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Synthesis of a large pore phenyl-modified mesoporous silica and its characterization by nitrogen and benzene sorption†

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Phenyl-modified porous silicas have been synthesized at room temperature by the co-condensation of a siloxane and an organosiloxane in the presence of a surfactant. Mesitylene was employed as a pore swelling agent to produce a mesostructured material. The product has been characterized by powder XRD, nitrogen sorption at 77 K and benzene sorption at 293 K. Powder XRD data yielded a d_{100} spacing of 52.0 Å for the as-synthesized material and 49.5 Å after template removal. Nitrogen sorption is characterized by a type IV isotherm indicating mesoporosity with a BET specific surface area of 942 m^2 g^{-1} and a Gurvitsch pore volume of 0.67 cm^3 g^{-1}. Benzene sorption also produced a type IV isotherm with a BET specific surface area of 1051 ± 50 m^2 g^{-1} and a Gurvitsch pore volume of 0.75 cm^3 g^{-1}. The discrepancy in the total pore volume values may be due to the structure of the adsorbed benzene. Samples produced in the presence of tetradecane or in the absence of any pore swelling agent have pores in the microporous range.

Since the synthesis of the mesoporous aluminosilicates designated M41S (by researchers at Mobil Research and Development Corporation in 1992),[1] research in this area has concentrated on the use of these materials in catalysis. Early attempts to incorporate catalytically active guest species in the channels of MCM-41 resulted in low guest loadings probably due to the absence of specific interactions between host and guest. The use of organically functionalized mesoporous materials may alleviate this problem and the synthesis of hybrid inorganic–organic mesoporous silicas has recently been reported.[2] A phenyl-modified MCM-41 type material was synthesized at room temperature by the hydrolysis and co-condensation of a siloxane and organosiloxane in the presence of a surfactant. Nitrogen, water vapour and benzene sorption studies[3] carried out on that material indicated that it was microporous (average pore diameter *ca.* 20 Å), suggesting that the incorporation of phenyl groups resulted in a reduction in pore diameter.

One of the most desirable characteristics of unmodified MCM-41 is that its pore diameter can be tailored in the mesoporous range thus making the material suitable for the catalysis of large organic molecules. In one of the original papers by the Mobil group,[4] mesitylene was used as a solubilizing agent to swell the pores of MCM-41. Beck *et al.*[4] demonstrate that when a mesitylene/surfactant molar ratio of 2.5 is employed an increase in the pore diameter of *ca.* 20 Å is observed. In this study, a mesitylene/surfactant molar ratio of 6 was employed in order to produce a solid with pores large enough to accommodate structural phenyl groups while retaining pore diameters in the mesoporous range. Ulagappan and Rao[5] report the use of straight chain alkanes as pore-swelling agents and demonstrate that when an alkane/surfactant molar ratio of 1 is employed an increase in pore diameter is observed when using *n*-alkanes containing up to 14 carbons. Indeed, the increase in pore diameter expected if the lengths of the alkane chain and surfactant tail were to be additive in the formation of the micelle template is observed. In this study, tetradecane was therefore employed in a 1 : 1 molar ratio with the surfactant. We now report the synthesis and characterization of a phenyl-modified porous silica using mesitylene and tetradecane as auxiliary organics to produce a mesostructured material.

Experimental

Materials

Silica sources were tetraethoxysilane, 98% (TEOS, Aldrich) and phenyltriethoxysilane, 98% (PTES, Lancaster). The quaternary ammonium surfactant used as the templating agent was a 25 mass% aqeous solution of cetyltrimethylammonium chloride, $C_{16}H_{33}(CH_3)_3NCl$ (CTMACl, Aldrich). The auxiliary organics used as pore swelling agents were mesitylene, 98+% (Lancaster) and tetradecane, 99+% (Aldrich). All chemicals were used as received.

Syntheses

Mesoporous phenyl-modified silicas, containing 20 mol% PTES in the original synthesis composition, were prepared at room temperature. The preparations of mesitylene-swollen, tetradecane-swollen and an unswollen material are reported below.

Unswollen phenyl-modified silica. CTMACl solution (2.4 cm^3, 25 mass%) was added to a solution of 8 g of NaOH(aq) (1.0 mol dm^{-3}) in 28 g H_2O; 2.8 cm^3 TEOS and 0.8 cm^3 PTES were then added and the solution was stirred, open to the atmosphere, at room temperature for 48 h. The white solid product was recovered by filtration, washed with deionized water and dried in an oven at 100 °C. Surfactant extraction was performed by stirring a suspension of the as-synthesized product in HCl in EtOH (1.0 mol dm^{-3}) at 70 °C for 24 h. The extracted material was recovered by filtration, washed with ethanol and dried *in vacuo* at 100 °C.

Mesitylene-swollen phenyl-modified silica. The above procedure was repeated, but with addition of 1.5 cm^3 of mesitylene to the reaction mixture following addition of the siloxane.

Tetradecane-swollen phenyl-modified silica. The above procedure was repeated, but with addition of 0.47 cm^3 of tetradecane to the reaction mixture following addition of the siloxane.

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Instrumentation

Powder X-ray diffraction data were obtained on a computer-driven step-scanning diffractometer with a Philips PW1050/25 goniometer and using Cr-Kα radiation, ($\lambda = 2.29$ Å). Data were collected at every 0.1° of 2θ (dwell time = 4 s) and diffraction profiles were transferred to a personal computer for further analysis.

^{29}Si direct polarisation (DP) MAS NMR spectra were recorded at 59.582 MHz (spin rate = 4.8 kHz, pulse angle = 90°) on a Varian Unity 300 instrument fitted with a Doty MAS probe. A relaxation delay of 300 s was employed.

Nitrogen sorption was realized at 77 K using an automated Micromeritics Gemini 2375 Surface Area and Porosimetry Analyzer. The sample was purged of physisorbed vapour using the Micromeritics Flowprep 060 at 373 K under flowing N_2(g) for 6 h prior to analysis.

Benzene sorption at 293 K was performed using a McBain–Bakr gravimetric balance built in-house (University of Exeter). A water-cooled oil diffusion pump backed up by a two-stage rotary oil pump was used to attain pressures of *ca.* 1×10^{-3} Pa. The sample was outgassed at 373 K under vacuum for several hours to remove physisorbed vapour prior to adsorption. The adsorptive was exposed to three 'freeze–pump–thaw' cycles to remove dissolved gases before sorption studies. For each data point on the isotherm the sample was exposed to the adsorptive and allowed to reach equilibrium. Equilibrium was defined as the point at which no further drop in pressure and no further increase in the mass of the sample was observed (the time taken to reach equilibrium was generally 1–3 h).

Results and Discussion

Powder X-ray diffraction data (Table 1) indicate that a single phase is formed for both the swollen and unswollen materials. Following template removal, structural order is maintained and a small degree of lattice contraction is observed. It is evident from the XRD data that the addition of mesitylene as an auxiliary organic increases the d_{100} spacing, which is directly related to pore diameter. In contrast, the addition of tetradecane does not result in an increase in d-spacing suggesting that tetradecane is not a suitable pore-swelling agent for the formation of phenyl-modified mesostructured silica.

^{29}Si DP MAS NMR spectra of the mesitylene-swollen sample before and after template removal (Fig. 1) display distinct peaks due to the siloxane [$Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2$–4] and due to the organosiloxane [$T^m = RSi(OSi)_m(OH)_{3-m}$, $m = 1$–3] (Table 2). Q^2 and T^1 resonances are observed only after template removal. (A.S. spectrum was adequately modelled by a decomposition involving four Gaussian components.)

Nitrogen sorption results are given in Table 1. The type IV isotherm (Fig. 2) given by the mesitylene-swollen sample displays a small degree of hysteresis and indicates that the sample is mesoporous. Both the unswollen and tetradecane-swollen samples yield isotherms exhibiting type I characteristics (Fig. 3), indicating that the products are microporous.

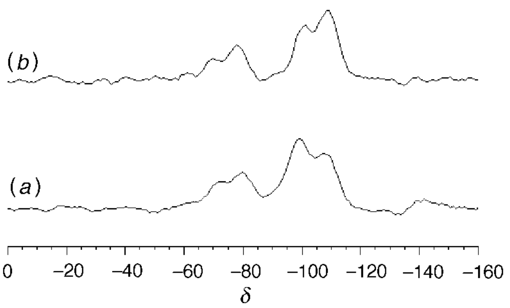

Fig. 1 ^{29}Si DP MAS NMR spectra of MES-swollen phenyl-modified mesoporous silica (*a*) as-synthesized and (*b*) after template removal

Table 1 Powder XRD and nitrogen sorption data for phenyl-modified mesoporous silicas: as-synthesized (A.S.) and after template removal (S.E.)

			nitrogen sorption		
swelling agent		XRD d_{100}/Å	isotherm type	BET surface area /$m^2\ g^{-1}$	Gurvitsch pore volume /$cm^3\ g^{-1}$
mesitylene	A.S.	52.0	—	—	—
	S.E.	49.5	IV	942	0.67
tetradecane	A.S.	37.5	—	—	—
	S.E.	32.0	I	760	0.42
unswollen	A.S.	37.5	—	—	—
	S.E.	36.0	I	990	0.50

Table 2 ^{29}Si DP MAS NMR data for MES-swollen phenyl-modified mesoporous silica: as synthesized (A.S.) and after template removal (S.E.)

	δ^a					
	T^1	T^2	T^3	Q^2	Q^3	Q^4
A.S.	—	−70.6	−79.7	—	−98.8	−108.9
S.E.	−61.6	−69.8	−78.2	−92.0	−100.3	−109.0

^{a}TMS as external reference.

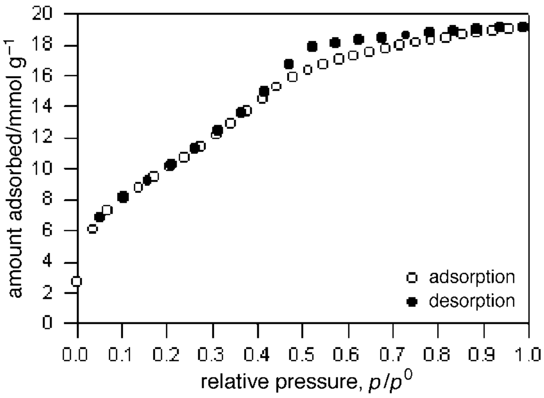

Fig. 2 Nitrogen sorption at 77 K on MES-swollen phenyl-modified silica

The final plateau of the nitrogen isotherm gives a Gurvitsch pore volume of 0.67 $cm^3\ g^{-1}$ for the mesitylene-swollen sample, which is a considerably higher value than that obtained on the Burkett material (0.45 $cm^3\ g^{-1}$)[3] and on the tetradecane-swollen and unswollen materials (Table 1).

Benzene sorption carried out on the mesitylene-swollen sample also yielded a type IV isotherm (Fig. 4) exhibiting H2 hysteresis,[6] confirming the sample's mesoporosity. A BET specific surface area of $1051 \pm 50\ m^2\ g^{-1}$‡ was obtained. Problems arise in the calculation of surface areas when using benzene, because of the inability to assign an accurate value to the cross-sectional area, a_m, of the benzene molecule. The area of the surface occupied by the benzene molecule is dependent on whether the molecule is lying flat or is oriented perpendicular to the surface. In this study the value of $a_m(C_6H_6) = 43$ Å^2 (recommended by McClellan and Harnsberger[7]) has been employed. Application of the Gurvitsch rule to the benzene isotherm gave a total pore volume of 0.76 $cm^3\ g^{-1}$, once again significantly larger than that obtained from benzene sorption on the original Burkett material

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‡ Uncertainty arises from the error margin of ± 3 Å^2 assigned to the molecular area of benzene by McClellan and Harnsberger.[7]

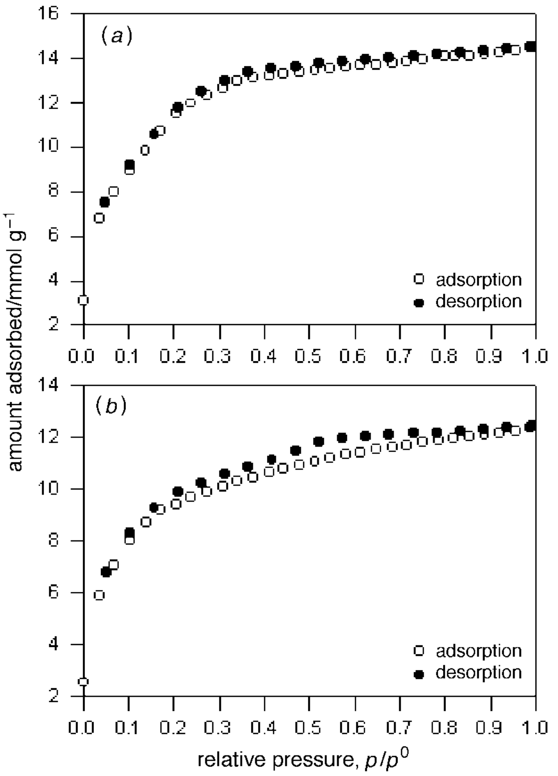

Fig. 3 Nitrogen sorption at 77 K on (*a*) unswollen and (*b*) TET-swollen phenyl-modified silica

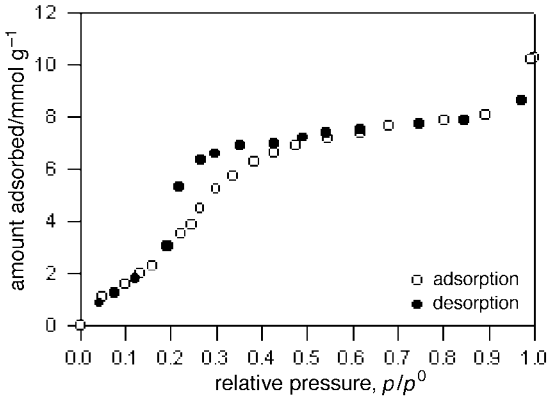

Fig. 4 Benzene sorption at 293 K on MES-swollen phenyl-modified silica

(0.31 cm^3 g^{-1}).[3] The discrepancy in the values of the total pore volumes obtained from the nitrogen and benzene isotherms is probably due to the structure of the adsorbed benzene.

If the Kelvin equation is applied to the benzene isotherm at the inception of hysteresis ($p/p^0=0.2$), a Kelvin pore diameter, $2r_k$, of 26 Å is obtained. It should be noted that this is not a true pore diameter, d, as a value for the thickness of the adsorbed benzene monolayer, t, is not available [$d=2(r_k+t)$].[8] In reality, the pore diameter of this material is likely to fall in the range 30–40 Å, well within the mesoporous regime. The value of the Kelvin pore diameter obtained from the characteristic type IV benzene isotherm combined with the total pore volume values and the XRD data, confirms that by using mesitylene as a solubilizing agent it is possible to produce a mesoporous phenyl-modified silica. In contrast, in the absence of any solubilizing agent, or in the presence of tetradecane, phenyl-modified silicas with pore diameters in the microporous range are produced.

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