Synthesis and Characterization of Crystalline, Tin-silicate Molecular Sieves with MFI Structure

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Tin-containing, medium pore molecular sieves (Si/Sn ratios above 30) with MFI structure have been synthesized; changes in unit cell volume, IR and catalytic activity data indicate that a part of the tin is well-anchored within the silicate framework.

Substitution of tin for aluminium in the framework of molecular sieve zeolites enhances adsorbent and catalytic properties useful in hydrocarbon conversion processes.[1,2] Attempts to incorporate tin in aluminosilicates were restricted to treatment of different zeolites with chlorides or fluorides of tin,[2,3] secondary synthesis process of substitution of Sn for Al by digestion of respective zeolites with NH_4SnF_3[1] and the synthesis of two types of crystalline $NaSn_3Si_{12}O_{34}\cdot nH_2O$, designated as Sn–A and Sn–B from a basic sodium stannosilicate gel.[4] The latter exhibit properties characteristic of a condensed felspathoid and contain both tetrahedral Si and octahedral Sn. Substitution of Sn^{IV} for P^{V} in the $AlPO_4$-5 structure in the tetrahedral coordination to produce a material with Brönsted and Lewis acid sites has also been reported.[5] In the case of Al-free MFI, only a few studies have clearly evidenced the incorporation of another tetravalent element (Ti^{4+} and Ge^{4+}).[6,7] Substitution of Si by Sn is not reported in zeolite, unless a trivalent element (*e.g.* Al^{3+}) is present in the framework. We report here our preliminary results on the synthesis of medium porous, Sn-containing silicalite-1 (MFI structure) molecular sieves, their characterization by XRD, IR and ^{119}Sn NMR spectroscopy and catalytic activity in the hydroxylation of phenol.

The hydrothermal synthesis of Al-free tin-silicates was carried out using gels with molar compositions: 1.0 $SiO_2 : x$-$SnO_2 : 0.45$ TPAOH : 35 H_2O, $x = 0.005$ to 0.03 and TPAOH (Pr_4NOH) as the organic template. In a typical synthesis, 0.68 g of $SnCl_4\cdot 5H_2O$ (Loba chem.) was added to a solution of 15 g of tetraethyl orthosilicate (Aldrich, 99.99%) under stirring. 40.27 g of TPAOH (20% aq. solution, Aldrich) was then added under vigorous stirring. This mixture was stirred for 1 h and 10 g of water was then added to the resultant clear solution. The homogeneous reaction mixture (pH 12.3) was charged into a stainless steel autoclave and heated at 433 K for 60 h to complete crystallization. After crystallization, the product was filtered, washed with deionised water, dried at 383 K and calcined at 773 K. The product yield was between 70 and 80 mass %. Five such Sn-silicate samples with Si/Sn input ratios of 33, 50, 70, 100 and 133 were prepared. For comparison, a silicalite-1 (S-1) sample and a Sn-impregnated silicalite-1 sample were prepared. The latter was prepared by impregnation of S-1 with $SnCl_4$ solution followed by calcination at 773 K.

The XRD profiles of the Sn-silicate samples match well with that of Sn-free silicalite-1 (MFI) structure.[8] The only difference is that the XRD peaks are narrow and sharp for S-1, indicating that the crystallite size is larger than those of Sn-containing samples. Indeed, the SEM showed that the particles were 3–5 μm in the case of S-1 and 0.2–0.5 μm for all Sn-silicate samples. Table 1 shows the orthorhombic unit cell volumes of the MFI-type Sn-silicates V_{uc}, which increases with the number of Sn atoms in the sample (total Sn per unit cell). If at least a part of the tin is located within the framework of the silicalite-1 structure, such an increase should take place (Shannon ionic radii, 0.55 Å for Sn^{4+} and 0.26 Å for Si^{4+}). Based on a theoretical calculation of unit cell volume expansion, an estimated one fifth of the Sn atoms are expected to be in the framework positions in our samples to account for the observed increase in the unit cell. The framework IR spectra of the Sn samples (KBr pellets, Nicolet) indicate a clear shift of the wavenumber of the T–O–T lattice vibration towards lower values with increasing tin content per unit cell (Table 1). An analogous shift observed for other MFI-type metallosilicates has been attributed to heteroatom incorporation into the MFI framework.[9,10] In addition, we have also observed a shoulder at around 975 cm^{-1} in the IR spectra of Sn-silicate samples. A similar observation for Ti and V-silicates with MFI and MEL structures has been attributed to Si–O–M vibrations from the possible substitution of heteroatom (M) in the Si–O–Si units,[7,12] substitution of the Sn^{4+} cation within the oxygen framework of MFI was not evidenced in an earlier study.[12]

The N_2 adsorption isotherms of Sn-silicate samples are characteristic of microporous materials. The surface areas are in the range of 500–525 $m^2\,g^{-1}$ as against a value of 385 $m^2\,g^{-1}$ recorded for Sn-free S-1 sample (Table 1). While an increase of about 40 $m^2\,g^{-1}$ is expected from the smaller particle size of Sn-silicate samples, a still higher area is probably due to the formation of defect sites during the synthesis and subsequent calcination of the samples. The mesopore (t-area) contribution is rather small in all the cases. The amounts of H_2O, n-hexane and cyclohexane adsorbed on these samples at 298 K

Table 1 Sample composition and physico-chemical characteristics

Sample	Sn per us[a]	μ_{uc}/Å^3	μ_{T-O-T}/ cm^{-1}	Sorption mass% H_2O	Capacity[b] Cyclohexane	Capacity[b] n-hexane	δ^c (^{119}Sn)	Surface area/ $m^2\,g^{-1}$	Mesopore area/ $m^2\,g^{-1}$
Sn Sil(33)[d]	3.29	5371	1099	8.0	6.0	16.5	−685	527	42
Sn Sil(50)	2.06	5365	1100	7.5	4.8	16.0	—	522	38
Sn Sil(70)	2.13	5354	1102	7.0	4.5	15.2	−693	518	65
Sn Sil(100)	0.81	5361	1108	6.8	4.4	14.5	—	506	42
Sn Sil(133)	1.13	5346	1108	6.5	4.2	13.5	—	500	51
Silicalite-1	—	5345	1110	4.8	4.0	12.5	—	384	18
Sn-impreg.-Sil (50)	2.06	—	—	—	—	—	−604	—	—

[a] Total amount in the product. [b] Gravimetric adsorption at $p/p_o = 0.5$ and at 298 K. [c] Chemical shift with respect to Me_4Sn. [d] Si/Sn molar ratio of the gel in parentheses.

Table 2 Hydroxylation of phenol[a]

Sample	Phenol conversion[b] mol %	H_2O_2 selectivity[c] mol %	Product distribution[d] (%)			
			BQ	CAT	HQ	CAT/HQ
Sn-Sil(50)[e]	20	55	6.0	72	22	3.3
Sn-impreg.-Sil(50)	1.0	3	nd[h]	70	30	2.3
SnO_2[f]	0.5	1.5	nd	65	35	1.9
Ti-Sil(48)	25	68	nd	53	47	1.1

[a] Reaction conditions: catalyst = 100 mg; solvent (water) = 5 g; phenol/H_2O_2 (mole) = 3; temp. = 348 K; reaction time = 24 h; reaction carried out in a 100 ml batch reactor. [b] Based on the formation of all products. [c] For the formation of benzoquinone (BQ), catechol (CAT) and hydroquinone (HQ), excluding tar. [d] Break up (mass%) of products excluding tar. [e] Si/M ratio in parentheses. [f] For similar amount of Sn as in the case of Sn-Sil(50). [g] Titanium silicalite-1, for comparison. [h] Not detected.

and at p/p_0 of 0.5 (gravimetric, Cahn electrobalance) are included in Table 1. The comparable sorption capacities for *n*-hexane and cyclohexane between S-1 and Sn-silicates indicate that the micropores are maintained and that occluded SnO_2-type of species may not be present in these samples.

The X-ray photoelectron spectra of the samples showed typical doublets for Sn $3d_{3/2}$ and $3d_{5/2}$ electrons with the binding energies of 495.8 and 488.0 ev, respectively, confirming the presence of Sn in the 4+ oxidation state on the surface. The calculated surface chemical compositions compare well with the bulk composition of samples with Si/Sn > 70 and confirm the presence of Sn^{4+} in the bulk of the samples. For Sn Sil(33) and Sn Sil(50) samples, the surface appears to be enriched with Sn^{4+} ions. Extraction with conc. HCl did not remove any tin from the samples, confirming the absence of Sn^{2+} ions in our samples.

The ^{29}Si and ^{119}Sn solid state MASNMR spectra of the samples were recorded in a Bruker 300 MHz instrument. The ^{29}Si NMR spectra showed spectral broadening in the low field region and the presence of defect groups at around -105 ppm[7] for all the Sn-containing samples both in the as-synthesized and calcined forms. ^{119}Sn NMR observations are not conclusive at present. For both SnO_2 and Sn impregnated silicalite-1 samples the isotropic peak with a chemical shift at -604 ppm (with respect to Me_4Sn) show the presence of Sn essentially in octahedral coordination.[13] The spectra of the Sn-silicate samples, showed spinning side bands of sufficient intensity to enable the principal component of the chemical shift tensor to be determined at around -685 and -693 ppm (Table 1), which is in overlap with the reported range for octahedral tin. It is probable to think of tin incorporation at or very close to the defect sites than of a tetrahedral substitution in the lattice.

Catalytic activity studies are often indicative of the framework and extra-framework location of the substituting elements in the silicalite structure.[6] Hydroxylation of phenol with H_2O_2 (often carried out as a test reaction for Ti-silicalites[14]) is performed over a Sn-silicate-1 (50) sample (Table 2). For comparison, data obtained on pure SnO_2, Sn-impregnated silicalite-1- and on a Ti-silicalite-1 (TS-1) are included in Table 2. The results show that both SnO_2 and Sn-impregnated silicalite-1 samples have negligible activity in this hydroxylation reaction and that the phenol conversion on Sn-silicate-1 sample is only marginally lower (20 mol%) than on TS-1 (25 mol%) for similar Si/M ratios and under similar conditions. A higher catechol to hydroquinone ratio in the product distribution on Sn-silicate-1 sample indicates the presence of a considerable amount of surface Sn species (as against their presence in the channels) which are quite active in the hydroxylation reaction probably because they are isolated and are well dispersed.

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References

1 G. W. Skeels and E. M. Flanigen, *Stud. Surf. Sci. Catal.*, 1989, **49A**, 331; EP 321,177 (1989); *US Patent Appl.* 133,372 (1987).
2 *US Patents*, 4,933,161 (1990); 5,192,519 (1993).
3 I. G. K. Andersen, E. K. Andersen, N. Knudsen and E. Skou, *Solid State Ionics*, 1991, **46**, 89; *Solid State Ionics*, 1989, **35**, 51.
4 *Handbook of Molecular Sieves*, ed. R. Szostak, Van Nostrand Reinhold, New York, 1992, p. 434.
5 N. J. Tapp and C. M. Cardila, *Zeolites*, 1990, **10**, 680.
6 G. Perego, G. Bellusi, C. Corno, M. Taramasso, F. Buonomo and A. Esposito, *Stud. Surf. Sci. Catal.*, 1986, **28**, 129.
7 Z. Gabelica and J. L. Juth, *Stud. Surf. Sci. Catal.*, 1989, **49A**, 421.
8 W. Meier and D. Olson, Atlas of Zeolite structure types, *International Zeolite Association*, 1976.
9 R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, 1989.
10 G. Vorbeck, J. Janchen, B. Parlitz, M. Schneider and R. Fricke, *J. Chem. Soc., Chem. Commun.*, 1994, 123.
11 P. R. Hari Prasad Rao, A. V. Ramaswamy and P. Ratnasmy, *J. Catal.*, 1992, **137**, 225.
12 V. Valtchev, *God. Sofii Univ.* 'Sv. Kliment Okhridski', *Geol.-Geogr. Fak.*, 1992, **83**, 87 (Bulg.); CA 120:40697k.
13 N. J. Clayden, C. M. Dobson and A. Fern, *J. Chem. Soc., Dalton Trans.*, 1989, 843.
14 D. R. C. Huybrechts, I. Vaesen, H. X. Li and P. A. Jacobs, *Catal. Lett.*, 1991, **8**, 237.