Ozone treatment for the removal of surfactant to form MCM-41 type materials

Matthew T. J. Keene, Renaud Denoyel and Philip L. Llewellyn*

Centre de Thermodynamique et de Microcalorimétrie du CNRS, 26 rue du 141ème RIA, 13331 Marseilles, cedex 3, France.
E-mail: pllew@ctm.cnrs-mrs.fr

Ozone has been used to remove the organic surfactant species at 250 °C from as synthesised organic/inorganic composite (or mesophase) materials to form mesoporous MCM-41 type solids with higher surface area, larger pores and narrower pore size distribution than those obtained by conventional calcination at 550 °C.

The relatively large interest of MCM-type mesoporous materials that has arisen since 1992[1,2] lies in the fact that they can be tailored to form pores of narrow distribution, from 2 to 10 nm. This opens up a field of fundamental and applied science where a narrow mesopore size distribution and high surface area could be required. Surprisingly for these tailor-made materials where a control of the pore size can be important, a limited number of studies have been published concerning the specific removal of organic material from the as synthesised organic/inorganic composite or mesophase.[3–6] In effect, the removal of the 'templating' surfactant molecules, occluded within this material during the synthesis, is quite often carried out by thermal methods. Commonly, a heating ramp of 1 °C min^{-1} up to a plateau temperature of 550 °C in air is used.[1,2] However, methods such as plasma and supercritical fluid extraction[3] are other possible means to remove this organic material. Several studies have also used washing or ionic exchange of the surfactant.[4–7]

Ozone, is commonly used as a treatment in numerous applications ranging from environmental technology (*e.g.* ozone in water treatment[8]) to physics (*e.g.* cleaning of polished flat surfaces). To date, however, ozone treatment has not been used to eliminate organic species from porous materials. For microporous materials such as zeolites, the elimination of the organic template could be hampered by the steric hindrance of the micropores themselves. This is not the case for slightly larger pores where the elimination of the organic moieties from the pores is hindered to a far lesser extent. The present preliminary study has used ozone at room temperature to remove the organic surfactant to form mesoporous MCM-41 type materials.

The silica mesophase was prepared using the synthesis outlined by Grün *et al.*[9] This particular synthesis route uses tetraethoxysilicate as the silica source and is carried out at 25 °C. The surfactant used was cetyltrimethylammonium bromide (CTABr). After filtering and washing in distilled water, the sample was dried in air at 20 °C overnight. For comparison, part of the sample was calcined under a nitrogen flow, at a heating rate of 1 °C min^{-1}, up to a 550 °C plateau for 4 h. For the ozone treatment, around 0.1 g of sample was placed on a watch glass which was then placed for 24 h under a UV lamp (electrical power 20W : UV power 6.8 W at 254 and 180 nm) whose wavelength is known to create ozone from atmospheric oxygen. To verify the effect of the UV light on the sample, a separate sample was treated by a flow of gaseous ozone produced by an electric arc. Both samples showed similar results on further characterisation. The sample was characterised by X-ray diffraction (Fig. 1), DRIFT (Fig. 2) and argon adsorption manometry at 77 K (Fig. 3). The ozone treated sample was also treated by thermogravimetry up to 1000 °C that showed a 1% weight loss, essentially from silanol condensation forming water.

The XRD patterns shown in Fig. 1 are typical for hexagonal mesoporous materials. For the ozone treated sample, the d_{100} spacing of 4.15 nm is surprising in that it is the same as that found in the initial mesophase. Normally, thermal extraction and ion exchange of the template leads to an appreciable shrinkage of the structure of up to 25%.[4] This is illustrated in the lower pattern obtained for a traditionally calcined sample with a d_{100} spacing of 3.67 nm.

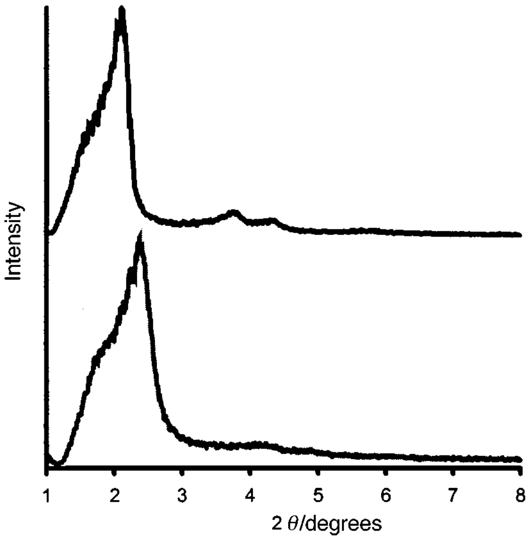

Fig. 1 X-Ray powder diffraction patterns of an ozone treated sample (upper curve) and a sample calcined to 550 °C (lower curve)

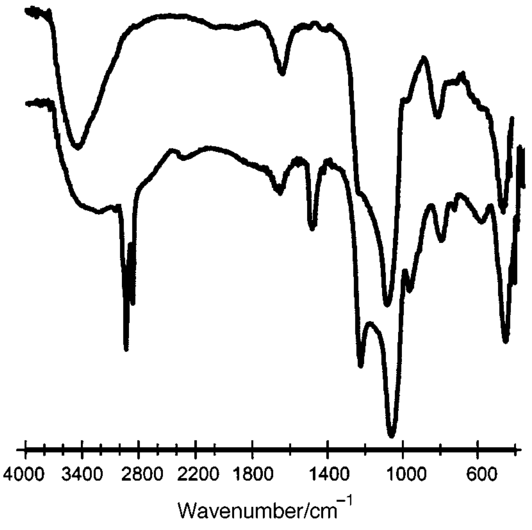

Fig. 2 DRIFT spectra of an ozone treated sample (upper curve) and original mesophase (lower curve)

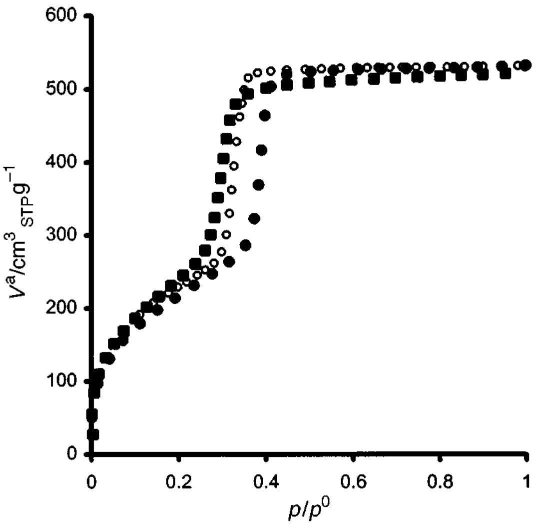

Fig. 3 Argon adsorption–desorption isotherm obtained at 77 K for (i) an ozone treated sample: (●) adsorption, (○) desorption, and (ii) a sample calcined at 550 °C: (■) adsorption

The IR spectrum of the silica mesophase before ozone treatment (lower curve, Fig. 2) clearly shows the peaks resulting from C–H stretching (2924 and 2854 cm^{-1}) as well as a broad signal (3600–3200 cm^{-1}) assigned to hydrogen bonded Si–OH groups.[10] After ozone treatment (upper spectrum, Fig. 2), the C–H peaks are no longer observed whereas a large signal assigned to hydrogen bonded Si–OH persists.

The argon adsorption isotherms at 77 K obtained with the ozone treated sample (circles) and a traditionally calcined sample (squares) (Fig. 3) are both of type IV character[11] and show distinct capillary condensation steps. The capillary condensation step obtained with the ozone treated sample is in reality sharper and slightly higher in relative pressure (p/p^0 = 0.37 compared with 0.30) than that obtained for a sample calcined using a standard thermal treatment. This would seem to indicate that a larger pore size and a narrower pore size distribution can be obtained for MCM41 using ozone treatment. The *t*-plot analysis shows that there are no micropores and relatively little external surface area (*ca.* 25 m^2 g^{-1}) when compared to the calcined sample (*ca.* 40 m^2 g^{-1}). The argon BET surface area obtained is 710 m^2 g^{-1} for the ozone treated sample, which is similar for the same sample calcined using a standard treatment. Using the geometric formula for the diameter $d = 4V/A$, leads to a pore diameter of 3.6 nm for the ozone treated material.

These results highlight that for mesoporous materials, such as MCM-41, treating by ozone could prove interesting from several points of view. First of all, such treatment is relatively strightforward, as a simple UV lamp can be used. Secondly, it could be envisaged that samples *in situ* can be treated after the synthesis of the mesophase. That is to say that, the elimination of the organic template can be possible within the synthesis medium limiting the total number of synthesis steps required. Thirdly, the ozone treatment is carried out at room temperature, although the temperature reached within the pores themselves could be higher. For this reason ozone treatment could prove well adapted to materials with a fragile structure where, for example, the nature of metal species occluded within the walls during synthesis could be altered on thermal treatment. Finally, this ozone treatment is a clean technology for the removal of organic species as the majority of products formed are thought only to be water and carbon dioxide. However, questions remain of in what forms the nitrogen and bromine are eliminated from the pores. From these points of view ozone treatment could prove more cost effective with respect to thermal treatment for the removal of organic species from these materials.

The authors would like to thank Dr J. Blanchard at the University of Frankfurt for the XRD spectra and the EC TMR program (ERB FM RX CT 960084) for financial support of M. T. J. K.

Notes and References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 J. S. Beck, J. C. Vartulli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3 S. Kawi and M. W. Lai, *Chem. Commun.*, 1998, 1407.
4 C.-Y. Chen, H.-X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 17.
5 R. Schmidt, D. Akporiaye, M. Stöcker and O. H. Ellestad, *Stud. Surf. Sci. Catal. A*, 1994, **84**, 61.
6 S. Hitz and R. Prins, *J. Catal.*, 1997, **168**, 194.
7 P. T. Tanev and T. J. Pinnavaia, *Chem. Mater.*, 1996, **8**, 2068.
8 S. E. Manahon, *Environmental Chemistry*, Willard Grant Press, Boston, 3rd edn., 1979, ch. 8.
9 M. Grün, I. Lauer and K. Unger, *Adv. Mater.*, 1997, **9**, 254.
10 X. S. Zhao, G. Q. Lu, A. K. Whittaker, G. J. Millar and H. Y. Zhu, *J. Phys. Chem. B*, 1997, **101**, 6525.
11 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.

Received in Bath, UK, 4th August 1998; 8/06118A