Synthesis and characterization of the mesoporous chromium silicates, Cr-MCM-41

N. Ulagappan and C. N. R. Rao*

CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560 012, India and Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

Mesoporous chromium-containing silicates of the MCM-41 type (pore size *ca.* 2.8 nm) with redox catalytic properties are synthesized and characterized.

Since the discovery of silica-based mesoporous molecular sieves such as MCM-41 by Kresge *et al.*[1] and Beck *et al.*[2] in 1992, some other related mesoporous materials have been reported in the literature. These include MCM-41 derivatives where Si is substituted by Al, Ti, V, Mn or Fe.[3–7] Recently, titanocene has been grafted on to MCM-41 to prepare titanium-containing MCM-41.[8] Most of these mesoporous solids exhibit interesting redox catalytic properties. We have prepared and characterized chromium-containing mesoporous silicates (Cr-MCM-41) for the first time, in view of the known catalytic properties of chromium in the presence of peroxide oxidants.[9,10]

In a typical synthesis of Cr-MCM-41, 4.9 ml of tetraethylorthosilicate was mixed with 0.19 g of NaOH and 0.15 g of chromium nitrate nonohydrate ($x = 0.02$) with 10 ml of water. The mixture was stirred for 10–15 min and 1.56 g of tetradecyltrimethylammonium bromide (TDTMABr) in 10 ml of water added to the mixture, followed by stirring for 20–30 min. Several homogeneous gels of the composition $x/2$ $Cr_2O_3 : SiO_2 : 0.25Na_2O : 0.25TDTMABr : 60H_2O$ ($x = 0.0$–0.10) were prepared by this procedure. The homogeneous gels were transferred to leak-proof polypropylene containers and heated at 363 K for 24 h. The solid products were thoroughly washed and dried overnight at 383 K. These solids were pale green and are designated Cr-MCM-41(1). Another set of chromium-containing MCM-41 materials were prepared starting with CrO_3 instead of $Cr(NO_3)_3$. The solids obtained with CrO_3 were pale yellow and are designated Cr-MCM-41(2). The as-synthesized Cr-MCM-41 samples were calcined in air at 873 K for 12 h. Thermogravimetric analysis indicated the loss of the template around 723 K; the mass loss was high (*ca.* 52%), suggesting that the product was likely to be porous (measured surface area *ca.* 550 $m^2\ g^{-1}$). On calcination, the Cr-MCM-41(1) preparations changed from pale green to pale yellow.

Typical X-ray diffraction patterns of as-synthesized and calcined samples of Cr-MCM-41 shown in Fig. 1 are comparable to the diffraction pattern of pure silica MCM-41.[1,2] There is a decrease in the d_{100} by *ca.* 0.3 nm on calcination. The d_{100} values and unit-cell parameters of the Cr-containing MCM-41 compositions prepared are listed in Table 1. The unit-cell parameter increases with increasing Cr content, demonstrating that chromium is incorporated in the framework. Definitive evidence for the hexagonal mesoporous nature of Cr-MCM-41 was obtained from transmission electron microscopy.

^{29}Si MAS NMR spectra of calcined Cr-MCM-41 show a main signal at δ -109 due to silicon surrounded by 4 Si (Q_4) and a small shoulder which can be attributed to Si surrounded by 3 Si and 1 Cr in the framework structure. IR spectra of the as-synthesized and the calcined samples of Cr-MCM-41 show bands characteristic of siliceous materials, with no significant information on Cr-substitution similarly to Ti-MCM-41.[11] In order to establish the oxidation state of Cr, we recorded diffuse reflectance spectra as well as EPR spectra of the Cr-MCM-41(1) and (2) samples. As-synthesized Cr-MCM-41(1) shows bands around 440 and 620 nm (Fig. 2) corresponding to the $^4\Gamma_2 \rightarrow {}^4\Gamma_4(F)$ and $^4\Gamma_2 \rightarrow {}^4\Gamma_5$ transitions of Cr^{III} respectively. Samples of Cr-MCM-41(2) and calcined Cr-MCM-41, on the other hand, show a main band around 370 nm; a less intense shoulder around 450 nm is seen in some of the samples (Fig. 2). The band at 370 nm is due to the charge-transfer absorption of Cr^{VI}, with the feature at 450 nm arising from the presence of a small proportion of Cr^{III}. The EPR spectrum of the as-synthesized Cr-MCM-41(1) shows a signal at $g = 1.94$ with $A = 462.5$ G (see inset of Fig. 2), characteristic of Cr^{III}; as expected, Cr-MCM-41(2) does not show this signal.

Catalytic properties of calcined Cr-MCM-41 ($x = 0.04$) were examined by carrying out a few typical reactions such as the oxidation of phenol, 1-naphthol and aniline with 30% H_2O_2 as

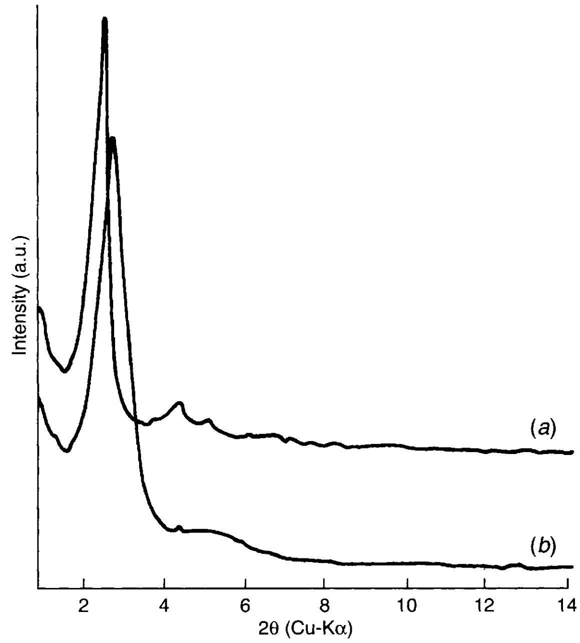

Fig. 1 X-Ray diffraction patterns of (*a*) as-synthesized Cr-MCM-41 and (*b*) calcined Cr-MCM-41 ($x = 0.04$)

Table 1 Unit-cell parameters of Cr-MCM-41 materials corresponding to different Si : Cr ratios

Si : Cr (in gel)	Cr-MCM-41(1)[a]		Cr-MCM-41(2)[b]	
	d_{100}/nm	a_0/nm[c]	d_{100}/nm	a_0/nm
100	3.53	4.07	3.46	3.99
50	3.57	4.12	—	—
30	3.66	4.22	3.67	4.24

[a] Cr^{III} source. [b] Cr^{VI} source. [c] Calculated using $a_0 = 2d_{100}/\sqrt{3}$.

the oxidant in the liquid phase with water or acetone as the solvent. The reaction conditions were: H_2O_2 : reactant = 3 (molar ratio), solvent : reactant = 10 (molar ratio), reactant : catalyst = 10 (*m/m*), T = 343 K and t = 2 h. The products were separated and analysed by gas chromatography. 1-Naphthol gave *ca.* 13.3% conversion with 75% selectivity for 2,4-naphthoquinone similarly to V-MCM-41,[5] while phenol gave a conversion of 7.4% with equal amounts of catechol and hydroquinone as the only products. Aniline gave 18.6% conversion with 61% selectivity for azobenzene. These catalytic properties suggest Cr-MCM-41 to be a potentially good redox catalyst system.

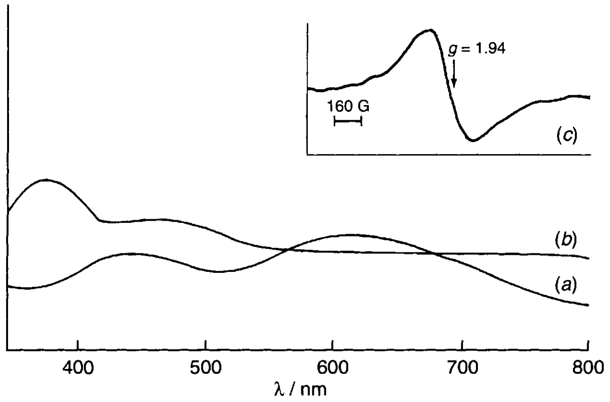

Fig. 2 Diffuse reflectance spectra of (*a*) as-synthesized Cr-MCM-41(1) and (*b*) Cr-MCM-41(2). Inset (*c*) shows the EPR spectrum of as-synthesized Cr-MCM-41(1).

References

1 C. T. Kresge, M. E. Leonwicz, W. J. Roth, J. C. Vartuli and J. C. Beck, *Nature*, 1992, **359**, 710.

2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. J. 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 R. Schmidt, D. Akporiaye, M. Stocker and O. H. Ellestad, *J. Chem. Soc., Chem. Commun.*, 1994, 1493.

4 P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.

5 K. M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1994, 1059.

6 D. Zhao and D. Goldfarb, *J. Chem. Soc., Chem. Commun.*, 1995, 875.

7 Z. Y. Yuan, S. Q. Liu, T. H. Chen, J. Z. Wang and H. X. Li, *J. Chem. Soc., Chem. Commun.*, 1995, 973.

8 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.

9 R. A. Sheldon, *Top. Curr. Chem.*, 1993, **164**, 21.

10 J. D. Chen, J. Dakka, E. Neelman and R. A. Sheldon, *J. Chem. Soc., Chem. Commun.*, 1993, 1379.

11 J. Blasco, A. Corma, M. J. Navarro and J. Perez-Pariente, *J. Catal.*, 1995, **156**, 65.

Received, 31st January 1996; Com. 6/00754F