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Different neutral surfactant template extraction routes for synthetic hexagonal mesoporous silicas

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The co-condensation of a tetraethoxysilane molecule on a neutral n-octylamine surfactant template is a convenient synthetic methodology for mesostructured material preparations. Distinct routes of template removal were investigated. The neutral surfactant was removed by calcination, hot solvent extraction, heating at 150 °C, *in vacuo* at room temperature and at 100 °C, and air drying, with the products assigned as HMM, HMS, HME, HMV1, HMV2 and HM, respectively. ^{29}Si NMR, infrared, surface area, pore diameters and pore volume determinations were employed to characterize each sample. Elemental analysis detected the presence of amine residues of 1.8, 1.2, 0.2, 1.6 and 0.30 mmol g^{-1} for HMA, HME, HMS, HMV1 and HMV2, respectively. The HMM, HMS and HMV2 samples presented a low amount of amine residues, and HMS and HMV2 have the great advantage of permitting template removal without calcination.

Introduction

Silica gel has been widely used as a support for covalent organic chain attachment, providing new materials that can be explored from the scientific, technological and environmental property points of view. These synthesized materials can be applied in catalytic processes,[1] chromatographic operations,[2] for removing and separating inorganic contaminants from solvents,[3,4] for the preconcentration of these contaminants,[5] such as preconcentration of pesticides,[6] as well as in agrochemical immobilization with the purpose of developing new compounds with low degrees of toxicity.[7,8]

Porous inorganic solids with controlled structures present better results than traditional modified surfaces, whose properties have been extensively investigated for both scientific and practical applications. Thus, mesoporous silicas formed by supramolecular neutral templating mechanisms have been prepared for evaluation.[9–13] The templates are often formed from neutral surfactant molecules.[14] The ability of this special class of molecules, having a polar head and a long, non-polar hydrocarbon tail, is to form micelles in polar solvents by placing the water-repelling hydrocarbon tails together in the center of a sphere, or sometimes a cylinder, to avoid water contact.[14] The diameter of the micelles depends on the exact nature of the surfactant, which is normally in the range of 2–4 nm.[14] These mesoestructured materials with ordered pores have been investigated for a wide range of scientific and practical interests[15–17] and in many types of heterogeneous catalyses.[18–21]

Mesoporous materials are normally synthesized by employing cationic surfactants as the template agent, around which a sol–gel process takes place. However, to remove this type of surfactant, another operation is required, *i.e.*, calcination. Recently, this same methodology has been used to develop new materials based on a co-condensation process, by using a simple neutral surfactant as a template.[14–18] This proposed neutral templating route enabled surfactant removal by a series of methods, beyond calcination. In addition, incorporation of organic groups into the mesoporous structures is also possible before the normal synthetic operation. This very elegant methodology is associated with functional group incorporation during the co-condensation process, and the observed yield is much higher than traditional postmodification procedure.[14]

The present investigation reports the synthesis of hexagonal mesoporous silicas by employing neutral surfactants. Several different processes were employed to remove the template in order to obtain a good removal operation with regard to environmental concerns, due to the fact that the chemist has a key role to play in maintaining and improving the quality of life.[22]

Experimental

Chemicals

Tetraethoxysilane (TEOS) (Aldrich) was used as the silica source. The surfactant n-octylamine (Aldrich) and ethanol (Merck) were employed. All other reagents grade were also used.

Synthesis

The parent mesostructure was prepared by stirring n-octylamine (23.2 mmol) in 200 cm^3 of water for 30 min until an opalescent solution was obtained. TEOS (106 mmol) was then added and the mixture was stirred for 24 h. The resultant solid was filtered and dried in air for 24 h.[23]

Template extraction

The amine extraction was carried out using different methods: (i) air drying for 72 h, (ii) drying in an oven at 423 K for 72 h, (iii) drying *in vacuo* at 298 K for 12 h; (iv) drying *in vacuo* at 373 K for 12 h, (v) washing by a hot ethanol reflux in a Soxhlet system for 72 h; and (vi) calcining at 903 K for 4 h. After which, each sample was submitted to a washing process with water. This procedure was adopted to give analogous conditions for all final products.

Characterization

Powder X-ray diffraction patterns were measured on a Shimadzu XRD-6000 diffractometer using CuKα radiation.

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A JEOL JSMT-300 scanning electron microscope studied the morphology of the obtained materials after sputter coating with a thin conducting layer of gold. The surface area of the hexagonal mesoporous materials was obtained using the BET equation on a Flowsorb 2300 analyser. The pore size was obtained by the mercury intrusion technique in a Micromeritics 9320 porosimeter. The degree of amine residue in the hexagonal mesoporous silicas was based on the carbon and nitrogen content, determined through elemental analysis on a PE-2400 elemental analyser. The infrared spectra of the solid samples were obtained using a diffuse reflectance system by accumulating 200 scans on an MB-Bomem FTIR spectrophotometer.

Nuclear magnetic resonance spectra of the solid samples were obtained on an AC 300/P Bruker spectrometer at room temperature. For each run, approximately 1 g of each mesoporous silica was compacted into a 7 mm zirconium oxide rotor. The measurements were obtained at a 59.61 MHz frequency for silicon with a magic-angle spinning speed of 4 Hz. In an attempt to increase the signal-to-noise ratio of the solid-state spectra, the CP-MAS technique was used, with a pulse repetition of 1 s and a contact time of 5 ms.[7,8]

Results and discussion

The general procedure for the synthesis of the proposed idealized hexagonal mesoporous silicas through a neutral template at room temperature is schematically illustrated in Fig. 1. The normal synthetic procedure used required tetraethoxysilane solubilization in a large amount of water for 24 h in order to cause a complete hydrolysis of all the ethoxy groups in the presence of the desired amine template molecule. The amine surfactant micelles guide the formation of the silanol groups around the polar head of the micelle. Outside each pore, the hydrolysed silicon atoms form siloxane groups, resulting in a crosslinked framework. The high density of the silanol groups dispersed over the pores form a homogeneous material. After synthesis, the neutral surfactant molecule was removed using the six different procedures, taking into account the aim of obtaining cheaper and more ecologically friendly processes than the traditionally employed methods. Each different removal process yielded products with different chemical and physical characteristics and different amounts of surfactant residue.

The mesoporous silicas obtained by the co-condensation process normally present hollow spheres of distinct shell thickness, as extensively reported before;[9,15,17,24] a simplified method of which consists of using n-octylamine as the template.[24] A representative scanning electron microscopic image of the materials obtained can be seen in Fig. 2. All the synthesized materials present the same features in these images, indicating the good homogeneity of the spheres formed, with aggregates of particles and with a flaky morphology.

The presence of residual amine can be detected in the infrared spectra, shown in Fig. 3, for all the HM samples, with the exception of HMM. The first peak at 1450 cm^{-1} is attributed to C–N stretching and the other, at 2950 cm^{-1}, is assigned to amine C–H stretching.[7,8] Both peaks confirm the presence of n-octylamine as an impurity in these materials as a consequence of the non-effective removal of the template, in spite of the use of the different extraction methods. However, in the HMM spectrum, the peaks in the ranges 3600–3400 and 1180–1080 cm^{-1} are typically representative of the existence of pure silica materials. The same sequence of peaks appears in the other spectra in addition to those related to the presence of amine. This fact is related to the removal method used for HMM, which is based on the use of a very high temperature and which eliminates any residues of amine inside the material.

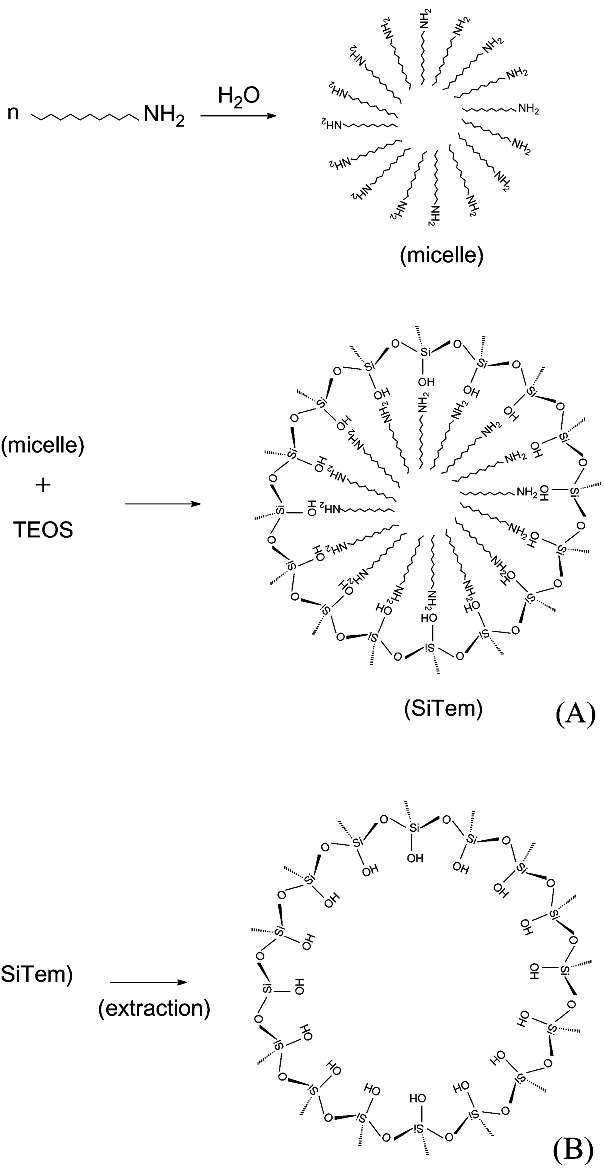

Fig. 1 Proposed scheme of hexagonal mesostructure formation with n-octylamine as template (A) and after template removal (B).

Quantitative amounts of surfactant were obtained for elemental analysis, the data are listed in Table 1. The results show that the traditional calcination method fully eliminates

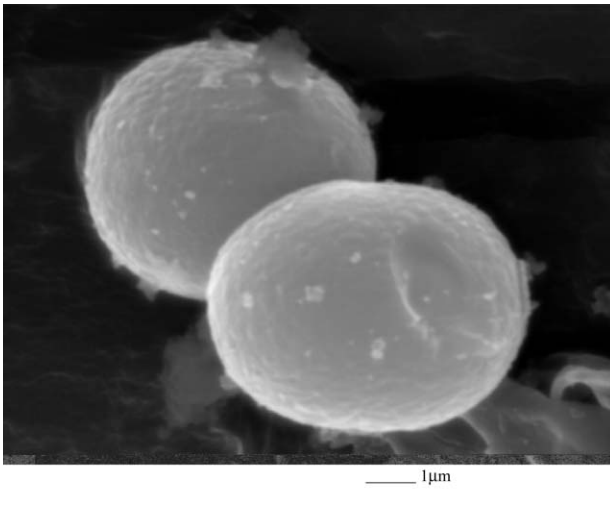

Fig. 2 Scanning electron micrographs for the HMS sample.

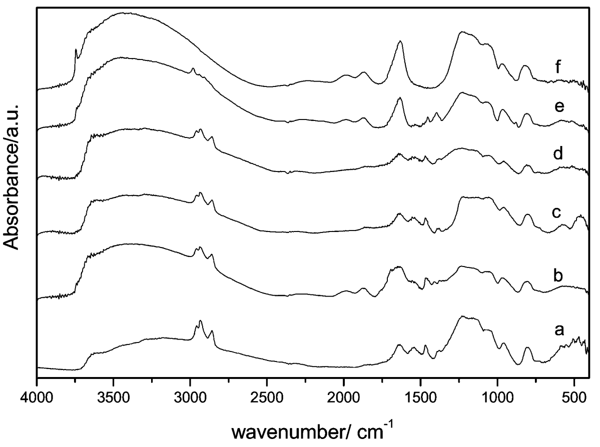

Fig. 3 Infrared spectra for hexagonal mesoporous silicas: HMA (a), HME (b), HMS (c), HMV1 (d), HMV2 (e), and HMM (f) samples.

the amine, as clearly is illustrated for the HMM product. However, with the other methods used for template extraction, there are always some traces of surfactant left. With the HMA, HME and HMV1 materials the amount of amine remaining was more than 1.0 mmol g^{-1}. However, the HMV2 and HMS silicas contained low amounts of n-octylamine and in the calcinated product, HMM, the template molecule was absent. Specifically in the HMV2 case, the product was obtained with a non-traditional method of template removal. Only a low amount of amine was detected, and this method has the advantage of removing the template agent without using any solvent during the extraction. This method of extraction thus permits a reduction of organic solvent use in the chemical process, which is one of the principles of green chemistry operations,[25] where, before introducing them into the marketplace, an improvement in the chemical process is needed leading to a reduction of chemicals in the environment.[26]

High surface areas for all samples were observed, with the exception of the HME material, which presented a lower value than for most mesoporous silicas. HMA presented a medium surface area. All the data are listed in Table 1. On inspection, it is clearly seen that the majority of all materials presented high surface areas, around 900 $m^2\ g^{-1}$. These high values are very much appreciated in material science in order to apply them in many reactions, such as in catalytic processes.[14]

With the exception of HME, all the silicas presented a similar pore size, showing that in the removal processes the n-octylamine did not alter the basic structure of this type of mesoporous material, as can be seen by the very similar porosimetry curves, shown in Fig. 4. An average pore diameter of around 2.4 nm was obtained for these synthetic materials. However, HME was the poorest template removal process, which was reflected in the low pore diameter obtained, 2.15 nm. The nitrogen adsorption–desorption isotherm and the Horvath–Kawazoe pore silica distribution for a typical process, is here represented by the HMS silica in Fig. 4. A well-defined step occurs in the P/P_o adsorption between 0 and 0.3, which is an indicative of the filling of the framework confined mesopores with an Horvath–Kawazoe average pore size of around 2.4 nm. The mercury adsorption properties are fundamentally similar for all the other obtained products.

Table 1 Properties of hexagonal mesoporous silicas obtained by using n-octylamine as a template. The interplanar distance (d_i), surface area (A_s), porous diameter(d_p), porous volume (V_p) and residual amine (RA) are presented

Sample	d_i/nm	A_s/$m^2\ g^{-1}$	d_p/nm	V_p/$cm^3\ g^{-1}$	RA/mmol g^{-1}
HMA	2.81	683 ± 82	2.33	0.29	1.8 ± 0.2
HME	3.68	346 ± 16	2.15	0.30	1.21 ± 0.4
HMM	2.99	862 ± 26	2.32	0.32	—
HMS	2.99	983 ± 55	2.42	0.32	0.2 ± 0.1
HMV1	2.93	916 ± 43	2.46	0.29	1.6 ± 0.1
HMV2	2.87	935 ± 38	2.51	0.26	0.3 ± 0.1

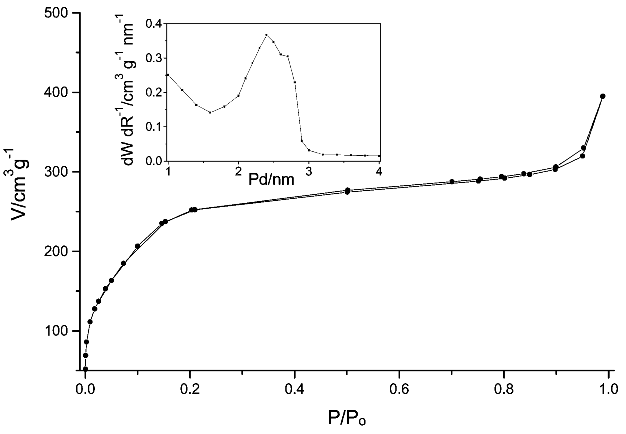

Fig. 4 Mercury adsorption–desorption isotherms for an HMS silica. Relative pressure is P/Po where P is the equilibrium pressure of the adsorbate and P_o is the saturation pressure of the adsorbate at the temperature of the adsorbent. Insert, the corresponding Horvath–Kawazoe pore size distribution curves (dW/dR) for the normalized adsorbate volume with respect to the pore diameter.

The X-ray diffraction powder patterns of the synthesized products are presented in Fig. 5. For all the samples, a single diffraction peak appeared in the low 2θ region, showing the formation of periodic mesostructures for all the products.[27] As observed above, the HME material differed from the other samples, showing here a broad and undefined peak. This fact may be explained by the removal process applied, which was evaporation of the surfactant at 150 °C. In this case, the material turned a dark yellow colour during the thermal operation. This change in colour may be attributed to amine oxidation and, consequently, this might cause a disturbance in the basic structure of the material, by altering the original structure to give a more pronounced amorphous character. Possibly, this change could reflect a little perturbation in the micelle structure, which caused a condition favourable to amine oxidation. On the other hand, all the other materials showed a single lattice peak around 2.9 nm, which is the characteristic diffraction peak for a hexagonal structure. It is worth pointing out that these extraction methods did not influence the hexagonal mesoporous structure. The similarities between the X-ray diffraction patterns

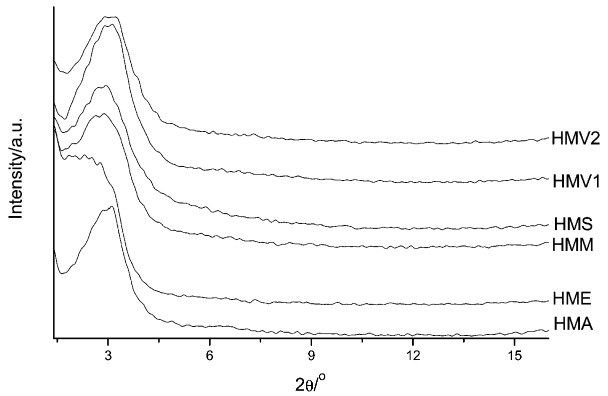

Fig. 5 X-ray diffraction patterns for the silicas.

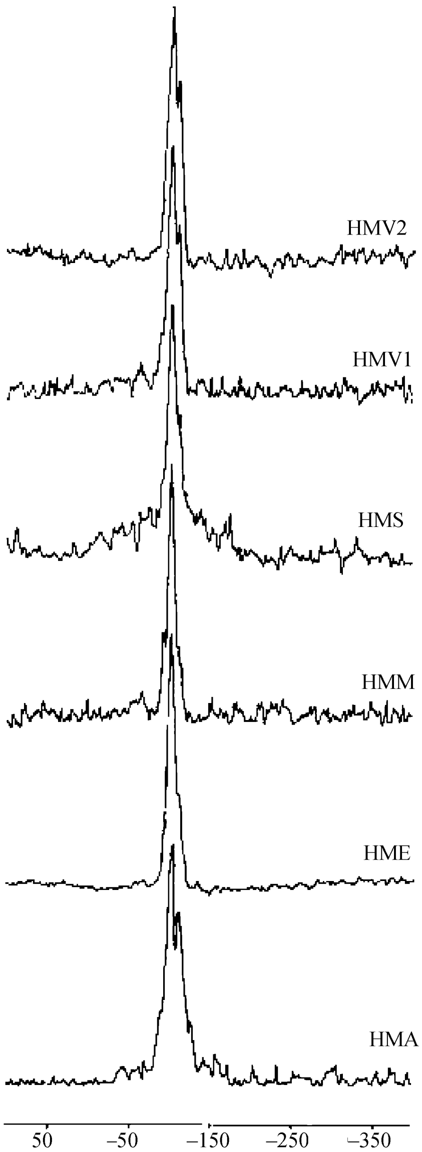

Fig. 6 Solid state ^{29}Si NMR spectra for the silicas.

for this series of materials confirmed the success of the amine substitution strategy in producing isostructural compounds.[28]

The ^{29}Si NMR spectra for all the materials obtained are shown in Fig. 6. All the spectra show the series of typical silica signals: (i) $Si(OSi)_4$, (Q^4) at −116 ppm, (ii) a surface signal, $Si(OSi)_3OH$, (Q^3) at −106 ppm, and (iii) weak shoulders at −95 ppm assigned to the Q^2, $Si(OSi)_2(OH)_2$ structural units.[29] Usually, in hexagonal mesoporous silica a Q^4 peak has a higher intensity than a Q^3 one. However, in this work, all the samples were extensively washed with water after the template removal process. Indeed, the increase in the Q^3 peak intensity can be explained as a result of the hydrolysis of the siloxane Q^4 groups. Then, in such an operation, silanol groups, Q^3, are produced as a consequence of the washing procedure.[30]

Conclusion

All the routes of neutral surfactant removal yielded good silicas, with the exception of that obtained by the oven drying process at 150 °C, HME, which might have resulted in a partial oxidation of the amine due to the heating process. In this case, a hexagonal mesoporous material of low quality and homogeneity was obtained. The purpose of the removal of the template by different methods was to show that the traditional one, which employs calcination (HMM), is the best in order to eliminate completely any template residue. However, this route does not allow the production of modified mesoporous materials during the co-condensation process. However, another traditional template removal procedure, Soxhlet extraction (HMS) and an untraditional method, under vacuum at 100 °C (HMV2), yielded product with a low amount of template residue, and were successful in producing modified hexagonal mesoporous silicas during the co-condensation process. Furthermore, HMV2 has the great advantage of being a synthesis procedure that does not require the use of organic solvents during the template removal process.

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