

A novel synthetic route for negatively charged ordered mesoporous silica SBA-15

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Ordered mesoporous silica SBA-15 functionalized with a high density of carboxylate groups has been prepared by a one-pot synthesis of a cyano-functionalized SBA-15 followed by treatment with sulfuric acid that removes the template and hydrolyses the cyanide group in one step.

Ordered mesoporous silica-based materials¹ have become one of the most important scaffolds for the construction of advanced materials on the nanometer scale.² After the initial efforts to expand the range of structures and framework compositions, the focus in more recent work has been directed towards expanding their functionality by surface modification, incorporating functional organic/inorganic compounds,^{3,4} and their use as templates for metal-^{5,6} or carbon-based materials.⁷

Surface modification of mesoporous silica through silylation with functional silanes provides a way of rationalizing the design of functional materials. For example, the weakly acidic nature of the silica surface can be altered by attaching a functional group that exhibits the desired polarity in a certain pH range.⁶ Silica functionalized with carboxylate groups (–COOH) has a negatively charged surface in neutral to basic environments. In addition to being capable of removing cationic species from aqueous solution, –COOH groups in the pore structure may serve as anchor sites for biomolecules and for polypeptide syntheses.⁸ For such applications, large-pore mesoporous silica is advantageous.

MCM-41 functionalized with –COOH groups has been synthesized by a procedure involving the hydrolysis of cyanide-modified parent silica.⁹ Very recently, a sol-gel preparation of a mesoporous silica film with a –COOH-terminated pore surface has been reported.¹⁰ In both cases, the pore size of functionalized silicas is smaller than 3.0 nm. To our knowledge, no direct synthesis of –COOH-functionalized, large-pore SBA-15 has yet been reported. Furthermore, these methods require that the template is removed from a –CN-containing hybrid by solvent extraction, a procedure which is not straightforward for SBA-15.¹¹

Here we report a novel route for –COOH-functionalized siliceous SBA-15. It involves a one-pot synthesis of –CN-functionalized hybrid material followed by treatment with sulfuric acid. The latter is capable of efficiently removing the template *via* ether cleavage and serves to hydrolyse the –CN groups in one step. The synthesis started from the preparation of a hydrochloric acid solution of the triblock copolymer Pluronic P-123 (P-123). 2-Cyanoethyltriethoxysilane (CTES, Gelest) was then added to the solution. After stirring for 30 minutes, tetraethylorthosilicate (TEOS) was slowly added into the mixture. The molar composition of the mixture was (1 – *x*) TEOS : *x* CTES : 5.9 HCl : 193 H₂O : 0.017 P-123, where *x* = 0.1 and 0.2. The reaction was performed at 40 °C for 20 hours, followed by aging at 90 °C for one day. The product was filtered, washed with water and acetone, and dried at 90 °C. For removal of the template and hydrolysis of the –CN groups, 1.0 g dried sample was re-dispersed in 120 mL 48 wt% H₂SO₄ solution, and the mixture was heated to 95 °C for one day. Subsequently, the product was recovered by washing with water until the eluent became neutral, and finally dried at 90 °C.

As-synthesized –CN-containing SBA-15 (CN/SBA-15) shows a highly ordered hexagonal structure. Fig. 1 shows the

powder X-ray diffraction (PXRD) pattern of the sample functionalized with 20% CTES (20CN/SBA-15). The cell parameter calculated from the position of the (100) reflection is 11.1 nm. No change of the cell parameters is observed after H₂SO₄ treatment but the (110) and (200) reflections increase in intensity. The nitrogen sorption isotherm of the H₂SO₄-treated sample (20CA/SBA-15) shows a sharp step with a hysteresis loop corresponding to the filling of ordered mesopores (inset in Fig. 1). For the sample functionalized with 10% CTES (10CA/SBA-15), the definition of X-ray reflections and the steepness in N₂ sorption step are even more pronounced than for 20CA/SBA-15 (data not shown). Table 1 summarizes the physicochemical properties of the –COOH-functionalized samples. Both the materials have large pores, high surface areas and thick pore walls. It shows that the incorporation of –COOH groups does not interfere with the formation of SBA-15.

The effect of H₂SO₄ treatment on the template removal and hydrolysis of –CN groups was followed by ¹³C and ²⁹Si solid state NMR. The results for the sample synthesized with 20% CTES in the starting mixture (20CN/SBA-15 and 20CA/SBA-15) are shown in Fig. 2. The ¹³C CP/MAS NMR spectrum of 20CN/SBA-15 contains the lines from the P-123 template and the cyanoethyl group. In addition, it indicates that some of the –CN groups have already been hydrolysed prior to the H₂SO₄ treatment. After acid treatment, almost no P-123 copolymer is present in the sample, proving that effective removal of P-123

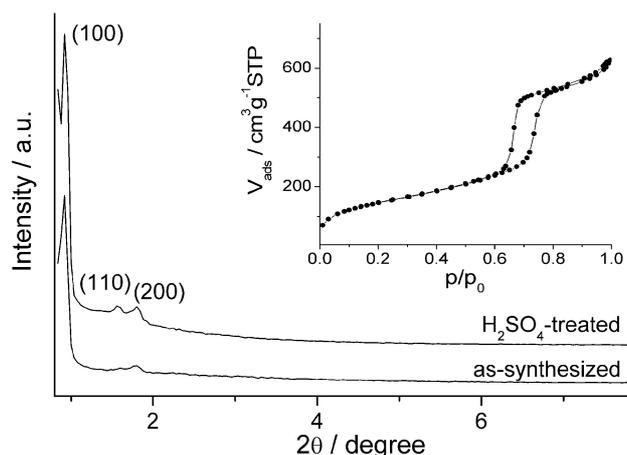


Fig. 1 PXRD patterns of functionalized SBA-15 with 20% CTES before and after H₂SO₄ treatment. The inset shows the N₂ sorption isotherm of the H₂SO₄-treated sample (20CA/SBA-15).

Table 1 Physicochemical properties of –COOH-functionalized SBA-15

Sample	Cell parameter/ nm	Pore diameter ^a / nm	Surface area ^b / m ² g ⁻¹	Pore volume/ cm ³ g ⁻¹	Wall thickness/ nm
10CA/SBA-15	11.5	7.4	588.8	1.01	4.1
20CA/SBA-15	11.1	7.0	532.2	0.92	4.1

^a BJH pore diameter calculated from the desorption branch. ^b BET surface area calculated from the adsorption branch.

can be accomplished through ether cleavage by concentrated sulfuric acid. In addition, all the $-\text{CN}$ groups are hydrolysed to $-\text{COOH}$ groups. The ^{29}Si NMR spectrum (20CA/SBA-15) shows that the lines assigned to T-groups are only slightly affected by the treatment, indicating that the functional groups are strongly anchored. Furthermore, the relative intensities of Q^2 and Q^3 lines decrease after the H_2SO_4 treatment, suggesting that during the treatment at 95°C , the acid does not just cleave the template and hydrolyses the $-\text{CN}$ groups, but also facilitates a further condensation of silanol groups in the pore walls.

The concentration of the $-\text{COOH}$ functional groups in SBA-15 was evaluated by thermogravimetric analysis (TGA) and titration. Both samples contain more adsorbed water (6–10 wt%, estimated from the weight loss up to 200°C) than calcined SBA-15 (2–3 wt%). The weight losses for 10CA/SBA-15 and 20CA/SBA-15 measured in the temperature range between $200\text{--}500^\circ\text{C}$ were about 8.2% and 15.8%, respectively, corresponding to the decomposition of the functional group. This gives a concentration of 1.1 mmol g^{-1} and 2.2 mmol g^{-1} for 10CA/SBA-15 and 20CA/SBA-15, respectively. If all these groups are assumed to be located on the surface, the surface densities of $-\text{COOH}$ groups in the two samples are *ca.* 1.1 nm^{-2} and 2.4 nm^{-2} . These data are in reasonable agreement with the T/Q ratio derived from the ^{29}Si NMR spectra. On the other hand, the $-\text{COOH}$ densities estimated by titration with diluted sodium hydroxide solution were *ca.* 0.8 mmol g^{-1} and 1.7 mmol g^{-1} . The values derived from titration may be smaller because the sample weight is over-estimated due to the chemisorbed water on the charged pore surface, it is difficult to correctly judge the titration endpoint, and some buried carboxylate groups could be inaccessible due to further silanol condensation during acid treatment.

A material functionalized with carboxylate groups should have cation-exchange properties. In order to assess these, 10CA/SBA-15 was exchanged with monovalent Na^+ ion, and was then used for ion-exchange with divalent Ca^{2+} . The measurement was conducted with a total normality of 0.1 N (adjusted by CaCl_2 and NaCl) at 25°C , and the amount of Ca^{2+} in solution was determined by titration with standardized EDTA

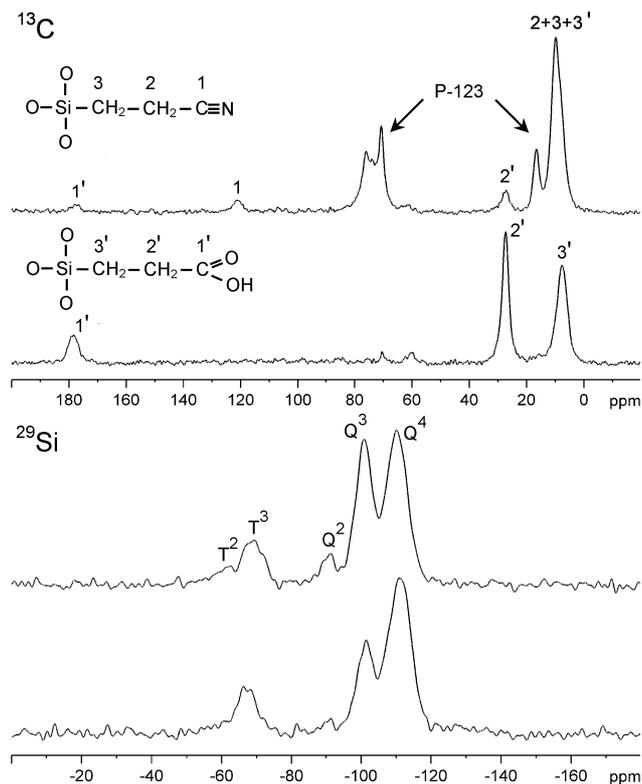


Fig. 2 ^{13}C CP/MAS and ^{29}Si MAS NMR spectra of 20CN/SBA-15 (top) and 20CA/SBA-15 (bottom).

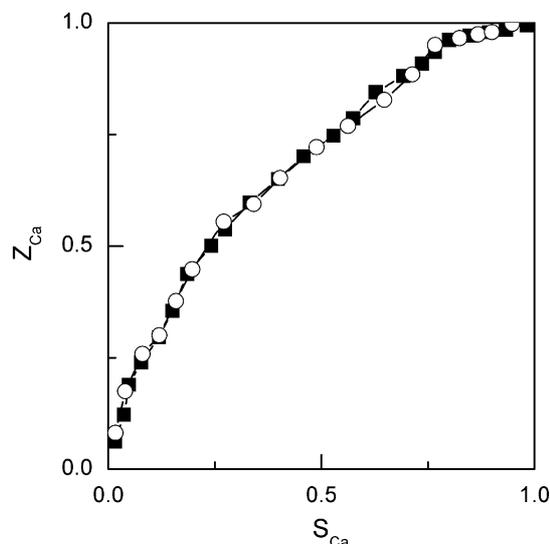


Fig. 3 Na/Ca binary ion-exchange isotherm of 10CA/SBA-15 at 25°C with total normality of 0.1 N. Z_{Ca} and S_{Ca} represent the fractions of Ca^{2+} in the solid phase and solution phase, respectively.

solution. The measurement was repeated twice, and the resulting ion-exchange isotherms are shown in Fig. 3. It shows a selectivity for Ca^{2+} over Na^+ . Since the group density is relatively high, this may be due to a chelating effect of the carboxylate groups. The selectivity for Ca^{2+} is not very pronounced. At low $\text{Ca}^{2+}/\text{Na}^+$ it is much lower than for some zeolites used as water softeners, while at high $\text{Ca}^{2+}/\text{Na}^+$ the selectivity is higher and full exchange can be achieved.

In conclusion, we demonstrate a novel route to synthesize large-pore $-\text{COOH}$ -functionalized SBA-15 with a high density of $-\text{COOH}$ groups that shows high cation-exchange capacity. The template removal *via* ether cleavage as well as the $-\text{CN}$ hydrolysis can be achieved by one-step H_2SO_4 treatment.

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