Macroporous silica–alumina composites with mesoporous walls

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Abstract. Macroporous silica–alumina composites with mesopores have been prepared by employing polymethylmethacrylate beads as templates in the presence of the cationic surfactant, N-cetyl-N,N,N-trimethylammonium bromide. The Si/Al ratio in the composites has been varied between 4.5 and 48 and the occurrence of mesopores has been verified by X-ray diffraction. The surface areas of the samples vary between 676 and 1038 m² g⁻¹, with the highest value in the sample with Si/Al = 48.

Keywords. Macroporous materials; mesoporous materials; silica–alumina composites.

1. Introduction

Macroporous materials of oxides such as TiO₂, SiO₂ (Holland *et al* 1998, 1999) and ferroelectric PbTiO₃ (Gundiah and Rao 2000) are attracting much attention. Macroporous solids with micropores or mesopores would make useful adsorbents or catalyst supports. Recently, Stein and coworkers have reported the synthesis of macroporous silica containing mesoporous walls by treating a solution containing the silica precursor with an aqueous mixture of cetyltrimethylammonium hydroxide and tetrapropylammonium hydroxide and pouring the solution over an ordered array of polystyrene beads (Holland *et al* 1999). We have attempted to make macroporous aluminosilicates containing mesoporous walls. For this purpose we have employed an ordered array of polymethylmethacrylate spheres in the presence of the cationic surfactant N-cetyl-N,N,N-trimethylammonium bromide (CTAB). We describe the macroporous–mesoporous silica–alumina composites with satisfactory/high surface areas.

2. Experimental

Polymethylmethacrylate (PMMA) spheres of diameter 275 nm were obtained from Soken Chemicals, Japan. These were taken as 1% wt : wt in distilled water and sonicated for 30 min to disperse the spheres. This sol was centrifuged at 1000 rpm for 6–8 h. The water above the spheres was removed with a pipette carefully and the spheres were left to dry under ambient conditions. These formed millimeter sized colloidal crystals which were used for further reactions.

The silica–alumina gel was synthesized in the following manner. To a solution of 0.5 g of CTAB in 10 ml H₂O, 0.1 g of Al₂(SO₄)₃·16 H₂O was added and stirred until a

homogenous solution was obtained. 1 ml of tetraethyl-orthosilicate was added to this mixture and the stirring continued. Finally, a few drops of NH₃ (25% solution) were added to make the pH ~ 8. The turbid solution was poured on the colloidal crystals to allow it to percolate through the voids between the spheres. This was left to dry at room temperature. The dried products were calcined at 400°C for 2 h, which resulted in sample A shown in table 1. By a similar procedure, we prepared two other silica–alumina samples (B and C) with different Si/Al ratios.

Powder X-ray diffraction (XRD) patterns of the samples were obtained using CuK α radiation (Rich-Siefert, XRD-3000-TT). Thermogravimetric analysis (TGA) was carried out (Mettler Toledo, TG-850) in flowing oxygen atmosphere (50 ml·min⁻¹) at a heating rate of 10 K min⁻¹. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis were carried out using a Leica scanning electron microscope fitted with EDX spectrometer and a Link ISIS detector. Nitrogen adsorption studies were carried out at liquid nitrogen temperature on these samples using a Cahn-2000 Electrobalance. Solid state MAS NMR measurements were performed on a Bruker DSX-300 MHz Spectrometer. Tetramethylsilane (TMS) and Al(H₂O)₆³⁺ were used as external standards.

3. Results and discussion

Table 1 lists the compositions of the various samples prepared by us. In figure 1a we show the SEM image of the templating PMMA spheres employed by us. The spheres are of uniform diameter and are ordered into arrays. In figure 1b we show the SEM image of sample B after the spheres were treated with the silica–alumina gel, dried and calcined. The networks are fairly well ordered.

The diameter of the pores is slightly smaller (~ 150 nm) than that of the initial PMMA spheres. The shrinkage occurs during the removal of the template during calcination. The SEM image of the samples A and C too were similar to the image in figure 1b. There was no noticeable change in the external morphology on increasing the amount of aluminum in the samples. The SEM images clearly establish the presence of macropores probably connected in three dimensions.

XRD patterns of the as-synthesized and calcined samples are presented in figure 2. The as-synthesized

Table 1. Properties of macroporous $\text{SiO}_2\text{-Al}_2\text{O}_3$ with mesoporous walls.

	Si/Al		d (Å)		Surface area ($\text{m}^2 \text{g}^{-1}$)
	Gel	Product	As-synth.	Calcined	
A	18.5	48.0	38.94	35.60	1038
B	12.4	15.3	35.26	32.64	804
C	9.3	4.5	38.15	33.52	676

Figure 1. a. SEM image of PMMA spheres of 275 nm diameter and b. SEM image of sample B after removal of the templates.

samples of A, B and C show single peaks with d -values 38.94, 35.26 and 38.15 Å respectively. The low-angle peak is similar to that shown by hexagonal mesoporous solids. There is a decrease in the d -value after calcination due to removal of template CTAB molecules, d -values being 35.5, 32.64 and 33.52 Å respectively for A, B and C. The presence of the low angle peak after calcination indicates that the mesoporous phase is reasonably intact after removal of the template. We know of three materials, A, B, and C, which are macroporous-mesoporous.

TGA curves of the aluminosilicates A and C are shown in figure 3. The as-synthesized samples show a single weight loss from 250–350°C due to the loss of the PMMA and CTAB templates. The weight loss above 350°C is due to the condensation of the silanol that occurs after 350°C. The TGA curve for the calcined samples show a single weight loss corresponding to the adsorbed water. The amount of template removed was calculated to be above 95%.

We performed MAS NMR studies to determine the coordination of aluminium and silicon in the framework. ^{29}Si MAS NMR of the as-synthesized sample A showed two broad peaks at -101 and -110 ppm corresponding to the Q^3 and Q^4 species respectively. The intensity of the Q^3 species was greater than the Q^4 species indicating that the silanol groups had not condensed fully. On calcination, the relative intensity of the Q^4 species increased, showing

Figure 2. XRD patterns of the as-synthesized and calcined samples A, B and C.

Figure 3. TGA curves of the aluminosilicate samples A and C.

that on calcination the silanol groups condense to form Si–O–Si species. ^{27}Al MAS NMR of the calcined sample A showed a large narrow peak at -7 ppm corresponding to octahedrally coordinated aluminium species and a very small, broad feature centred at 46 ppm due to tetrahedrally coordinated aluminium. On integrating these peaks, the areas under the peaks were found to be in the ratio of $1 : 0.2$ of the octahedral to the tetrahedral species. It appears only 20% of the Al is present in the framework. Most of the Al is therefore present as Al_2O_3 in composite form with SiO_2 . This is because of the limitation due to the pH and temperature employed in the preparation. We may therefore consider A, B, and C as composites of SiO_2 and Al_2O_3 with a small proportion of aluminosilicate. Even though the amount of aluminium in the framework is small, the composite materials that we have made have macroporous–mesoporous characteristics described earlier.

Nitrogen adsorption isotherms of the samples A, B and C are presented in figure 4. These are typical type IV isotherms characteristic of mesoporous materials. The isotherms exhibit little or no hysteresis, showing thereby that the pores may not be very ordered. The surface areas

Figure 4. Nitrogen adsorption isotherms for samples A, B and C. The dark circles represent the adsorption cycle and the open circles represent the desorption cycle.

calculated by the BET method are in the range of 676 – $1038 \text{ m}^2 \text{ g}^{-1}$ for the three samples. There is a decrease in the surface area with the increasing aluminum content, consistent with the observations of Janicke *et al* (1999), who observed that the surface areas decrease as we decrease the Si/Al ratios.

4. Conclusions

We have demonstrated the synthesis of macroporous aluminosilicates containing mesoporous walls. Though the amount of aluminium in the framework is small, the presence of macropores as well as mesopores makes these composites suitable as catalyst supports. The presence of macropores would aid in the diffusion of species to the active sites of the catalyst. The study opens up scope for preparing macroporous–mesoporous structures by doping other transition metals such as Ti, V, Cr, etc into the silica framework. The only limiting factor is that the reaction

has to be carried out at a temperature below which the template decomposes.

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