

Sn-MFI molecular sieves: synthesis methods, ^{29}Si liquid and solid MAS-NMR, ^{119}Sn static and MAS NMR studies

N.K. Mal, V. Ramaswamy, P.R. Rajamohanam, A.V. Ramaswamy *

National Chemical Laboratory, Pune 411008, India

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Abstract

Four different methods of the hydrothermal synthesis of Sn-sil-1 (MFI structure) ($\text{Si}/\text{Sn} > 15$) molecular sieves are described. Three of the methods are in a basic medium ($\text{pH} = 12.4$) and the last is in a fluoride medium ($\text{pH} = 6.4$). The procedure in which $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is dissolved first in $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) before hydrolysis by tetrapropyl ammonium hydroxide (method A) seems to be the most suitable in terms of the crystallinity of the resulting material and its activity in the hydroxylation of phenol by aqueous H_2O_2 (72% efficiency for H_2O_2). The course of hydrolysis of TEOS and SnCl_4 is studied systematically by ^{29}Si liquid NMR spectroscopy. It is inferred that as soon as SnCl_4 is partially hydrolysed, it combines with monomeric $\text{Si}(\text{OH})_4$ (Q^0) species. This combination leads to the formation of Q^1 , Q^2 and Q^3 species and a clear solution. The liquid NMR data provide direct evidence for the interaction of Sn species with silicate species in the synthesis mixture. Further, ^{29}Si MAS NMR and ^{119}Sn static and MAS NMR spectral studies of the crystalline product indicate that the Sn^{4+} ions are probably attached to the defect silanol groups in a tetrahedral coordination, but tend to assume five- or six-fold coordination very easily due to their large size. © 1997 Elsevier Science B.V.

Keywords: Gel formation; Liquid and solid ^{29}Si NMR; Sn-sil-1 molecular sieves; ^{119}Sn static and MAS NMR; Synthesis

1. Introduction

Tin-containing molecular-sieve zeolites are interesting materials as they could be useful as adsorbents [1], as ionic conductors [2] and as catalysts in the hydroxylation of phenol, phenol ethers [3] and in many other chemical reactions [4–6]. The hydrothermal synthesis of tin-containing molecular sieves in the presence of an alkali metal was first reported by Dwyer and Jenkins [7]. Exxon has claimed the synthesis of stannosilicates of a

novel structure in the presence of an alkali metal and Al or Ga, where Sn^{4+} ions are reported to be octahedrally coordinated [1]. Recently, Skeels et al. [4] have reported the post-synthesis treatment of ZSM-5 to prepare Al- and Sn- or Cr-containing MFI silicalites and their use in the cracking, hydrocracking and alkylation of both aromatics and isoparaffins. They have demonstrated the substitution of Sn in place of Al in the framework of the molecular sieve via treatment with fluoride salts. However, no details of the characterization of these materials with respect to the location and the environment of Sn^{4+} ions in the metallosilicate molecular sieves are given in these reports. For the

* Corresponding author. Fax: +91 212 334761.

preparation of Al-free metasilicate molecular sieves such as TS-1, VS-1 and CrS-1, different procedures of hydrothermal synthesis have been described in the literature. We discuss four different methods of the synthesis of Sn-sil.

Various techniques have been used for the determination of the nature and concentration of silicate species in aqueous solutions [8,9]. High-resolution ^{29}Si NMR has been the most successful technique to identify such species present in the solution phase. Barrer [10] has postulated that zeolite nuclei are formed from the precursors present as soluble aluminosilicate species in the synthesis solutions in the case of aluminum-containing zeolites. The soluble silicate species (Q^0 , Q^1 , Q^2 , Q^3 and Q^4) in solution are in equilibrium with each other and the distribution of such silicate species depends on the pH, the nature of the silica source, the nature of the templates, the metal ions and the temperature [9]. Booxhorn et al. [11] have observed a redistribution of the silicate species in a TPA (tetrapropylammonium) silicate solution after the addition of methanol, ethanol or dimethyl sulfide. A sharp signal observed at $\delta = -98$ ppm in the ^{29}Si NMR spectrum of a DMSO/TPA silicate mixture has been assigned to the double five-membered ring (D5R) silicate species [11]. However, no report or evidence is available for the participation of any detectable precursor silicate species present in the reaction mixture (clear aqueous solution) during the synthesis of tin-silicate molecular sieves. Since Sn-sil-1 (MFI structure) can be synthesized from aqueous solution [12], it is easier to understand the species responsible for the Si–O–Sn bond formation. The purpose of this study is to understand the interaction between the soluble silicate species (Q^0 , Q^1 , Q^2 , Q^3 and Q^4) formed in the gel during the hydrothermal synthesis of Sn-sil-1 by ^{29}Si liquid NMR and coordination around Sn^{4+} ions of the resultant crystalline material by solid ^{29}Si and ^{119}Sn MAS NMR spectroscopy.

2. Experimental

2.1. Synthesis

Hydrothermal syntheses of Sn-sil-1 (MFI structure) molecular sieves were carried out in 100 ml

stainless-steel autoclaves under autogenous pressure and static conditions.

2.1.1. Method A

In a typical preparation, 0.76 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 5 g of H_2O was added to 15.3 g of tetraethylorthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS). After 30 min, 33 g of tetrapropylammonium hydroxide (TPAOH, 20% aqueous) was added to the reaction mixture under continuous stirring during addition and for 1 h afterwards. Finally, 14 g of H_2O was added under vigorous stirring for 30 min. The clear gel obtained was transferred to an autoclave and placed in an oven for crystallization at 433 K for two days. The autoclave was then removed from the oven and quenched with cold water. The contents were filtered, washed thoroughly with deionised water and dried at 393 K for 5 h. The chemical composition of the reaction mixture (gel) was found to be $0.45\text{TPAOH} : 0.03\text{SnO}_2 : 1.0\text{SiO}_2 : 35\text{H}_2\text{O}$.

2.1.2. Method B

In a typical preparation, 15.3 g of TEOS was hydrolyzed with 33 g of TPAOH under vigorous stirring for 30 min. Then, 0.76 g of $\text{SnCl}_4 \cdot \text{H}_2\text{O}$ in 10 g of H_2O was added to this mixture and stirred for 1 h. Finally, 9 g of H_2O was added and stirred for another 15 min. This clear gel was placed in an autoclave in an oven at 433 K for two days. After crystallization, the material was filtered, washed with deionized water and dried at 393 K.

2.1.3. Method C

In this procedure, acetylacetone was used as a complexing agent. 33 g of TPAOH was added to 15.3 g of TEOS and hydrolyzed for 30 min while stirring. Then, 0.76 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 10 g of water was added to 0.64 g of acetylacetone ($\text{acac}/\text{SnO}_2 = 3$). This complex was added to the TEOS+TPAOH mixture and stirred for 1 h. Finally, 9 g of H_2O was added and stirred for another 15 min. The resultant gel was charged in an autoclave and placed in oven at 433 K for two days. After crystallization, the contents of the autoclave were filtered, washed with distilled water and dried at 393 K.

2.1.4. Method D

This method was used to prepare Sn-silicalite-1 in a fluoride-ion ($\text{pH} < 7$) medium. In a typical preparation, 3.8 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 10 g of H_2O was added to 5.34 g of NH_4F in 25 g of H_2O under vigorous stirring. Then, 9.78 g of tetrapropylammonium bromide (TPABr) in 56 g of H_2O was added to the mixture and stirred for 30 min. Finally, 8.64 g of fumed silica (Sigma) was gradually added to the mixture under vigorous stirring and the resultant gel was further stirred for 3–4 h until a homogeneous gel was obtained ($\text{pH} = 6.4$). The gel was sealed in a Teflon-lined autoclave and heated at 473 K for six days. The crystalline product was filtered, washed with distilled water and dried at 393 K for 5 h. The chemical composition of the reaction mixture (gel) was found to be $1.0\text{SiO}_2:0.1\text{SnO}_2:0.25\text{TPABr}:1.0\text{NH}_4\text{F}:70\text{H}_2\text{O}$.

All the samples prepared by the above four methods (A, B, C and D) were calcined at 773 K for 16 h in air. Some preliminary tests were carried out to examine the course of hydrolysis of TEOS and SnCl_4 in presence of TPAOH. The results are shown in Table 1. The four methods of synthesis of Sn-sil-1 molecular sieves are shown schematically in Fig. 1.

2.2. Characterization

^{29}Si liquid NMR spectra of the clear gel were recorded in a Bruker MSL 300 FT-NMR spec-

Table 1
Hydrolysis of TEOS and SnCl_4

	Reactants	Observation
1	$\text{Si}(\text{OEt})_4 + \text{TPAOH}$	Clear solution
2	$\text{SnCl}_4 + \text{Si}(\text{OEt})_4$	Clear solution
3	$\text{SnCl}_4 + \text{TPAOH}$	Precipitate
4	$\text{SnCl}_4 + \text{NaOH}$	Precipitate
5	$[\text{SnCl}_4 + \text{Si}(\text{OEt})_4] + \text{TPAOH}$	Clear solution
6	$[\text{Si}(\text{OEt})_4 + \text{TPAOH}] + \text{SnCl}_4$	Turbid
7	$[\text{Si}(\text{OEt})_4 + \text{TPAOH}] + \text{SnCl}_4$ in acetylacetone	Clear solution
8	$\text{SnCl}_4 + (\text{TPABr in H}_2\text{O})$	Clear solution
9	$\text{Si}(\text{OEt})_4 + (\text{TPABr in H}_2\text{O})$	Clear solution
10	$\text{SnCl}_4 + \text{NH}_4\text{F}$	Clear solution
11	$(\text{SnCl}_4 + \text{NH}_4\text{F}) + \text{TPABr}$	Clear solution
12	$(\text{SnCl}_4 + \text{NH}_4\text{F} + \text{TPABr}) +$ fumed silica	Homogeneous gel

trometer operated at 293 K. ^{29}Si spectra were collected using a 30° pulse with a 1 s recycle delay time. In order to avoid the glass background signal, ^{29}Si solution spectra were recorded using a conventional, static, wide-line probe. The samples were taken in 10 mm o.d. plastic tubes with a tight cap, and 200–2000 FIDs were accumulated. The chemical shift was recorded with respect to tetramethyl silane (TMS).

The samples synthesized during the course of the work were analyzed for quantitative and qualitative phase identification by X-ray powder diffraction recorded on a Rigaku X-ray powder diffractometer (model D MAX III VC, Ni-filtered $\text{Cu K}\alpha$ radiation and graphite a monochromator).

Both AAS (Hitachi) and ICP (John Yvon JYU-38 VHR) instruments were used for wet chemical analysis of the samples. The Si/Sn ratios of the calcined samples were obtained by XRF (Rigaku, model 3070).

^{29}Si MAS NMR spectra were recorded at 59.6 MHz on a Bruker MSL-300 NMR spectrometer. ^{119}Sn MAS NMR spectra were obtained at 111.82 MHz. Typically, around 16 000–18 000 transients were accumulated before Fourier transformation. The chemical shift (in the case of Sn) was referenced externally to tetramethyl tin.

2.3. Catalytic oxidation reaction

The hydroxylation of phenol was carried out batchwise in a (100 ml capacity) glass vessel fitted with a mechanical stirrer, a condenser and a feed pump (Sage Instruments, USA) at 348 K using mainly water as the solvent. Aqueous H_2O_2 (26%) was added (phenol to H_2O_2 mole ratio of 3) in one lot after maintaining the temperature of the reaction. The reaction was carried out for 24 h. The products were diluted with a solvent and analyzed in a capillary GC (HP 5880) using a 50 m long silicon gum column. Invariably, the conversion of H_2O_2 was found to be almost 100% after 24 h. The activity data are presented in terms of H_2O_2 efficiency for the formation of dihydroxybenzenes (Table 2).

3. Results and discussion

Table 2 summarizes some of the properties of the Sn-sil-1 molecular sieves prepared by the four

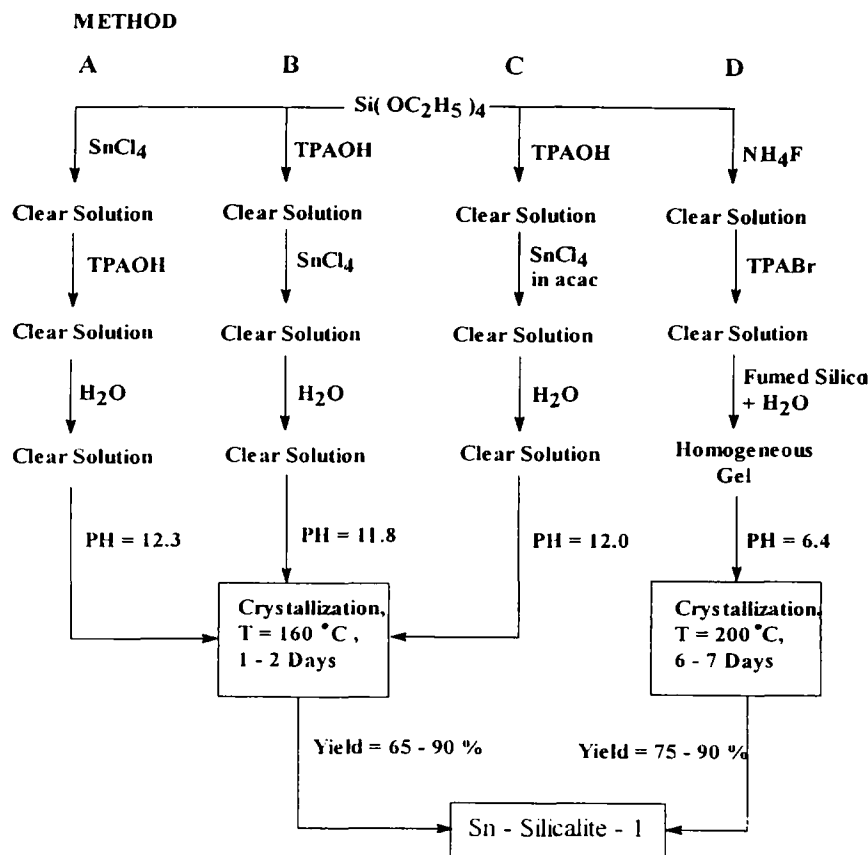


Fig. 1. Schematic representation of the different hydrothermal procedures for the synthesis of Sn-silicalite-1.

different methods (A–D) described above. Samples prepared using method A were assumed to have 100% crystallinity and they gave a higher H_2O_2 efficiency (72%) in comparison to samples prepared by other methods. Samples synthesized using methods B, C and D show 60, 95 and 100%

crystallinity and 43.2, 64.8 and 28.8% H_2O_2 efficiency, respectively, in the hydroxylation of phenol. The difference in the hydroxylation activity may be related to the nature and location of Sn^{4+} ions in the MFI structure of the samples prepared by the different methods. In the sample

Table 2
Physicochemical characteristics of Sn-silicalite-1 molecular sieves

Method	Si/Sn output	Crystallization time	Crystallinity ^a (%)	Average particle size ^b (μm)	Surface area ($\text{m}^2 \text{g}^{-1}$)	H_2O_2 efficiency ^c (mol%)
A	28.0	1–2 days	100	0.15	527	72.0
B	25.0	1–2 days	60	1.5	415	43.2
C	27.8	1–2 days	95	0.3	510	64.8
D	15.0	6–7 days	100	5×10	310	28.8

^aCrystallinity was calculated with respect to the sample prepared using method A.

^bDetermined by scanning electron microscopy.

^cEfficiency is expressed in terms of the hydroxylation of phenol to dihydroxy benzene with aqueous H_2O_2 at 348 K.

prepared using method A, some isolated Sn^{4+} species are tetrahedrally coordinated (in the framework position) and the rest are uniformly linked to defect silanol groups. These are the active centers in the hydroxylation of phenol [13]. Most of the Sn^{4+} ions are probably present on the surface in the sample prepared using method B and are octahedrally coordinated, whereas the nature of the Sn species prepared using method C is similar to that prepared using method A. This sample is equally crystalline and active in the hydroxylation of phenol (Table 2). The lower activity of sample B in the hydroxylation of phenol may also be due to the low crystallinity of the sample, whereas the lower activity of sample D may be due to a larger particle size ($5 \times 10 \mu\text{m}$) compared to sample A ($0.15 \mu\text{m}$). In the case of titano-silicates (TS-1), it is known that larger particles of TS-1 show lower activity in the hydroxylation of phenol [14]. Thus, method A used for the synthesis of Sn-sil-1 was found to be the most suitable.

3.1. ^{29}Si liquid NMR spectra

The synthesis of Sn-sil-1 comprises a gel of the molar composition $1.0\text{SiO}_2:0.45\text{TPAOH}:0.03\text{SnO}_2:35\text{H}_2\text{O}$. The possible Si species which were formed in the reaction mixture of Sn-sil-1 synthesis and their corresponding NMR signals (ppm) with respect to TMS are given in Table 3. Fig. 2(a) shows a sharp peak at -82.5 ppm for TEOS. Addition of TPAOH to $\text{Si}(\text{OEt})_4$ solution under stirring for 1 min induced approximately 15% hydrolysis of $\text{Si}(\text{OEt})_4$ to monomeric

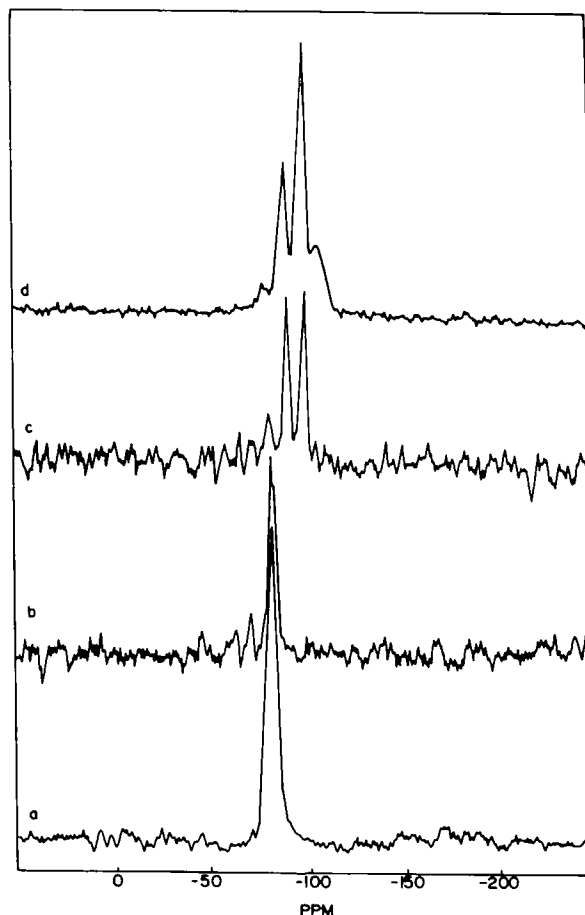


Fig. 2. ^{29}Si liquid NMR spectra of (a) TEOS, (b) 1.0 TEOS:0.45 TPAOH stirred for 1 min, (c) reaction mixture (b) stirred for 30 min, and (d) reaction mixture (b) stirred for a further 2 h.

Table 3
The silicate species in the reaction mixture detected by ^{29}Si liquid NMR^a

	Species (M = Si or Sn)	Chemical shift ($-\delta$) (ppm)	Identification
1	$\text{Si}(\text{OEt})_4$	-82.5	TEOS
2	$\text{Si}(\text{OH})_4$	-72.2	Q^0 (monomer)
3	$(\text{OH})_3\text{Si}-\text{O}-\text{M}(\text{OH})_3$	-80.2	Q^1 (dimer)
4	$(\text{OH})_2\text{Si}-[\text{OM}(\text{OH})_3]_2$	-89.1	Q^2
5	$(\text{OH})_1\text{Si}-[\text{OM}(\text{OH})_3]_3$	-98.7	Q^3
6	$\text{Si}-[\text{OM}(\text{OH})_3]_4$	-106.5	Q^4
7	Double five-membered ring silicate species	-98.7	D5R

^aReferenced to tetramethyl silane.

Si(OH)_4 species only (Fig. 2(b)). Further stirring for 30 min resulted in the formation of Q^1 , Q^2 and Q^3 species, while a small amount of Q^0 was left in the reaction mixture. The concentration of Q^2 and Q^3 species was almost the same (Fig. 2(c)). It was rather difficult to control the hydrolysis of Si(OEt)_4 to the monomeric Si(OH)_4 species only. Once the monomeric species are formed, they immediately react further to combine with other monomeric species to form Q^1 , Q^2 , Q^3 and Q^4 species. It was not possible to locate precisely the time at which only monomeric species (Q^0) are likely to be present in the reaction mixture during the hydrolysis of TEOS by TPAOH under these reaction conditions. In such a situation, further addition of a metal source (SnCl_4) in the presence of monomeric Si(OH)_4 (Q^0) species (obtained by hydrolysis) was not possible. However, when the reaction mixture of TEOS and TPAOH was stirred for an additional 2 h, Q^3 species predominated over Q^2 species and a small fraction of Q^4 species were formed, while the Q^0 species disappeared completely (Fig. 2(d)). Ultimately, solid silicalite-1 was crystallized (at 433 K, 1–2 days) with a low yield (55%).

Fig. 3 illustrates the influence of the addition of SnCl_4 to the reaction mixture of TEOS and TPAOH. When 0.03 M SnCl_4 solution was added to the solution after 30 min of stirring (1.0TEOS:0.45TPAOH) (Fig. 3(a)) and then stirred for a further 2 h, the formation of Q^3 species was favored. When Q^4 species appeared, the Q^0 species disappeared (Fig. 3(b)). A comparison of the ^{29}Si NMR spectra (Fig. 3(b) and (c)) shows that the addition of SnCl_4 to the reaction mixture of TEOS and TPAOH (Fig. 3(a)) only results in the broadening of Q^4 peaks, while the other spectral features remain unchanged. It was found that when a solution of TEOS and TPAOH (1.0TEOS:0.45TPAOH) was stirred vigorously for more than 1 h and then SnCl_4 was added, a turbid solution was formed due to the precipitation of SnO_2 (the availability of free Si(OH)_4 groups being insufficient to form bonds with Sn), leading to a limited amount of Sn^{4+} incorporation to form Sn-sil-1. On the other hand, when a solution of TEOS and TPAOH is stirred for only 30 min and then SnCl_4 is added, a clear solution (with no

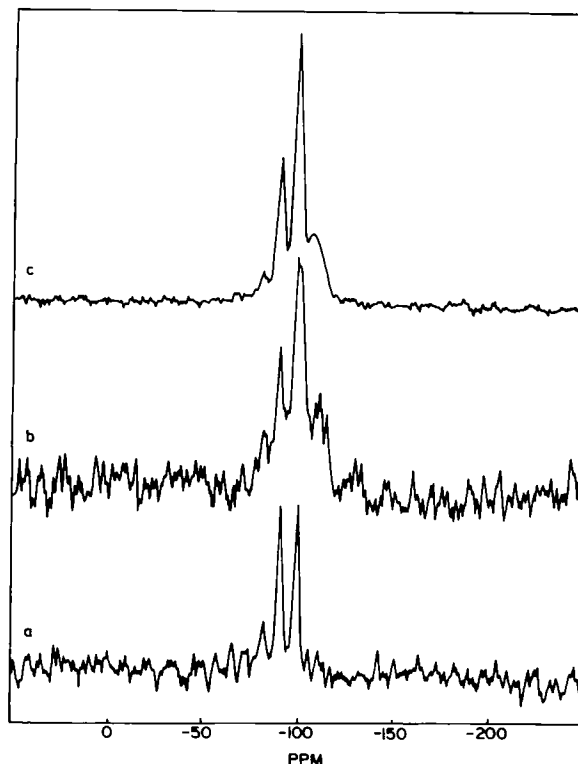


Fig. 3. ^{29}Si liquid NMR spectra of (a) 1.0TEOS:0.45TPAOH stirred for 30 min, (b) 0.03 M SnCl_4 solution added to (a) and stirred for a further 2 h, and (c) reaction mixture (a) stirred for a further 2 h.

turbidity) results due to incomplete hydrolysis of TEOS. Fig. 4 shows that the addition of SnCl_4 to TEOS does not cause any effect on the NMR signal of TEOS. Thus, TEOS acts as a solvent for SnCl_4 and gives a clear solution.

In Fig. 5, spectra a, b and c show the effect of addition of TPAOH to a solution of 0.03 SnCl_4 :1.0TEOS stirred for 1 min and recorded after 10, 20 and 30 min, respectively, on the type of Si species formed. The addition of TPAOH causes the hydrolysis of SnCl_4 to $\text{Sn(OH)}_1\text{Cl}_3$, $\text{Sn(OH)}_2\text{Cl}_2$ and $\text{Sn(OH)}_3\text{Cl}$ but not to Sn(OH)_4 species (Fig. 5(a)). As soon as SnCl_4 is partially hydrolyzed it combines with monomeric Q^0 species, and this combination leads to the formation of Q^1 species and a small amount of Q^2 species (Fig. 5(b), spectrum recorded after 20 min). In the spectrum recorded after 30 min, Q^3 species appeared along with Q^1 and Q^2 species,

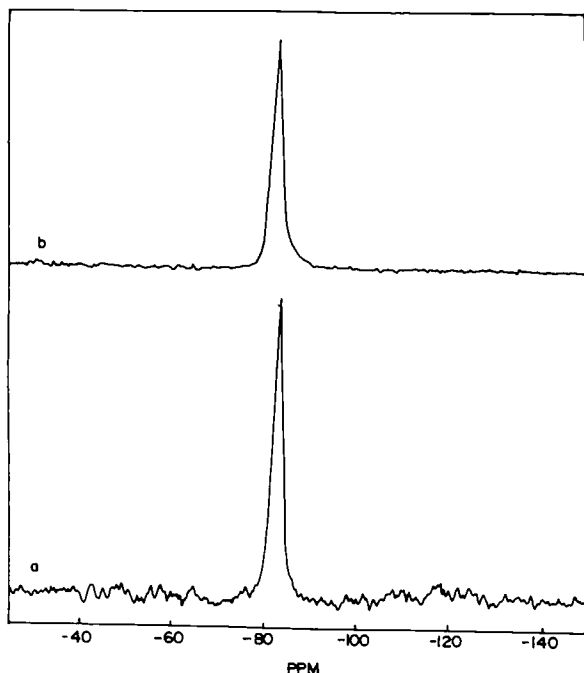


Fig. 4. ^{29}Si liquid NMR spectra of (a) TEOS and (b) 1.0TEOS:0.03SnCl₄ mixture.

resulting in a clear solution (Fig. 5(c)). Since Sn(OH)₄ is not stable in alkaline solutions, it may form solid SnO₂, but SnO₂ precipitation was not observed. Thus, it is reasonable to believe that a partially hydrolyzed SnCl₄ species combines with Q⁰, and then another Sn–Cl bond is hydrolyzed. On the other hand, when the solution is stirred for 30 min, the Q⁰ species almost disappear (Fig. 6(a)). The Q³ species predominate over Q², while the Q⁴ species are present in very small amounts. A comparison of the spectra shown in Figs. 2(b) and 5(a) gives direct evidence for the interaction of Sn species with silicate species in the reaction mixture.

Fig. 6 illustrates the time taken to complete the reaction in a reaction mixture of the molar composition 1.0TEOS:0.03SnCl₄:0.45TPAOH. The spectra given in Figs. 6(a)–(c) indicate that (1) Q⁴ Si species are stronger in the case of “b” and “c” than “a”, as indicated by the intense NMR peak at $\delta = -106.5$ ppm; (2) the reaction is almost complete within 30 min; (iii) aging of the solution (for three months) does not cause any change in the Si species present in the gel; and (iv) oligomers

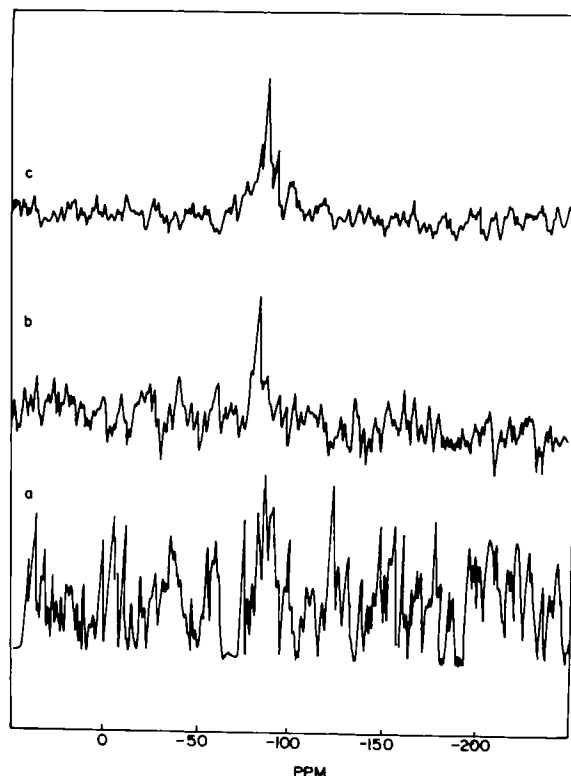


Fig. 5. ^{29}Si liquid NMR spectra of 1.0TEOS:0.03SnCl₄+0.45TPAOH stirred for 1 min. The spectra were recorded after (a) 10 min, (b) 20 min and (c) 30 min.

are formed probably through Si–O–Sn–O–Si and Si–O–Si–O–Si bonds, and not through Sn–O–Sn–O–Sn bonds. If Sn–O–Sn bonds were formed, turbidity or precipitation due to SnO₂ would have been noticed. A comparison of the spectra shown in Fig. 3(a) (solution prepared by mixing TPAOH with TEOS followed by the addition of SnCl₄; method B) and Fig. 6(a) (solution prepared by mixing SnCl₄ with TEOS followed by the addition of TPAOH; method A) indicates that the concentration of Q² and Q³ species is almost the same in the case of method B, whereas Q³ species predominate over Q² species in method A. This indicates that the presence of the heteroatom (Sn) favours the formation of Q³ species as compared to Q² species. Again, a comparison of Figs. 3(b) and 6(b) indicates that the abnormality in the formation of Q⁴ species observed in the case

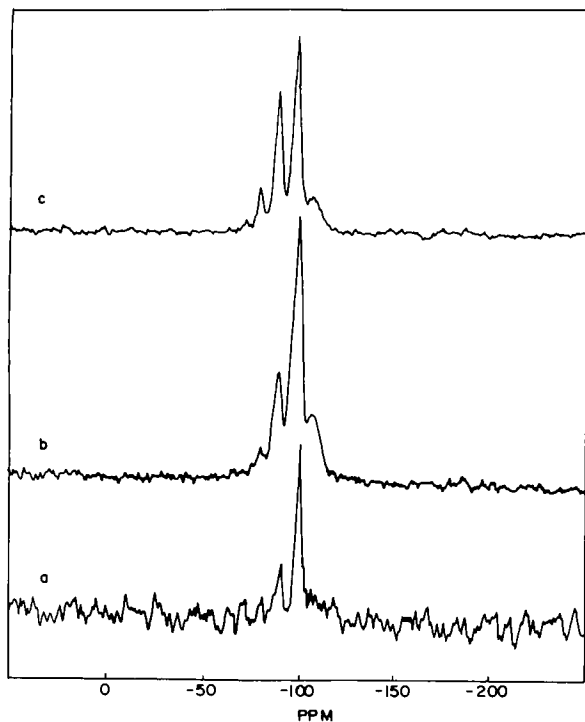


Fig. 6. ^{29}Si liquid NMR spectra of $1.0\text{TEOS}:0.03\text{SnCl}_4+0.45\text{TPAOH}$ (a) stirred for 30 min, (b) stirred for a further 2 h, and (c) reaction mixture (b) after aging for three months.

of method B is also not seen in the case of synthesis of Sn-free sil-1 (Fig. 3(c)) or Sn-sil-1 (Fig. 6(b)) following method A.

3.2. ^{29}Si , ^{119}Sn MAS NMR and ^{119}Sn static NMR studies

^{29}Si and ^{119}Sn MAS NMR spectra of some of the representative samples which were prepared using method A are shown in Fig. 7. Spectra a, b and c illustrate the ^{29}Si MAS NMR spectra of silicalite-1, as-synthesized Sn-sil-1 (Si/Sn=50) and calcined Sn-sil-1, respectively. ^{119}Sn MAS NMR spectra of the as-synthesized sample in a fluoride medium (prepared using method D) (Fig. 7(d)), calcined samples of Sn-sil-1 with Si/Sn=50 and Si/Sn=200 (curves e and f, respectively) are also included. The ^{29}Si MAS NMR spectrum of silicalite-1 shows the expected 24-fold crystallographic multiplicity of a monoclinic ZSM-5 lattice

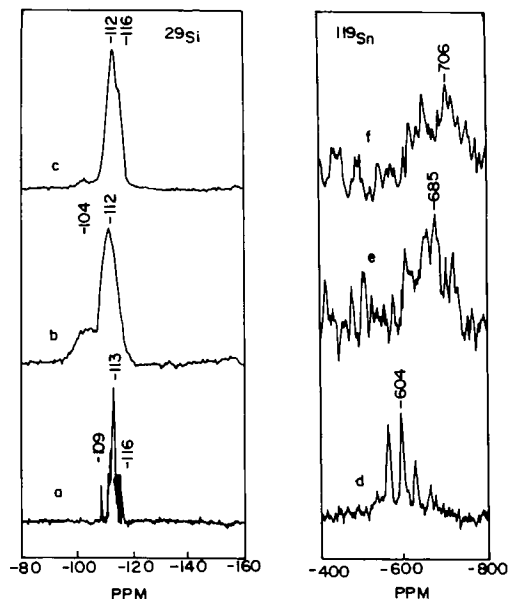


Fig. 7. ^{29}Si MAS NMR spectra of (a) silicalite-1, (b) as-synthesized Sn-sil-1 (Si/Sn=50) and (c) calcined Sn-sil-1 (Si/Sn=50). ^{119}Sn MAS NMR spectra of (d) sample synthesized in a fluoride medium, (e) calcined Sn-sil-1 (Si/Sn=50) and (f) calcined Sn-sil-1 (Si/Sn=200).

(Fig. 7(a)). A similar spectrum was obtained for the sample prepared in a fluoride medium (not shown in Fig. 7). The ^{29}Si MAS NMR spectrum of the as-synthesized Sn-sil-1 (Sn/Sn=50) sample exhibits an intense resonance at -112 ppm flanked by low-field resonance at approximately -104 ppm (with respect to Me_4Si) (curve b). Upon calcination, the intensity of the low-field resonance is reduced (curve c). The broad high-field resonance at -112 ppm is due to the $\text{Si}(\text{OSi})$ environment. The resonance at -104 ppm arises primarily from Si at defect sites, containing $\text{Si}(\text{OH})$, $\text{Si}(\text{OH})_2$ and $\text{Si}-\text{O}-\text{R}$ [15,16]. The Si (1Sn) environment, even if present, is not clearly detectable in the ^{29}Si NMR spectrum due to the high Si/Sn ratio of the sample. However, after calcination, a very weak shoulder develops at around -116 ppm (Fig. 7(c)). In the case of TS-1, this peak at -116 ppm has been attributed to the distorted silicon environment in the tetrahedra containing $\text{Si}-\text{O}-\text{Ti}$ bonds [17–19]. The ^{29}Si MAS NMR spectrum thus merely indicates the presence of terminal silanol groups at which tin may be

located, as further evidenced by ^{119}Sn MAS NMR studies.

Despite the high Si/Sn ratio of the samples, ^{119}Sn NMR signals are detectable owing to the large sensitivity associated with the spin-1/2 of the ^{119}Sn nucleus, which allows us to probe the tin environment directly. For both SnO_2 - and Sn-impregnated silicalite-1 samples, the isotropic peak with a chemical shift at $\delta = -604$ ppm shows the presence of Sn in essentially octahedral coordination. The ^{119}Sn MAS NMR spectrum of the sample synthesized in a fluoride medium shows a chemical shift at -604 ppm with spinning side bands on either side (Fig. 7(d)). This matches well with the tin resonance in pure SnO_2 [20]. For the calcined Sn-sil-1 samples, in spite of overnight data collection the signal-to-noise ratio was poor due to the small concentration of Sn species (Fig. 7(e) and (f)). The ^{119}Sn NMR peaks were located in the range -685 to -706 ppm for all the samples. For octahedrally coordinated tin in the mineral sorensonite, a chemical shift value of -706 ppm has been reported [16]. In many ternary oxides, the octahedral tin environment resonates in the chemical-shift range -450 to -700 ppm [21]. Thus, there is a range of approximately 300 ppm for one particular type of coordination for Sn^{4+} , although the overall ^{119}Sn chemical-shift range spans several thousand ppm [20]. The observed chemical shift for calcined Sn-sil-1 suggests the presence of octahedral tin.

However, static ^{119}Sn NMR spectra of the hydrated and dehydrated form of Sn-sil-1 (Si/Sn = 50), shown in Fig. 8(a) and (b), respectively, are different from the ^{119}Sn MAS NMR spectra. The hydrated form of Sn-sil-1 shows sharp resonances at -687 and -573 ppm (approximately 20% of the -687 ppm peak) (Fig. 8(a)). After dehydration, the peak at -688 ppm remains unchanged, but the peak at -573 ppm is shifted to -439 ppm. This peak at -688 ppm may be associated with an octahedral environment around the ^{119}Sn nucleus. For the dehydrated sample, the ^{119}Sn resonance at -439 ppm may be due to the tetrahedral environment of the Sn^{4+} nucleus, which is shifted to -574 ppm (which may be five-fold coordinated) on hydration. On the basis of other characterization techniques such as XRD (expan-

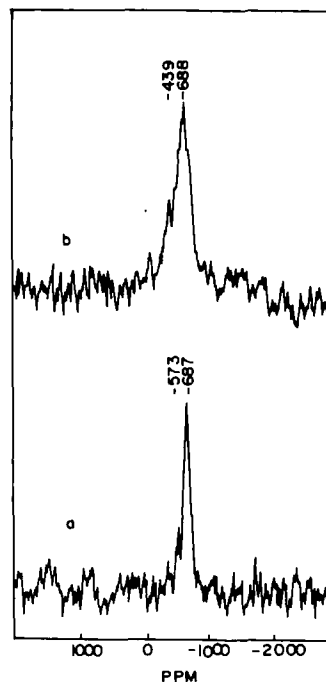


Fig. 8. Static ^{119}Sn NMR spectra of the (a) hydrated and (b) dehydrated forms of Sn-sil-1 (Si/Sn = 50).

sion of the unit cell), FT-IR [12] and Mössbauer spectroscopy [22], we concluded that at least a part of Sn^{4+} ions are in the framework position (Td coordination), which is probably responsible for the signal at -439 ppm in the static ^{119}Sn NMR spectrum. The Sn species linked to the defect silonols seem to be in octahedral coordination, indicated by the MAS NMR signal at -688 ppm. The coordination of Sn^{4+} ions in Sn-sil-1 when exposed to air becomes octahedral (oh) because of its hydrophilic nature and the strong tendency of Sn^{4+} ions to expand their coordination on interaction with moisture. So, in ^{119}Sn MAS NMR, we have observed only the -688 ppm peak assigned to oh coordination. However, when the sample was dehydrated under vacuum and sealed in a glass tube and then exposed to ^{119}Sn static NMR, it gave an additional peak at -439 ppm assigned to Td coordination. Dehydrated Sn-sil-1 (under sealed conditions) cannot be exposed to ^{119}Sn MAS NMR techniques. Hence, both ^{119}Sn static and MAS NMR studies are required.

Thus, Sn^{4+} ions either in substitutional, corner- or edge-sharing positions of the silicate structure or linked to defect silanols tend to assume five- or six-fold coordination with ligands such as $-\text{OH}$ or H_2O very easily due to their larger size. This is supported by the charge transfer (CT) absorptions at 225 and 255 nm, which have been assigned to penta- and hexa-coordinated Sn^{4+} ions [20], respectively.

4. Conclusions

The following conclusions can be drawn from the ^{29}Si liquid NMR spectral studies of Sn-silicalite molecular sieves: (1) TEOS is first hydrolyzed (by TPAOH) into monomeric species Q^0 . (2) SnCl_4 is hydrolyzed and oligomerized immediately into Q^2 and Q^3 species. Sn is probably incorporated into silicate species during oligomerization (SnO_2 is not precipitated in the solution). (3) For the synthesis of Sn-sil-1, the procedure described in method A is more suitable than other procedures. When partially hydrolysed SnCl_4 species combine with the monomer (Q^0) (obtained after the hydrolysis of a mixture of SnCl_4 and TEOS by TPAOH), this leads to the formation of Q^1 , Q^2 , Q^3 and Q^4 species with a clear solution: this is the critical point of method A because this leads to maximum number of possible Si–O–Sn–O–Si bond formations, which is necessary for the substitution of Si^{4+} in the framework of Sn-sil-1 and makes the catalyst more active than any other synthesis method.

^{29}Si solid MAS NMR, ^{119}Sn static and MAS NMR studies indicate that Sn^{4+} ions are probably located in the defect silanols in tetrahedral coordination, but tend to assume five- or six-fold coordination very easily due their larger size.

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