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Effect of the porosity and relative surface hydrophobicity of MCM-41 materials on the adsorption of [60]fullerene at the solid/toluene interface: comparison of Al- and Zr-doped silicates with the purely siliceous sample

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The adsorption of [60]fullerene from toluene on three MCM-41 type materials: purely siliceous, aluminosilicate and zirconiosilicate, is thought to occur primarily on the pore walls, and differences in the amount adsorbed between the three samples can be ascribed to the different size, volume and surface area of their pores rather than to the different hydrophobic character of their surfaces.

In spite of numerous theoretical and experimental studies on the physical and chemical characteristics of MCM-41 type mesoporous solids over the past five years, their interfacial properties have received much less attention. In view of their potential applications in selective catalysis and adsorption, it is necessary to describe the porous structure and hydrophilic–hydrophobic character of the MCM-41 materials prepared using different synthesis routes and incorporating (or not) heteroatoms in the silica matrix. In this paper the results of butanol adsorption from water and nitrogen gas adsorption–desorption measurements on three MCM-41 samples are reported in order to describe the porosity and hydrophobic character of their surfaces. These studies have been supplemented by X-ray diffraction and ^{27}Al MAS NMR spectroscopy. These properties are used to explain the adsorption of C_{60} fullerene at the solid/toluene interface.

The three MCM-41 samples were synthesized as follows. (1) Purely siliceous SiC14, prepared using Beck's method[1] using 45 g of deionised water; 14 g of sodium silicate solution, Na_2O 7.5–8.5%, SiO_2 25.5–28.5%, (Merck); 46.6 g (25 mass% solution) of *n*-tetradecyltrimethylammonium bromide (Lancaster); 0.9 g of 96% sulfuric acid (Carlo Erba). (2) Aluminosilicate SiAl29C14, prepared according to Klinowski and co-workers[2] using 50 g of deionised water; 5.9 g of sodium silicate solution (Merck); 4.5 g of fumed silica Cab-O-Sil M5; 35.9 g (25 mass% solution) of *n*-tetradecyltrimethylammonium bromide (Lancaster); 10 g of tetramethylammonium hydroxide, 25 mass% solution (Aldrich); 96% sulfuric acid (Carlo Erba); Amberlite IRA-420C strongly basic ion exchanger (Sigma); 0.42 g of aluminium sulfate. (3) Zirconiosilicate SiZr25C14, synthesised using the method developed by Maireles-Torres and co-workers[3] using 18.7 g of tetraethoxysilane 98% (Aldrich); 1.7 g of zirconium(IV) propoxide, 70 mass% solution in propan-l-ol (Aldrich); 5 ml of tetraethylammonium hydroxide 35 mass% solution in water (Aldrich); 15.1 g of *n*-tetradecyltrimethylammonium bromide (Lancaster); 26.1 ml of ethanol; 6.7 ml of *n*-propanol.

In syntheses (2) and (3) SiX*m*C14, *m* represents the atom ratio Si/X where X = Al, Zr. C14 indicates the 14 carbon atoms of the surfactant tail used in the synthesis.

An automated Philips diffractometer with Cu-Kα radiation was used to acquire X-ray powder diffraction data. X-Ray diffraction patterns of as-synthesised and calcined samples showed two or three peaks, which could be indexed in the hexagonal system. The unit cell parameter was calculated using $a_0 = 2d_{100}/\sqrt{3}$.[1] It is clear that the addition of aluminium and zirconium does not greatly affect this parameter.

^{27}Al MAS NMR spectroscopy of SiAl29C14 gave a signal at 53 ppm in both as-synthesised and calcined samples, indicating the presence of four-coordinate aluminium only.

Nitrogen adsorption–desorption measurements were performed on all calcined samples using an automated volumetric apparatus (Sorptomatic 1800) at 77 K. The isotherms are of type IV according to the IUPAC classification, do not exhibit hysteresis loops, and have a well marked capillary condensation step, indicating that the pore size distribution is very homogeneous in each case. The nitrogen adsorption isotherms served as a basis for determining some important parameters of the materials synthesised, including BET specific surface area (S_{BET}), pore surface area (S_{pore}), external surface area (S_{ext}), pore volume (V_{pore}), and the most probable pore diameter (d). The methods applied have been described previously.[4] These results are collected in Table 1. All the MCM-41 type materials prepared have high surface areas and the effective diameter of their pores is in the mesoporous size range.

Flow microcalorimetry was used to measure the enthalpy of butanol adsorption from water. Details of the experiment have been given elsewhere.[5] Adsorption from solution is known to have a competitive character. When adsorbed from water, the butanol molecules will be retained on the surface because their hydrophobic moieties are expelled from an aqueous environment and simultaneously attracted by the non-polar (hydrophobic) sites in the solid surface. The oncoming alcohol

Table 1 Interfacial properties of the MCM-41 materials

	SiC14	SiAl29C14	SiZr25C14
$S_{BET}/m^2\ g^{-1}$	761	1029	979
$S_{ext}/m^2\ g^{-1}$	116	11	13
$S_{pore}/m^2\ g^{-1}$	583	999	939
$V_{pore}/cm^3\ g^{-1}$	0.59	0.83	0.78
d/nm	2.8	3.3	2.8
a_0/nm	4.0	4.1	4.1
$\Delta_{dpl}H/mJ\ m^{-2}$	5.2	2.0	2.8
$\Gamma_{ads}/\mu mol\ g^{-1}$	2	11	3
$\Gamma_{des}/\mu mol\ g^{-1}$	−2	−10	−3

$\Delta_{dpl}H$ = integral molar enthalpy (per unit surface area of the adsorbent) of adsorption of *n*-butanol from water using a $10\ g\ l^{-1}$ solution at 298 K; Γ_{ads} = amount of C_{60} adsorbed on the adsorbent surface from $0.7\ mmol\ l^{-1}$ toluene solution at 298 K; Γ_{des} = amount of C_{60} desorbed from the adsorbent surface by the adsorbing toluene molecules at 298 K.

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molecules will displace interfacial water. The butanol concentration used in the study corresponds to the formation of a monolayer on the hydrophobic part of the MCM-41 surface. Therefore, the integral enthalpy of displacement per unit surface area, *i.e.*, $\Delta_{\text{dpl}}H$, is proportional to the surface area of hydrophobic sites in the MCM-41 materials. The relative hydrophobicity decreases in the order SiC14 > SiZr25C14 > SiAl29C14. For SiC14, the relative hydrophobicity is about twice that of the samples doped with Al or Zr. The presence of Al or Zr species in the silicate structure is reported to induce the formation of Lewis acid sites.[2,3] The increased Lewis acidity of SiZr25C14 and SiAl29C14 compared with SiC14 causes the percentage of polar surface sites in the first two adsorbents to increase and, consequently, the number of butanol molecules adsorbed from water to be greatly reduced. As a result, the relative surface hydrophobicity decreases.

The same flow microcalorimeter equipment was used to determine the adsorption of C_{60} fullerene from a toluene solution. Previously reports have described the inclusion of [60]fullerene (C_{60}) in siliceous MCM-41 by sublimation of the former at 873 K under vacuum[6] and, unusually, grinding together of the two components.[7] The possibility of loading aluminophosphates with C_{60} from the liquid and gas phases has also been studied.[8] Here, the amount of C_{60} adsorbed was determined using an on-line UV detector at $\lambda = 404$ nm. The results are presented in Table 1. Fullerene adsorption seems to be reversible, but the amounts adsorbed are generally very small. However, there are pronounced differences in the amount adsorbed between the three samples, SiAl29C14 giving by far the greatest adsorption value. Using the BET specific surface area of each MCM-41 sample, the average surface area available to each adsorbed C_{60} molecule can be calculated. The following values have been obtained: SiC14, 634 nm^2; SiZr25C14, 580 nm^2; and SiAl29C14, 156 nm^2. These values are far from the 0.8 nm^2 which was determined from the projection of a C_{60} molecule in a hexagonal close-packed arrangement onto a flat surface.[5] Clearly, only a very small proportion of the total MCM-41 surface is occupied by the adsorbing C_{60} molecules under the dynamic conditions used. It is of interest to consider which part of the solid surface is responsible for C_{60} adsorption and, here, the different relative external and pore surface areas of the three samples are of use. The external surface area of SiC14 is about one order of magnitude greater than those of the other two solids. If the adsorption had been limited only to the external surface, SiC14 would have adsorbed many more C_{60} molecules than the others. On the contrary, this sample gives the lowest level of adsorption. Furthermore, this difference cannot be explained by the different hydrophobic character of the MCM-41 surfaces because SiAl29C14 and SiZr25C14, which have almost the same relative hydrophobicity, have very different adsorption affinities for C_{60}. It is more reasonable to relate such behaviour to different accessibility of the MCM-41 porous structure to C_{60} adsorption. The two materials having smaller pore sizes adsorb fewer C_{60} molecules, inferring that adsorption seems to occur mainly on the internal surface. Between these two samples, the amount adsorbed obtained with SiC14 is the smallest because this support has the lowest pore volume and surface area of the samples studied. The nature of active sites in the MCM-41 surface relevant to the phenomenon is still not clear and some additional studies are necessary. In particular, C_{60} adsorption and desorption at different bulk concentrations are currently being determined and compared with the related enthalpy effects. The results will be reported subsequently.

References

1 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppart, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.

2 Z. Luan, C. F. Cheng, W. Zhou and J. Klinowski, *J. Phys. Chem.*, 1995, **99**, 1018.

3 D. J. Jones, J. Jiménez-Jiménez, A. Jiménez-Lopez, P. Maireles-Torres, P. Olivera-Pastor, E. Rodriguez-Castellon and J. Rozière, *Chem. Commun.*, 1997, 431.

4 M. J. Meziani, J. Zajac, D. J. Jones, J. Rozière and S. Partyka, *Langmuir*, 1997, **13**, 5409.

5 J. Zajac and A. J. Groszek, *Carbon*, 1997, **35**, 1053.

6 F. Rachdi, L. Hajji, C. Goze, D. J. Jones, P. Maireles-Torres and J. Rozière, *Solid State Commun.*, 1996, **100**, 237.

7 J. Chen, Q. Li, H. Ding, W. Pang and R. Xu, *Langmuir*, 1997, **13**, 2050.

8 A. Gügel, K. Müllen, H. Reichert, W. Schmidt, G. Schön, F. Schüth, J. Spickermann, J. Titman and K. Unger, *Angew. Chem., Int. Eng. Engl.*, 1993, **32**, 556.

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