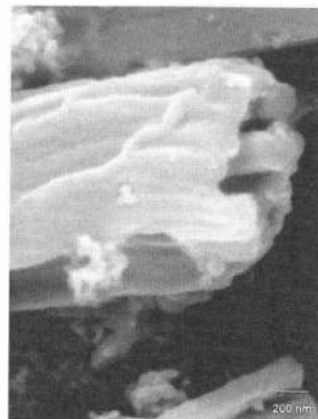


Fig. 2. SEM micrograph of stabilized LUS-1 showing the typical fiber-like morphology

Table 1
Morphology characteristics from N₂ adsorption-desorption and ²⁹Si MAS NMR data

LUS-1 Treatment (a)	Surface area m ² /g (b)	Porous volume cm ³ /g	Pore diameter (nm) (c)	Wall thickness (nm) (d)	C _{BET}	Q ₄ %	Q ₃ %	Q ₂ %	(Q ₂ +Q ₃)/ΣQ _i % (e)
Stabilized	33	/	/	/	32	59	24	17	41
873 K	1100	0.84	3.1	1.5	137	59	37	4	41
1173 K	935	0.67	2.9	1.7	70	83	14	3	17
1273 K	635	0.34	2.1	1.8	17	/	/	/	/

(a) as-made followed by stabilizing hydrothermal treatment and calcined at various temperature between 873 and 1273 K

(b) calculated using the BET equation for P/P₀ < 0.15

(c) calculated using the Kelvin-Thomson equation

(d) calculated from XRD and pore diameter

(e) chemical shift for Q₂, Q₃, Q₄ respectively at 92, 100, 109 ppm (ref. TMS)

is made of primary fiber of about 50 nm diameter merged together into secondary more or less bulky (some times hollow) fibers (figure 2) of about 1 μm diameter. These secondary fibers are themselves associated one with another in much larger fibers of rather heterogeneous diameter sizes centered at about 10 μm .

The ^{29}Si MAS NMR experiments performed on the different stabilized silicas. The stabilized state was of particular interest since it has been found to increase further the thermal stability of the material by about 100 K. For a calcination at 873 K the surface silanol groups undergo a strong rearrangement leading to an increase of the concentration of Q_3 species at the expense of the Q_2 species while the concentration of the Q_4 species remains constant. The OH density calculated from the surface area and the weight loss at 1273 K from TGA is 4.2 OH/nm^2 . However, after a calcination temperature of 1173 K, the number of Q_4 species is increased by about 50% mainly due to the condensation of the Q_3 species. The silanol density drops down to 0,25 OH/nm^2 , which confer to the material a rather hydrophobic nature characterized by a BET constant of 70 (instead of 137 after calcination at 873 K, table 1). For a higher calcination temperatures (1273 K), the silanol density drops even further and, concomitantly, the BET constant value decreases down to 17.

Further questions remains to be answered concerning the stability in boiling water since the OH density is almost the same as in MCM-41. It is believed that the difference lies on the localization of the silanol groups that might be rather internal to the wall in the LUS-1. A post hydrothermal treatment that decreases the resistance toward boiling water without changing the OH density according to ^{29}Si MAS-NMR would be interpreted as a rearrangement of the OH groups "moving" from internal to external position by successive OH condensations and siloxane bridge openings.

3. CONCLUSION

Super stable templated mesoporous silicas are obtained in a one-pot synthesis procedure using hydrophobic counterion believed to increase the hydrophobicity of the organic-inorganic interface and generate highly ordered silica mesophases. Lamellar and cubic mesophases obtained according to a similar recipe are currently under investigation.

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