Synthesis and Catalytic Properties of Mesoporous Tin Silicate Molecular Sieves

Tapan Kr. Das, Karuna Chaudhari, A. J. Chandwadkar and S. Sivasanker*

National Chemical Laboratory, Pune 411 008, India

The synthesis of mesoporous tin-silicates analogous to MCM-41 is reported, for which characterization studies indicate the incorporation of tin in the framework; the Sn-MCM-41 samples have excellent catalytic properties in the selective oxidation of aromatics and hydroxylation of phenol and 1-naphthol with peroxides.

Mesoporous molecular sieves designated as M41S were first reported by researchers at Mobil corporation.[1,2] The novelty of these materials lies in the fact that they possess well defined mesopores whose apertures can be tuned to the desired value in the range 18–100 Å by proper choice of the template. A number of publications describing the synthesis of MCM-41 (a member of M41S) containing elements such as aluminium,[3] iron,[4] titanium,[5] and vanadium[6] have appeared recently. We now report the synthesis, characterization and catalytic properties of Sn-analogues of MCM-41.

The hydrothermal synthesis of Sn-MCM-41 was carried out using gels with the following molar compositions; $SiO_2 : x\ SnO_2 : 0.089\ (CTMA)_2O : 0.155\ (TMA)_2O : 40\ H_2O$ where $x \leq 0.02$ and $(CTMA)_2O$ and $(TMA)_2O$ are organic templates.

In a typical synthesis tin tetrachloride $SnCl_4 \cdot 5H_2O$ (0.26 g, Loba Chemie, India) dissolved in water (15 g) was added to 16.7 g of a 24.6 mass% solution of cetyltrimethylammonium chloride/hydroxide [CTMACl/OH; 17.9 mass% Cl^-, 6.7 mass% OH^-; prepared by partial exchange of CTMACl (Aldrich) over ion-exchange resin] with stirring. To this mixture, tetramethylammonium hydroxide $TMAOH \cdot 5H_2O$ (2.08 g, 99%, Aldrich) was added followed by the addition of tetramethylammonium silicate TMA-silicate (17.3 g, 25 mass% solution, SACHEM. Inc.). This thick gel was allowed to stir for 15 min. Fumed silica (3.1 g, Sigma, 99% SiO_2) was added slowly to the above gel under stirring and the mixture stirred for 1 h (pH = 12.5). The mixture was then transferred to a stainless-steel autoclave and heated at 383 K for 5 days to complete the crystallization. After crystallization, the products were filtered, washed with deionized water, dried at 373 K and calcined at 823 K for 3 h in N_2 and 6 h in air. Three such Sn-MCM-41 samples with Si/Sn ratios of 83, 133 and 178 were prepared.

The XRD patterns of the synthesized Si-MCM-41 and Sn-MCM-41 samples matched closely with those reported by earlier workers[1,2] for MCM-41. The XRD d_{100} spacings for the samples are reported in Table 1. A slight shift in the d-spacings to lower 2θ values is noticed on incorporation of Sn, the shift increasing with increasing Sn content. Similar shifts were also reported by earlier workers with aluminium,[2,3] titanium[5] and vanadium[6] MCM-41. The N_2-adsorption isotherms of the samples showed single inflections characteristic of mesoporous materials with a uniform pore size. The average pore diameters calculated from N_2-adsorption isotherms using the BJH model[7] are also presented in the Table 1. The pore diameters also show an increasing trend with increasing Sn content of the samples. The increase in channel size on Sn-incorporation is probably due to the larger size of Sn^{4+} (0.55 Å) compared to Si^{4+} (0.26 Å).

Table 1 Composition and physico-chemical characteristics of the samples

sample	Sorption capacity[a] (mass %) H_2O	*n*-hexane	benzene	d_{100}	pore diameter (Å)
Sn-MCM-41(83)[b]	19.5	49.2	62.42	39.58	30.2
Sn-MCM-41(133)	17.53	47.02	60.52	39.39	29.6
Sn-MCM-41(178)	15.7	46.7	58.03	38.38	28.5
Si-MCM-41	13.8	45.1	56.1	36.77	27.0

[a] Gravimetric adsorption (Cahn electrobalance) at $p/p_0 = 0.5$ and at 298 K. [b] Si/Sn molar ratio in parentheses.

The framework IR spectra of the Si-MCM-41 and two Sn-MCM-41 samples are presented in Fig. 1. The T–O–T lattice vibration is found to shift to lower wavenumbers on incorporation of Sn. Earlier workers[8] have attributed such a shift to the incorporation of Sn in the lattice in the case of MFI system. Besides, the incorporation of Sn is also found to increase the intensity of a weak absorption noticed at around 970 cm^{-1}, attributed by Camblor *et al.*[9] to Si–O^- vibrations. This vibration has also been detected in Ti- and V-isomorphs of zeolites.[10–12] The amounts of H_2O, *n*-hexane and benzene sorbed by MCM-41 and Sn analogues are presented in Table 1. There is an increase in sorption of the molecules on incorporation of Sn due to the increase in channel volume. The XRD and IR results suggest that Sn is incorporated in the framework of MCM-41.

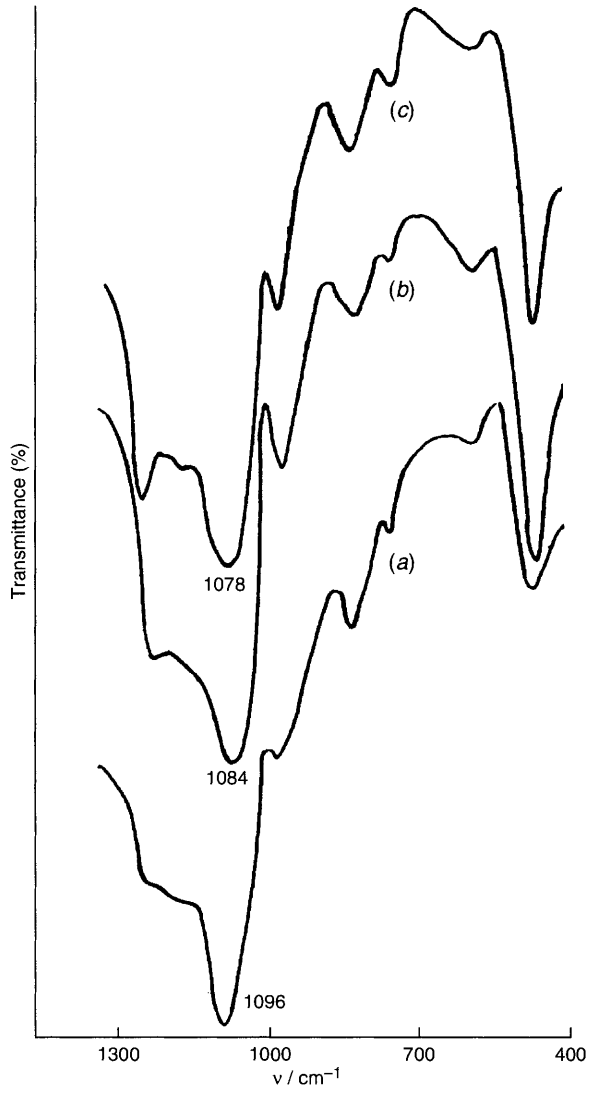

Fig. 1 Framework IR spectra of Si-MCM-41 (*a*), Sn-MCM-41(83) (*b*) and Sn-MCM-41(178) (*c*)

Earlier workers[8] have reported that Sn-MFI possesses selective oxidation properties when H_2O_2 is used as the oxidant. The catalytic activity of Sn-MCM-41 samples in the hydroxylation of phenol and 1-naphthol with H_2O_2 are presented in Tables 2 and 3. The experiments were carried out in a 50 ml batch reactor. Phenol conversions are high in the case of Sn-MCM-41 while the Sn-impregnated MCM-41 shows negligible conversion. This suggests that Sn is probably incorporated in the lattice and not merely occluded on the surface in Sn-MCM-41 samples. The catechol(CAT)/hydroquinone(HQ) ratios (Table 2) are >3.3 in the case of Sn-MCM-41 and is 1 in the case of Sn-impregnated MCM-41. The H_2O_2 selectivities are >50% as reported in the case of Ti-MFI[13] and V-MEL[14] zeolites.

The results of the hydroxylation of 1-naphthol establish that the active centres (Sn^{4+}) present in Sn-MCM-41 are accessible even to a large molecule such as 1-naphthol. This makes the Sn-MCM-41 samples useful in the oxidation of large molecules which normally would not enter the pores of the widely reported Ti- and V-analogues of MFI and MEL zeolites. The Sn-MCM-41 samples are also active in the oxidation of toluene and 2-methylnaphthalene with *tert*-butyl hydroperoxide (TBHP). Generally pore size restrictions preclude the use of TBHP in the oxidation of organic compounds using transition-metal analogues of MFI and MEL zeolites. The major product of the oxidation is benzaldehyde in the case of toluene and naphthaldehyde in the case of 2-methylnaphthalene.

One of us (T. K. D.) thanks CSIR, New Delhi for a research fellowship.

Received, 31st September 1995; Com. 5/05062F

Table 2 Activity of the samples in the hydroxylation of phenol[a]

sample	phenol conv. (mol %)	H_2O_2 select. (mol %)	product distribution (mass %) BQ	CAT	HQ
Sn-MCM-41(83)[b]	20.2	65.3	25.2	57.5	17.3
Sn-MCM-41(133)	17.4	55.8	26.4	57.4	16.2
Sn-MCM-41(178)	14.8	50.0	30.0	55.4	14.6
Sn-impregnated MCM-41	1.0	3.9	50.0	25.0	25.0
Si-MCM-41	no detectable activity				

[a] Reaction conditions: catalyst = 100 mg, solvent (water) = 10 g, phenol/H_2O_2(mol) = 3, T = 553 K, reaction time = 24 h, substrate = 1 g. [b] Si/Sn molar ratio in parentheses. BQ = benzoquinone; CAT = catechol; HQ = hydroquinone.

Table 3 Activity of the samples in the hydroxylation of 1-naphthol[a]

sample	1-naphthol conv. (mol %)	H_2O_2 select. (mol %)	product distribution (mass %) 1,4-naphthoquinone	1,4-dihydroxynaphthalene	1,2-dihydroxynaphthalene
Sn-MCM-41(83)[b]	17.1	85.5	83.0	12.3	4.7
Sn-MCM-41(133)	15.3	77.0	84.3	11.1	4.6
Sn-MCM-41(178)	14.2	73.0	88.0	7.7	4.3
Sn-impregnated MCM-41	1.0	4.0	50.0	50.0	—
Si-MCM-41	no detectable activity				

[a] Reaction conditions: catalyst = 100 mg, solvent (acetonitrile) = 10 g, 1-naphthol/H_2O_2(mol) = 3, T = 373 K, reaction time = 24 h, substrate = 1 g. [b] Si/Sn molar ratio in parentheses.

References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth and J. C. Vartuli, *US Pat.*, 5098684, 1992.
2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; J. S. Beck, J. C. Vartuli, W. J. Roth, M. W. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. U. Chu, D. H. Olsen, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3 R. B. Borade and A. Clearfield, *Catal. Lett.*, 1995, **31**, 267.
4 Zhong Yong Yuan, Shu Quan Liu, Tie Hong Chen, Jing Zhong Wang and He Xuan Li, *J. Chem. Soc., Chem. Commun.*, 1995, 973.
5 A. Corma, M. T. Navarro and J. Perez Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147.
6 K. M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1994, 1059.
7 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982, ch. 4.
8 N. K. Mal, V. Ramaswamy, S. Ganapathy and A. V. Ramaswamy, *J. Chem. Soc., Chem. Commun.*, 1994, 1931.
9 M. A. Cambler, A. Corma and J. Perez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1993, 557.
10 A. Thangaraj, R. Kumar, S. P. Mirajkar and P. Ratnasamy, *J. Catal.*, 1991, **130**, 1.
11 T. Sen, M. Chatterjee and S. Sivasanker, *J. Chem. Soc., Chem. Commun.*, 1995, 207.
12 P. R. H. Prasada Rao, A. A. Belhekar, S. G. Hedge, A. V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 1993, **141**, 595.
13 C. B. Khouw, H. X. Li, C. B. Dartt and M. E. Davis, *ACS Symp. Ser.*, 1993, **523**, 273.
14 P. R. H. Prasada Rao, A. V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 1992, **137**, 225.