Synthesis of a mesoporous MCM-48 material containing only tetrahedral aluminium

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A mesoporous MCM-48 is synthesised with an Si : Al ratio of 22, without observing octahedral aluminium in its as-synthesised form or after template removal by calcination at 540 °C.

The discovery of a new class of ordered mesoporous materials with pore sizes in the range 2–10 nm denoted as M41S materials by researchers of the Mobil Oil Company[1,2] has initiated an intensive research effort resulting in a significant number of publications. Hereby the main research effort has been concentrated on the member of the M41S class of materials having unidimensional hexagonal organised pores, denoted as MCM-41. Besides the systematic investigation of the synthesis of MCM-41 materials,[2–4] its application as model material for adsorption and pore-size determination studies,[5–8] the study of the incorporation of metal ions, *e.g.* trivalent aluminium,[9–11] and its subsequent use as catalysts for different catalytic applications were the major points of interest. In addition, Mobil researchers reported in their first papers[1,2] that another purely siliceous member of the M41S class of materials, MCM-48, having a regular three-dimensional pore system, could be prepared by using the same synthesis principles. However, until now only a very limited number of publications dealing with MCM-48 have been reported,[3,12–14] compared to the large number of papers dealing with MCM-41. For MCM-48 to be useful in respect to catalytic applications, it is essential to incorporate metal ions, *e.g.* trivalent aluminium, into the siliceous framework. Until now only Zhao and Goldfarb[13] have reported the synthesis of an Al-containing MCM-48 (Si/Al ratio of 46) without, however, stating the details of the synthesis conditions or reporting any characterisation data of this material.

We report here on the synthesis of a mesoporous MCM-48 material with an Si : Al ratio of 22 without observing any octahedral aluminium before or after the removal of the template by calcination at 540 °C.

The synthesis mixture was prepared using tetraethylorthosilicate [$Si(OEt)_4$, 98%, Aldrich], aluminium sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$, 99.4%, BDH Laboratory Supplies], hexadecyltrimethylammonium bromide ($C_{16}H_{33}Me_3NBr$, 98%, Fulka) and sodium hydroxide (NaOH, 98%, Eka Nobel). A gel with the following molar composition was prepared; $60\ SiO_2 : 1\ Al_2O_3 : 24.6\ C_{16}H_{33}Me_3NBr : 19.2\ Na_2O : 6000\ H_2O$.

The synthesis procedure was as follows: tetraethylorthosilicate (21.3 g) was added to a solution containing $C_{16}H_{33}Me_3NBr$ (14.9 g), NaOH (2.48 g) and H_2O (180.2 g), which was temperature equilibrated at 36 ± 1 °C. After 5 min stirring in a 500 ml beaker at 500 rpm, $Al_2(SO_4)_3 \cdot 18H_2O$ (1.1 g) was added, and the gel was stirred for another 55 min. The resultant gel was then loaded into a stoppered Teflon bottle and heated without stirring for 72 h at 100 °C. After cooling to room temperature the solid product was recovered by filtration, washed extensively with distilled water and dried at ambient temperature. Part of the material was calcined at 540 °C for 1 h in a flow of N_2 followed by 6 h in air (flow rates = 100 ml min^{-1}): a heating rate of approximately 10 °C min^{-1} was applied.

The powder X-ray diffraction patterns of the resultant as-synthesised and calcined materials are presented in Fig. 1 and correspond well to those reported for a purely siliceous MCM-48[3,12] and are consistent with an $Ia\bar{3}d$ cubic symmetry of the material, as found for the purely siliceous MCM-48.[3,12] Assuming this cubic symmetry the unit-cell size (*a*) was calculated to be 9.7 ± 0.05 nm for the as-synthesised and 8.9 ± 0.07 nm for the calcined material. The unit-cell contraction of about 0.8 nm upon removal of the template by calcination is found to be significantly lower compared to the unit-cell contraction observed for a purely siliceous MCM-48 material, which was found to be up to 2 nm.[12]

The surface area was determined to be 1157 $m^2\ g^{-1}$ by a full nitrogen adsorption–desorption isotherm using BET analysis. In accordance with the nitrogen[14] and argon isotherms[3] obtained on purely siliceous MCM-48 materials, a sharp increase in the adsorbed volume of N_2, due to capillary condensation of N_2 in the interconnecting pores of this material was observed (see Fig 2). As for the isotherms obtained on a purely siliceous MCM-48 no hysteresis in the adsorption and desorption cycle upon pore condensation was observed. The total adsorbed volume of N_2 of 0.96 $cm^3\ g^{-1}$ is in good agreement with the N_2 volume adsorbed on a purely siliceous MCM-48 (1.02 $cm^3\ g^{-1}$) with very good structural ordering.[12,14] The powder X-ray diffraction and N_2 adsorption studies and the comparison with a well structured siliceous sample indicate that the above described synthesis procedure results in a well ordered Al-containing MCM-48 material. The bulk Si : Al ratio was determined to be 22 by microprobe analysis in the as-synthesised and calcined samples. The ^{27}Al solid-state MAS NMR spectra were recorded at room temperature on a Varian VXR 300 S WB spectrometer (resonance frequency 78.157 MHz). The spectrometer was equipped with a Jakobsen MAS probe using a 7 mm zirconia rotor (MAS spinning speed 6 kHz) and applying a pulse length

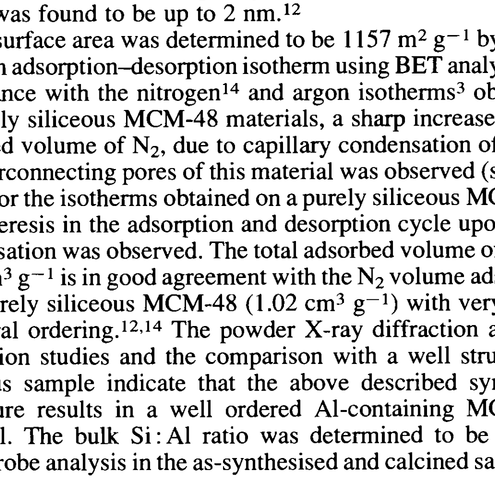

Fig. 1 Powder X-ray diffraction pattern of the as-synthesised and the calcined Al-containing MCM-48 sample

of π/20. As a reference a 1 mol dm^{-3} $Al(NO_3)_3$ (δ 0) solution was used. The as-synthesised sample was not thermally treated in any way (drying at room temperature). The calcined sample was saturated with water before recording the ^{27}Al MAS spectrum. In the ^{27}Al MAS NMR spectrum of the as-synthesised material (Fig. 3) only one peak centred around δ 50 can be observed, which represents aluminium in its tetrahedral coordination state.[9,10] Octahedrally coordinated Al, normally represented by a broad peak around δ 0[10] was not observed. Upon removal of the template by calcination at 540 °C still only tetrahedrally coordinated Al was observed, indicating that in contrast to aluminium-containing MCM-41 material,[9,10] no dealumination of the framework of the mesoporous MCM-48 took place (which would result in the formation of extraframework, octahedrally coordinated Al).

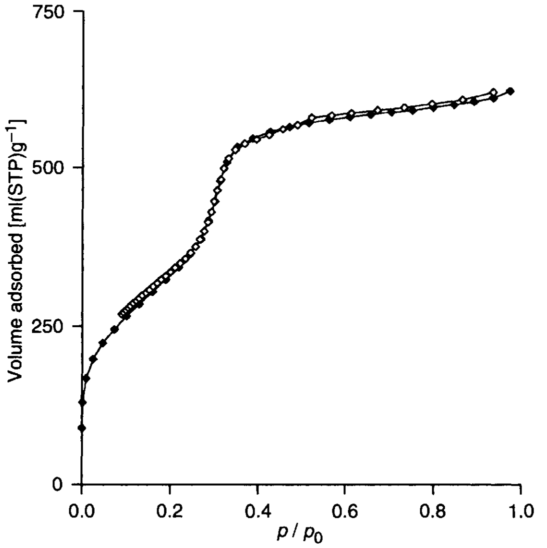

Fig. 2 N_2 adsorption isotherm of the calcined MCM-48 sample (◆ adsorption, ◇ desorption)

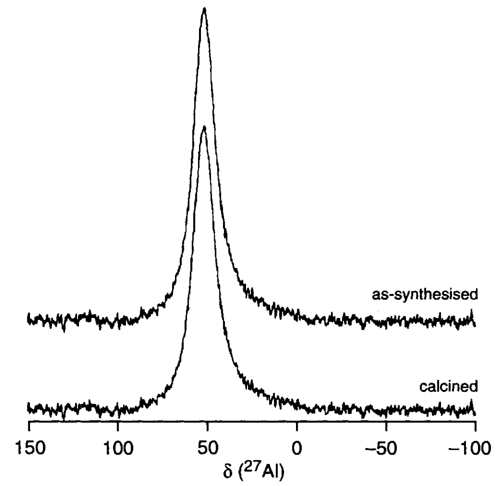

Fig. 3 ^{27}Al MAS NMR spectra of the as-synthesised and the water-saturated calcined MCM-48 samples

This might indicate that the Al incorporated into MCM-48 interacts in a different way with the siliceous framework compared to Al implemented into MCM-41, resulting in a possible difference of these materials as catalysts for acid-catalysed reactions. This will be the subject of our future studies. In conclusion, for the first time the detailed synthesis of a structurally well organised aluminium containing MCM-48 material, with an Si : Al ratio as low as 22, while only observing tetrahedally coordinated Al, is reported. During the removal of the template by calcination the aluminium is sustained in its framework positions.

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Received, 22nd January 1996; Com. 6/00507A