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Novel Non-Thermal Synthesis and Characterization of Mesoporous Sn(IV) Silicates

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Sn(IV) incorporated mesoporous molecular sieves with Si/Sn ratios of 10, 20, 40, and 80 have been successfully synthesized under non-thermal conditions at ambient temperature. They have been characterized by means of X-ray diffraction, nitrogen adsorption isotherms, FT-IR spectroscopy, transmission electron microscopy and thermogravimetry analysis. Nitrogen adsorption data and XRD patterns confirmed that, the framework, high surface area and uniform pore size distribution are maintained in the crystallized sample with Si/Sn ratios of 40 and 80.

Key Words: Mesoporous, Sn(IV) silicate, Non-thermal synthesis.

INTRODUCTION

The synthesis of a new family of mesoporous molecular sieves with exceptionally large uniform pore structures were reported by Mobil researches[1-3] in year 1992. Due to their high surface area they found good use as catalysts[4,5] and efficient adsorbent[6]. Since the discovery of MCM-41 (a member of the M41S family) possessing a hexagonal array of uniform pores, several reports have appeared on the isomorphous substitution of Si by other elements such as titanium[7-9], vanadium[10-12], tin[13], chromium[14,15] and zirconium[16].

Different procedures of preparation for mesoporous materials have been proposed[17]. Hydrothermal conditions have been employed to graft Sn(IV) into mesoporous MCM-41[18]. These procedures use expensive organic silicon compounds like tetramethylammonium silicate or tetraethylorthosilicate as a silicon source. We report here the preparation and properties of mesoporous Sn(IV) silicate using sodium silicate as the source of silicon and minimum amount of surfactant at ambient temperature.

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EXPERIMENTAL

All the chemicals used were of analytical grade from E. Merck (Germany) except cetyltrimethylammonium bromide (CTMABr) which was supplied by Aldrich (U.K.).

Synthesis: In a typical synthesis, 0.6 g CTMABr was dissolved in 23 mL of demineralized water, the mixture was stirred for 15 min (140 rmp) after that 3 g of sodium silicate was added to the mixture and it was further stirred for 0.5 h. The pH value of mixture was 11.5 which was decreased to 9 by adding sulphuric acid (2 M) solution. Then solution of $SnCl_4 \cdot 5H_2O$ (0.49 g in 50 mL demineralized water) was added dropwise. The stirring was continued for 4 h. A bulky white gelatinous precipitate was formed. It was filtered, washed five times with demineralized water and dried in air oven at 50°C for 48 h. Small portion of this material was calcined at 600°C for 6 h.

The molar composition of the materials was as follows: SiO_2: 0.12 CTMABr: (0.0125-0.1) $SnCl_4$: 0.03 H_2SO_4: 100 H_2O. The following Si/Sn molar ratios were used in the samples: 10, 20, 40 and 80. The samples were denoted as SnxMCM-41 where x indicated the Si/Sn molar ratio. In order to study the effect of addition of Sn(IV) in these types of materials, a sample only with silica in the framework was also prepared under the same conditions, it was denoted as Si-MCM-41.

Characterization: XRD was performed using a Philips X'pert powder diffractometer system with Cu-Kα ($\lambda = 1.541$ Å) radiation from 1.5° (2θ) to 10.0° (2θ). The sorption isotherm of N_2 at 77 K was studied using a quantachrome Nova instrument. Specific surface area was determined by applying the BET equation to the isotherm[19]. Pore size distribution was calculated using the adsorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) formula[20]. FT-IR spectra were recorded using a Bruker FT-IR spectrophotometer model Vector-22. Thermal analysis was done on a Rheometric Scientific modal STA-1500.

RESULTS AND DISCUSSION

The XRD patterns of the calcined SnxMCM-41 samples with different Si/Sn ratios (10, 20, 40, 80) and the pure silica MCM-41 are given in Fig.1. The samples (with Si/Sn ratios 40 and 80) produce relatively well-defined XRD patterns, with one major peak along with three small peaks identical to those of MCM-41 materials[1-3] Beck *et al.*[3] indexed these peaks for a hexagonal unit cell, the parameter of which was calculated from the equation $a_\circ = 2d_{100}/\sqrt{3}$. The unit-cell parameter and d spacing of the SnxMCM-41 samples and MCM-41are given in Table-1. The decrease in d spacing and unit-cell parameter of SnxMCM-41 compared with its pure silica analogue (Table-1) suggest the presence of tin in the framework. It is also observed that the unit-cell parameter decreases with increasing Sn content. However, a gradual loss of long-range ordering is observed with increasing incorporation of Sn in the SnxMCM-41 samples. This is probably due to an increasing number of defect sites and bond strain in these materials, as evidenced by decreasing intensities of the d_{100} peak as well as the higher angle peaks. Finally, at high Sn loading (Si/Sn ≤ 10) amorphous materials are obtained.

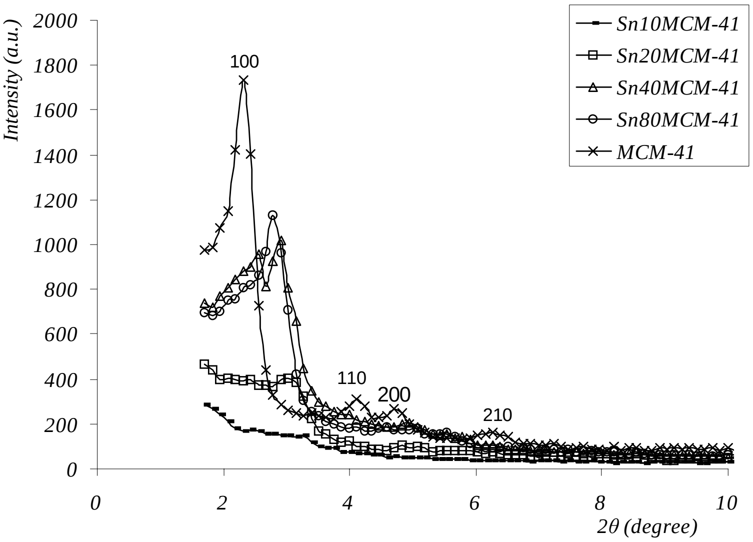

Fig.1 XRD patterns of the calcined mesoporous Sn(IV) silicates

TABLE-1
PROPERTIES OF THE SYNTHESIZED MESOPOROUS Sn(IV) SILICATES

Sample	Si/Sn ratio		XRD d_{100} (Å)	Unit cell parameter (a_o) (Å)	Pore volume (cc/g)	BET surface area (m^2/g)	Pore diameter (Å)
	gel	product					
Sn10MCM-41	10	19.4	26.12	30.2	0.30	223	17.9
Sn20MCM-41	20	47.2	27.76	32.0	0.41	522	18.1
Sn40MCM-41	40	151.7	28.99	33.5	0.57	814	18.1
Sn80MCM-41	80	184.0	30.03	34.7	0.58	831	18.1
Si-MCM-41	∞	∞	36.78	42.5	0.63	876	17.9

Nitrogen adsorption isotherms: Nitrogen sorption isotherm and corresponding pore size distribution of the synthesized Sn(IV) silicates are given in Fig.2. These isotherms show a typical IV-type adsorption profile consisting of a condensation behaviour due to the formation of mesopores. As the relative pressure increases ($P/P^o > 0.2$), the isotherms show inflection, where the P/P^o position of the sharpness of the isotherm in range $0.2 < P/P^o < 0.4$ corresponds to uniformity of mesopore size. It can be seen that as the tin content increases in the sample, the amount of adsorbed nitrogen is lowered at the same relative pressure and its sharpness are smaller[21]. Moreover, when the sample was synthesized under the same conditions but without tin, this sample showed similar isotherm. However there is a great difference between the sample with the higher quantity of Sn (Sn10MCM-41).

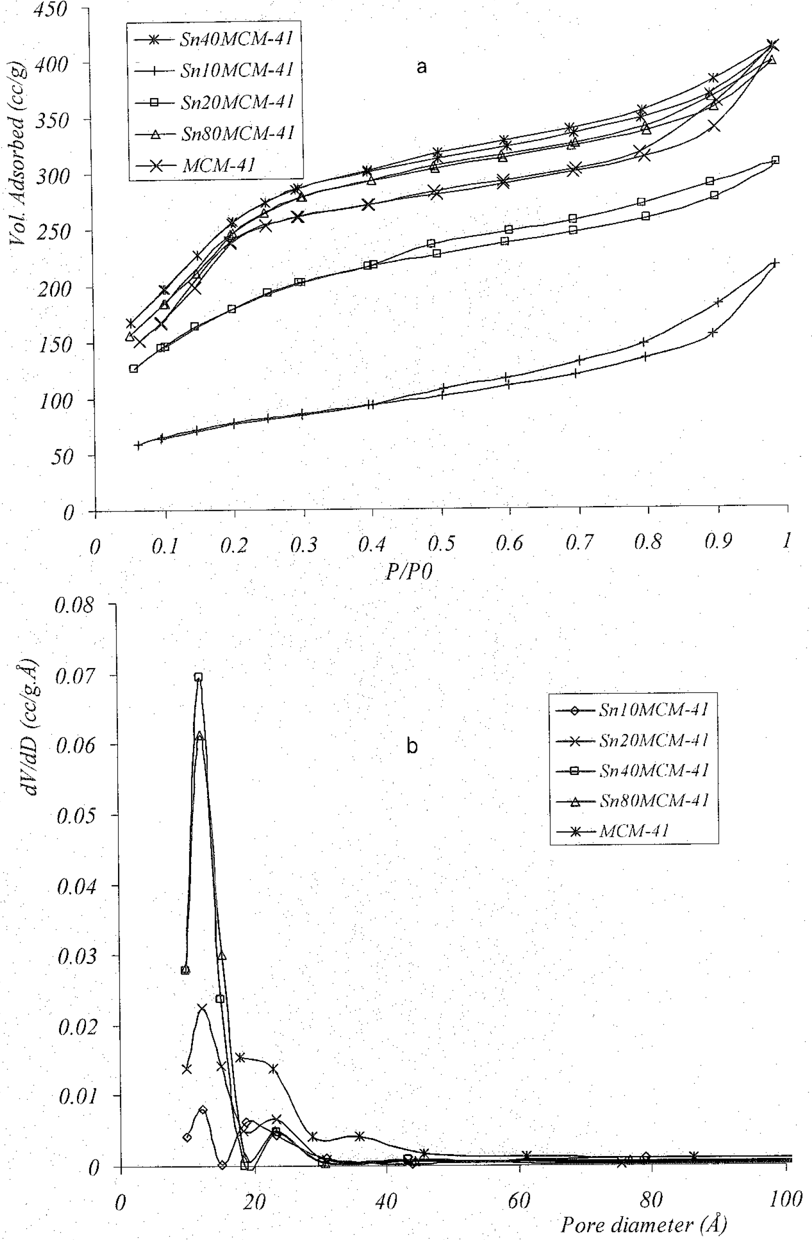

Fig. 2. (a) Nitrogen adsorption/desorption isotherm and (b) Pore size distribution of the synthesized mesoporous Sn(IV) silicates

Table-1 shows the specific surface area for all the samples. These data clearly illustrate that the use of Sn(IV) has an influence on the specific surface area. This parameter increases when the Si/Sn molar ratio increases.

Pore size distribution of the synthesized Sn(IV) silicates is shown in Fig.2(b). The pore size distribution is narrow for the samples between the range 17.9-18.1 Å. Table-1 shows the data of average pore size for all the samples. We can see that as the amount of Sn(IV) increases, the pore volume of samples shifts gradually to lower values.

FT-IR spectra: The infrared spectra of the synthesized mesoporous Sn(IV) silicates are given in Fig.3. The peaks appeared in the region of 1300-400 cm^{-1} are similar to vibrations of the framework structure of zeolites[22]. Similarly, mesoporous molecular sieves also show series of bands that are characteristics of the SiO_4 tetrahedral unit and its modification by introduction of metal ions. The spectrum shows five main absorption bands between the regions 1245-1210, 1090-1055, 970-960, 850-790, 465-440 cm^{-1}, similar to amorphous fumed silica[23-25]. The band in region 1245-1210 cm^{-1} is due to external asymmetric stretching vibrations of five membered Si-O rings, which is an evidence for the presence of 5 membered rings in the walls of MCM-41 structure. The band in region 1090-1055 cm^{-1} is due to internal asymmetric stretching mode of SiO_4 (TO_4) skeleton, appears to be the strongest band in the spectra of all silicates[25]. The (Si–O) bond stretching is not observed in the case of microporous molecular sieves. The peak in region 970-960 cm^{-1} is generally considered as a proof for the incorporation of the heteroatom into the framework[26]. Camblor *et al.*[26] have proposed that the band at 960 cm^{-1} is due to the (Si–O) stretching vibrations of (Si–OH) groups. The (Si–O–Si) lattice vibrations are found to shift to lower wavenumbers probably due to the incorporation of Sn into the channel walls, as (Sn–O) bond is longer than (Si–O) bond. It has also been observed the ν_{as}(Si-O-Sn) and/or ν(Si-OH) band intensity increase with respect to that of the ν_{as}(Si-O-Si) and/or ν(Si-OH) band when Sn content increases.

Thermogravimetric analysis: TG curves of the synthesized mesoporous Sn(IV) silicates are presented in Fig. 4. The TG curve of uncalcined sample shows a gradual weight loss up to 900°C. The TG curve of the samples show five steps of weight loss. These steps are 35-130, 130-300, 300-380, 380-480 and 480-600°C. The weight loss is *ca.* 4.0 % in the first step and is due to desorption of physisorbed water held in the pores. The weight losses in the second (*ca.* 20.0 %) and third (*ca.* 7.0 %) steps are mainly associated with oxidative decomposition of templates, in the fourth step, the weight loss (*ca.* 7.0 %) is due to removal of coke formed in the previous steps by the decomposition of templates. In the last step, the weight loss (*ca.* 2.0 %) is mainly due to water loss formed by the condensation of silanol groups. It can be noticed that the weight losses of both MCM-41 and SnxMCM-41 samples are similar, indicative of similar filling of SnxMCM-41 and MCM-41 samples.

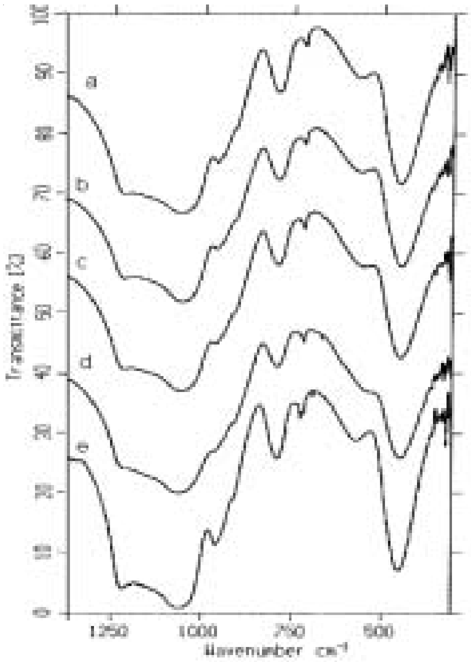

Fig. 3. FT-IR spectra of the synthesized mesoporous Sn(IV) silicates, (a) Sn80MCM-41 (b) Sn40MCM-41 (c) Sn20MCM-41 (d) Sn10MCM-41 (e) Si-MCM-41

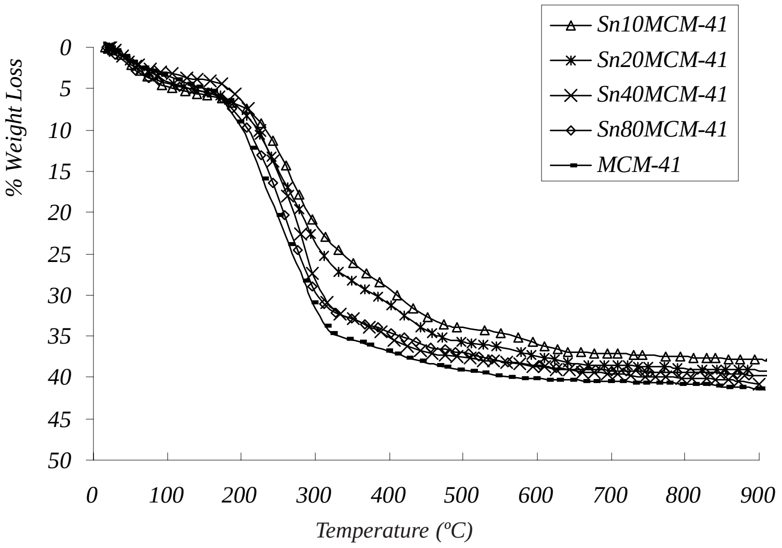

Fig. 4. Thermograms of the synthesized mesoporous Sn(IV) silicates

Conclusion

A simple, rapid and low cost non-thermal method has been developed to synthesize a new phase of Sn(IV) incorporated mesoporous molecular sieves (with Si/Sn ratios of 10, 20, 40 and 80) with high thermal stability and high surface area and pore volumes. The prepared material shows high potential to be used as a new promising sorbent in removal of heavy metals and further work is in progress.

REFERENCES

1. C.T. Kresge, M.E. Leonowics, W.J. Roth, J.C. Vartuli and J.S. Beck, US Patent 56,098,684 (1992).
2. C.T. Kresge, M.E. Leonowics, W.J. Roth, J.C. Vartuli and J.S. Beck, *Nature*, **359**, 710 (1992).
3. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowics, 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.*, **114**, 10834 (1992).
4. A. Corma, V. Fornes, M.T. Navarro and J.P.-Pariente, *J. Catal.*, **148**, 569 (1994).
5. S.S. Kim, W. Zhang and T.J. Pinnavaia, *Science*, **282**, 1302 (1998).
6. L. Mercier and T.J. Pinnavaia, *Adv. Mater.*, **5**, 500 (1997).
7. P.T. Tanev, M. Chibwe and T.J. Pinnavaia, *Nature*, **368**, 321 (1994).
8. A. Corma, M.T. Navarro and J.P.-Pariente, *J. Chem. Soc. Chem. Commun.*, 147 (1994).
9. S. Gontier and A. Tuel, *Stud. Surf. Sci. Catal.*, **97**, 157 (1995).
10. K.M. Reddy, I. Moudrakovski and A. Sayari, *J. Chem. Soc. Chem. Commun.*, 1059 (1994).
11. J.S. Reddy and A. Sayari, *J. Chem. Soc. Chem. Commun.*, 2231 (1995).
12. D.H. Park, C.F. Cheng and J. Klinowski, *J. Mater. Chem.*, **7**, 159 (1997).
13. K. Chaudhari, T.K. Das, P.R. Rajmohanan, K. Lazar, S. Sivasanker and A.J. Chandwadkar, *J. Catal.*, **183**, 281 (1999).
14. N. Ulagappan and C.N.R. Rao, *J. Chem. Soc. Chem. Commun.*, 1047 (1996).
15. T.K. Das, K. Chaudhari, E. Nandanan, A.J. Chandwadkar, A. Sudalai, T. Ravindranathan and S. Sivasanker, *Tetrahedron Lett.*, **38**, 3631 (1997).
16. D.J. Jones, J.J.-Jimenez, A.J.-Lopez, P.M.-Torres, P.O.-Paster, E.R.-Castellon and J. Roziere, *J. Chem. Soc. Chem. Commun.*, 431 (1997).
17. A.I. Bortun, L.N. Bortun and A. Clearfield, *Chem. Mater.*, **9**, 1854 (1997).
18. A. Corma, M.T. Navarro and M. Reuz, *J. Catal.*, **219**, 242 (2003).
19. S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, New York (1982).
20. E.P. Barrett, L.G. Joyner and P.P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
21. P.T. Tanev and T.J. Pinnavaia, *Chem. Mater.*, **8**, 2068 (1996).
22. E.M. Flanigen, in ed.: J.A. Pabo, Intrazeolite Chemistry and Catalysis; AS Monograph Series 171, Washington, DC, p. 80 (1976).
23. X. Chen, L. Huang, G. Ding and Q. Li, *Catal. Lett.*, **44**, 123 (1997).
24. C-Y. Chen, H-X. Li and M.E. Davis, *Microporous Mater.*, **2**, 17 (1993).
25. C-Y. Chen, H-X. Li and M.E. Davis, *Microporous Mater.*, **2**, 27 (1993).
26. M.A. Camblor, A. Corma and J.P.-Pariente, *J. Chem. Soc. Chem. Commun.*, 557 (1993).

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