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Synthesis of large-pore ordered mesoporous silicas containing aminopropyl groups

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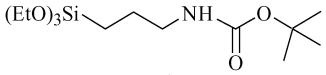
Ordered mesoporous silicas with large-pore diameters incorporating aminopropyl groups in variable quantity have been synthesized *via* the co-condensation of tetraethyl orthosilicate (TEOS) and 3-*tert*-butyloxycarbonylaminopropyltriethoxysilane templated with nonionic surfactant P123 under acidic conditions. The deprotection of amino groups was then quantitatively achieved either by thermal treatment or acid hydrolysis followed by Et_3N treatment, both routes leading to exactly the same materials. We showed that the free amino centers are fully accessible, by using the condensation of the amine function with benzaldehyde.

Introduction

Since the discovery of ordered mesoporous silica,[1] many research efforts have been made to modify interior pore surfaces of mesoporous materials. Postsynthesis grafting of an organotrialkoxysilane $RSi(OR')_3$ onto the pore surface was often used.[2] However, this method allows control of neither the loading nor the distribution of the functional groups.[3] More recently, an alternative approach in one step, overcoming the main restrictions of the postsynthesis method has been developed.[4–8] It consists of the co-polymerization of tetraethyl orthosilicate (TEOS) and an organotrialkoxysilane $RSi(OR')_3$ in the presence of a structure directing agent. However, this method requires that the R group is sufficiently hydrophobic to enter the core of the micelle and not too bulky to avoid its perturbation.

Among the variety of functional groups that have been incorporated into mesoporous materials by this route, the amino group gave rise to numerous studies. Indeed, it is a particularly useful functionality for many applications such as entrapping enzymes, selective catalysis and adsorption. Aminopropyl functionalized silicas were synthesized in the presence of dodecylamine,[5] cetyl-trimethylammonium bromide[9] or sodium dodecyl sulfate[10] as surfactant by co-condensation of TEOS and 3-aminopropyltriethoxysilane (APTES). However, the pore sizes of all these materials are relatively small (less than 3 nm), which is a drawback for many applications, in particular for catalysis[11] or immobilization of biomolecules. In an attempt to overcome this drawback, Zhao *et al.*[12] used the triblock copolymer P123 as surfactant under acidic conditions. However, they showed a strongly adverse effect of APTES on the formation of mesostructure under these conditions due to protonation of the amine functions. Recently, Katz *et al.*[13] reported the synthesis of imprinted amines in bulk silica by using the deprotection of carbamate groups, which are commonly used as protecting agents for amino groups in synthetic chemistry. These observations prompted us to investigate the co-condensation method on the protected amino group.

Here we report the synthesis of large-pore aminopropyl-functionalized ordered mesoporous silica by using co-condensation of TEOS and 3-*tert*-butyloxycarbonylaminopropyltriethoxysilane **1** in the presence of surfactant self-assemblies under acidic conditions. We show that the quantitative carbamate deprotection renders the amino centers fully accessible, which could allow the immobilization of bio-molecules.



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Experimental

General procedures

Triblock copolymer ($EO_{20}PO_{70}EO_{20}$ with PEO = poly(ethylene oxide) and PPO = poly(propylene oxide)) Pluronic P123, 3-aminopropyltrimethoxysilane, tetraethyl orthosilicate (TEOS) and di-*tert*-butyl dicarbonate were purchased from Aldrich and used as supplied. The CP MAS ^{29}Si solid state NMR spectra were recorded on a Bruker FTAM 300 as were CP MAS ^{13}C solid state NMR spectra, in the latter case by using the TOSS technique. In both cases, the repetition time was 5 and 10 s with contact times of 5 and 2 ms. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2010 analyser and the average pore diameters were calculated by the BJH method. The X-ray measurements and data treatment were performed at the "Groupe de Dynamique des Phases Condensées" in Montpellier. The X-ray diffraction experiments were carried out on solid powders in glass capillaries of 1 mm diameter in transmission configuration. A copper rotating anode X-ray source (4 kW) and 2D detector were used. The diffraction curves were obtained giving diffracted intensity as a function of the wave vector q. The diffracted intensity was corrected by exposure time, transmission and intensity background coming from diffusion by an empty capillary.

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Preparations

3-*tert*-Butyloxycarbonylaminopropyltriethoxysilane, 1. 3-*tert*-Butyloxycarbonylaminopropyltriethoxysilane **1** was prepared by mixing 3-aminopropyltriethoxysilane (11.30 g, 51.1 mmol) and di-*tert*-butyl dicarbonate (12.50 g, 57.3 mmol) in 50 mL of ethanol. The resulting mixture was stirred overnight at room temperature. The solvent was removed under vacuum and the residual liquid was distilled to afford 12.10 g of **1** (37.3 mmol, 73%) as a colorless liquid (bp 95 °C at 0.05 Torr). ^{1}H NMR (δ_{ppm}, 200 MHz, $CDCl_3$): 0.60 (m, 2H, CH_2Si), 1.20 (t, 9H, $^3J_{HH}$ = 6.90 Hz, OCH_2CH_3), 1.41 (s, 9H, $C(CH_3)_3$), 1.54 (m, 2H, $CH_2CH_2CH_2$), 3.09 (m, 2H, CH_2N), 3.79 (q, 6H, $^3J_{HH}$ = 7.00 Hz, OCH_2), 4.76 (s, 1H, N*H*). ^{29}Si NMR (δ_{ppm}, 40 MHz, $CDCl_3$):-45.40.

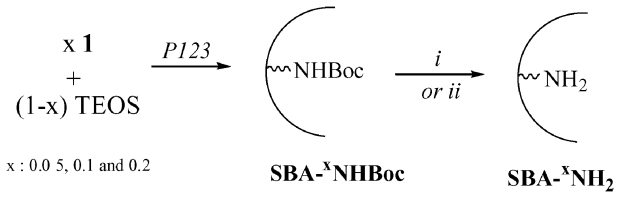
SBA-^{10}NHBoc. 4.0 g of P123 ($EO_{20}PO_{70}EO_{20}$) were dissolved in an aqueous HCl solution (160 mL, pH ≈ 1.5). This solution was poured on to a mixture of TEOS (8.41 g, 40.4 mmol) and **1** (1.44 g, 4.4 mmol) at ambient temperature. The molar composition of the reaction mixture was: 0.04 F^- : 1 TEOS : 0.11 **1** : 0.02 P123 : 0.12 HCl : 220 H_2O. The mixture was stirred for 2 h giving rise to a microemulsion. After heating this perfectly transparent solution at 60 °C, a small amount of NaF (75.4 mg) was added under stirring to induce the polycondensation. The mixture was left at 60 °C under stirring for 48 h. The resulting solid was filtered and washed with ethanol and ether. The surfactant was removed by hot ethanol extraction in a Soxhlet apparatus during 24 h. After filtration and drying at 60 °C under vacuum, 3.10 g (4.2 mmol, 95%) of SBA-^{10}NHBoc were obtained as a white solid.

SBA-^{10}NH$_2$ by thermal treatment. 2.00 (2.7 mmol) of solid SBA-^{10}NHBoc were introduced into a one-necked round bottomed flask. The flask was heated at 160 °C under vacuum during 12 h. The resulting solid was washed with ethanol and ether. After filtration and drying at 60 °C under vacuum, 1.65 g (2.6 mmol, 95%) of SBA-^{10}NH$_2$ were obtained as a white solid.

SBA-^{10}NH$_2$ by acidic hydrolysis. To a 6 M aqueous solution of HCl (40 mL) placed in a one-round bottomed flask, 2.05 (2.7 mmol) of solid SBA-^{10}NHBoc were introduced. The resulting mixture was heated at 100 °C during 12 h. The obtained solid was filtered and washed with water (3 × 100 mL) and then added to a solution (30 mL) of triethylamine–dichloromethane (1 : 5 v/v) to deprotonate the amino groups. After 1 h the solid was recovered by filtration and washed with ethanol and ether. After filtration and drying at 60 °C under vacuum, 1.45 g (2.3 mmol, 85%) of SBA-^{10}NH$_2$ were obtained as a white solid.

Results and discussion

First, we prepared SBA-15 mesoporous silica containing variable amounts of *tert*-butyloxycarbonylamino (NHBoc) groups called carbamate groups (Scheme 1). The synthesis of these materials was achieved by co-polymerization of **1** and tetraethyl orthosilicate (TEOS) in the presence of P123 as structure directing agent (see Experimental section). The surfactant was removed by washing to give the functionalized material denoted SBA-^{x}NHBoc (SBA to recall the P123 surfactant used, *x* to indicate the molar % of organic groups in the initial mixture and NHBoc for functional groups) in high yield.



Scheme 1 Preparation of SBA-^{x}NH$_2$ material by (*i*) thermal treatment or (*ii*) acid hydrolysis of SBA-^{x}NHBoc solid followed by Et_3N treatment.

Table 1 Textural and structural data for SBA-^{x}NHBoc and SBA-^{x}NH$_2$

Sample	S_{BET}/m^2 g^{-1}	D_p[a]/nm	V_p/cm^3 g^{-1}	d_{100}/nm
SBA-^{20}NHBoc	596	4.4	0.70	9.38
SBA-^{10}NHBoc	570	6.1	1.02	10.47
SBA-^{5}NHBoc	522	7.5	1.07	10.74
SBA-^{20}NH$_2$	550	4.0	0.62	9.84
SBA-^{10}NH$_2$	540	6.0	0.92	10.65
SBA-^{5}NH$_2$	420	7.5	1.00	10.92

[a] Calculated from desorption branch using the BJH method.

It is worth noting that no solid was obtained under the same conditions by using APTES instead of **1**. This result demonstrates the importance of the approach with protected amino groups. Some relevant textural and structural data for SBA-^{x}NHBoc are given in Table 1.

The powder small-angle X-ray pattern of SBA-^{10}NHBoc (Fig. 1a) exhibits an intense diffraction peak corresponding to d_{100} spacing (10.47 nm) and a second weak and broad peak centered at 5.96 nm. Further evidence for an ordered hexagonal structure was provided by transmission electron microscopy (TEM) image (see the inset in Fig. 2). The nitrogen adsorption–desorption isotherm for SBA-^{10}NHBoc is displayed in Fig. 2. The sample showed type IV isotherm with clear H_1-type hysteresis loop at relative high pressure, characteristic of mesoporous materials with large pores and narrow pores size distribution. The BET surface area increases, but pore volume and pore size decrease with increasing the concentration of **1** (Table 1).

The incorporation of carbamate groups in the mesoporous materials and the removal of surfactant were confirmed by solid-state NMR spectroscopy. The ^{13}C CP/MAS NMR spectrum of SBA-^{10}NHBoc (Fig. 3) demonstrates that the carbamate group remains intact as shown by the signals at 27.31 ppm (CH_3 resonances of *tert*-butyl), 158.00 ppm (carbonyl resonances) and three additional signals (43.00, 22.27 and 9.85 ppm) attributed to the propyl spacer. The ^{29}Si MAS NMR spectrum displays signals at −101.89 ppm and −111.60 ppm attributed to the substructures Q^3 and Q^4, respectively, denoting high cross-linking of the siloxane species. An additional signal at −66.75 ppm assigned to the substructure T^3 showed the fully cross-linked organosilsesquioxane species.

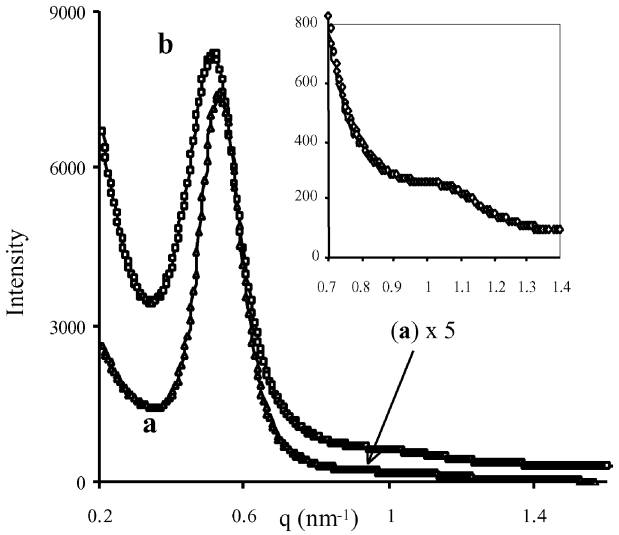


Fig. 1 SAXS patterns for (a) SBA-^{10}NHBoc and (b) SBA-^{10}NH$_2$.

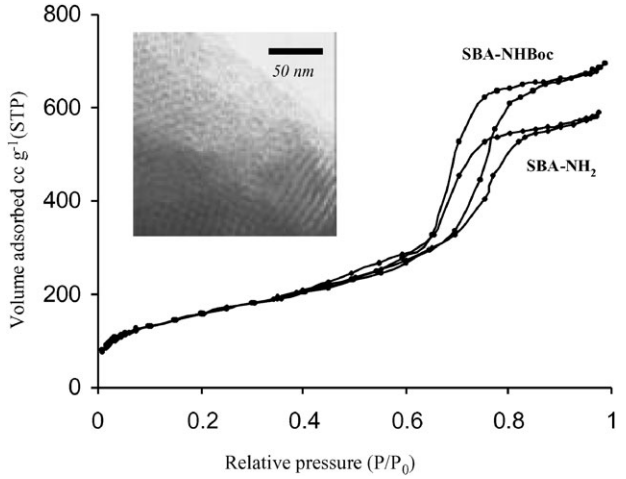


Fig. 2 N_2 adsorption–desorption isotherms of SBA-^{10}NHBoc and SBA-$^{10}NH_2$. The inset shows the TEM image of SBA-^{10}NHBoc.

Two independent routes for carbamate deprotection were used leading to exactly the same materials (Scheme 1). Thermal treatment of SBA-^{x}NHBoc at 160 °C under vacuum gave rise quantitatively to mesoporous silica containing aminopropyl groups (SBA-$^{x}NH_2$). The amino groups can also be recovered by treating SBA-^{x}NHBoc with a 6 M aqueous solution of HCl for 12 h under reflux. The resulting solids were then subsequently treated with CH_2Cl_2 triethylamine solution to deprotonate the amino groups giving rise to SBA-$^{x}NH_2$ in 95% yield. Some relevant textural and structural data for SBA-$^{x}NH_2$ are given in Table 1.

In both routes, the transformation of carbamate groups to the corresponding primary amine was quantitative. This is clearly reflected in the ^{13}C CP/MAS NMR spectrum (Fig. 3) by the disappearance of resonances associated with the carbamate protecting group (27.31 and 158.00 ppm) while the signals (42.72, 21.54 and 9.34 ppm) of the propyl spacer were retained.

Interestingly, no significant change was observed on the SAXS pattern for the SBA-$^{10}NH_2$ material (Fig. 1b) indicating a very stable structure even after chemical transformation. The nitrogen adsorption–desorption isotherm for SBA-$^{10}NH_2$ was

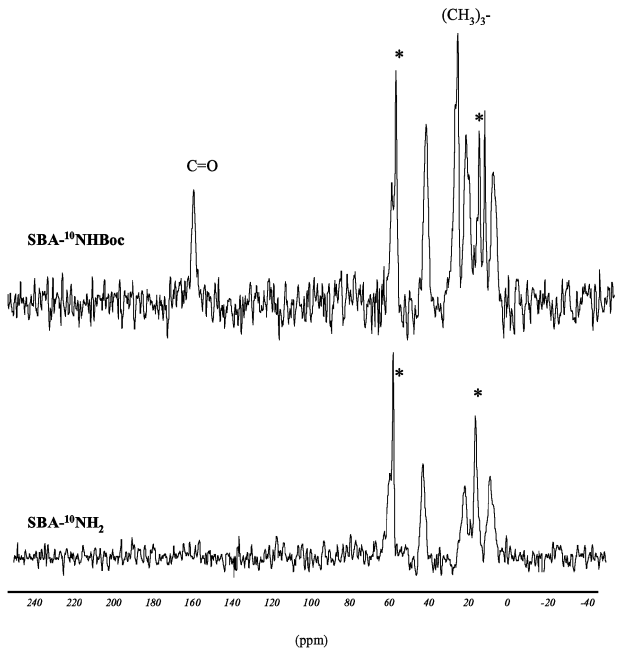
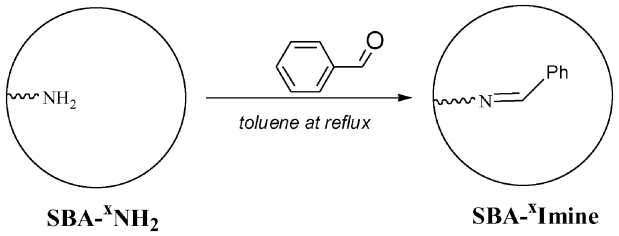


Fig. 3 ^{13}C CP/MAS NMR spectra of SBA-^{10}NHBoc and SBA-$^{10}NH_2$. Asterisks denote resonances corresponding to a residual amount of ethoxy groups.



Scheme 2 Imine formation by coupling between the amino groups of SBA-$^{x}NH_2$ materials and the benzaldehyde.

very similar (Fig. 2) to that of the starting material and revealed that the mesoporosity was maintained as well as a narrow pore size distribution.

The accessibility of the amino centers in SBA-$^{x}NH_2$ material was investigated by using the condensation reaction of the amine function with benzaldehyde to give imine (Scheme 2). The solid SBA-$^{x}NH_2$ were treated with an excess of benzaldehyde (2 equiv. of benzaldehyde per NH_2 moiety) in anhydrous toluene under reflux for 12 h. The resulting solids, called SBA-^{x}Imine, were copiously washed with toluene to eliminate the unreacted benzaldehyde. The filtrate including the excess benzaldehyde was analyzed by gas chromatography.

It was found that in all cases only one equivalent of benzaldehyde remained in solution. In addition, the ^{13}C NMR spectra of SBA-^{x}Imine revealed the presence of aromatic groups. These results indicate that all the amino groups were accessible. It is worth noting that the same reaction does not take place when SBA-^{x}NHBoc solids were used instead of SBA-$^{x}NH_2$. We observed that the lower the % ($x = 5$), the easier the transformation of amino groups in the imine, probably due to steric reasons. Thus, when $x = 5$ the whole transformation takes 4 h and when $x = 20$, it takes 12 h.

Conclusion

We have shown that it is possible to obtain large-pore ordered mesoporous silica functionalised with aminopropyl groups within the channel pores *via tert*-butyl carbamate as protecting agent. This protecting group allowed us not only to obtain material, whereas no material was obtained starting from the free amino group (under the same conditions), but to obtain an ordered material in spite of its bulk. Hydrolysis or thermal treatment of *tert*-butyl carbamate generates quantitatively the amine functions, which are fully accessible and could allow the immobilization of bio-molecules.

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