

An Improved Method for TS-1 Synthesis: ^{29}Si NMR Studies

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It is possible to incorporate up to eight Ti ions per unit cell, which is probably the maximum, into the MFI structure (TS-1) using our improved synthesis procedure; ^{29}Si NMR studies have helped in evolving the synthesis route.

The titanium silicate molecular sieve, TS-1, has been found to be a good catalyst for a number of oxidation reactions involving H_2O_2 .¹⁻⁵ Even though it has already found commercial applications,² a number of aspects about the Ti ions, which are believed to be the active centres, are still not clear. For example, what is the coordination of these ions?; and how much Ti can be incorporated into the MFI lattice? Recently, Behrens *et al.*⁶ concluded (based on XANES and EXAFS data) that Ti^{4+} ions are present mostly in octahedral coordination. They have also suggested that, as a result of the octahedral coordination of these ions, their incorporation in the tetrahedral lattice has to be limited. The highest titanium content reported in the literature is 2.5 Ti ions/unit cell (Si : Ti mole ratio = 39) by Taramasso *et al.*⁷

We have examined silico-titanium precursors used in the synthesis of TS-1 by ^{29}Si NMR studies and have optimized a synthesis procedure, which leads to incorporation of up to eight Ti ions/unit cell corresponding to a Si : Ti ratio of 11. We found that lower incorporation of Ti is due to the precipitation of TiO_2 during the preparation of the precursor mixture or during the crystallization of the precursor gel.

The precipitation of TiO_2 during the preparation of the precursor mixture of Si and Ti ions can be avoided by reducing the rate of hydrolysis of the alkoxides. We have modified the synthesis procedure of Taramasso *et al.*⁷ in three ways: First, $\text{Ti}(\text{OEt})_4$ was used as the source of titanium instead of $\text{Ti}(\text{OEt})_4$ as the rate of hydrolysis of the former is slower.⁸ Secondly, $\text{Ti}(\text{OEt})_4$ was dissolved in isopropyl alcohol to avoid the instantaneous hydrolysis of Ti-alkoxide to TiO_2 (once TiO_2 is formed, it is no longer available for incorporation into the framework). Thirdly, the addition sequence was modified, to avoid the formation of TiO_2 . Aqueous TPAOH was first added to $\text{Si}(\text{OEt})_4$ to hydrolyse the Si-alkoxide to monomeric $\text{Si}(\text{OH})_4$ species. Then $\text{Ti}(\text{OEt})_4$ in isopropyl alcohol was added to give a clear solution. At this stage, the monomeric silicate species oligomerize into D5R and 5-1 (pentasil) units, simultaneously incorporating the Ti ions as rapidly as they are produced by the hydrolysis of the

Ti-butoxide. A mismatch between the rate of polymerization of Si^{4+} ions and the hydrolysis of the Ti-alkoxide leads to non-inclusion of some Ti in the lattice. The titanium silicate species slowly crystallize into the MFI structure during autoclaving. Also, as crystallization from a silico-titanium gel has been avoided, the segregation of TiO_2 from the gel at the time of its dissolution during crystallization does not arise.

Investigations of the precursor species present in the synthesis mixture have been carried out by ^{29}Si NMR spectroscopy. Fig. 1(a) shows the ^{29}Si liquid NMR spectrum of $\text{Si}(\text{OEt})_4$ (a sharp peak at $\delta = -82.5$). Addition of aqueous TPAOH causes the immediate hydrolysis of the Si-alkoxide to monomeric $\text{Si}(\text{OH})_4$ (Q^0) and small amounts of the dimeric (Q^1) silicate species [Fig. 1(b)]. The addition of $\text{Ti}(\text{OEt})_4$ in isopropyl alcohol to the mixture of TPAOH and $\text{Si}(\text{OEt})_4$ gives a clear solution containing oligomerized silicate and titanium silicate species (mainly Q^2 and Q^3) [Fig. 1(c)]. As the ageing time increases, the concentration of the Q^3 species, the precursor for the MFI structure, increases.⁹ This method of

Table 1 Unit cell composition,^a volume^b and symmetry^d

Sample	Si/Ti	Unit cell composition	Unit cell volume/ \AA^3	Symmetry
A ^c	—	$\text{Si}_{96}\text{O}_{192}$	5344	M
B	99	$\text{Si}_{95.03}\text{Ti}_{0.97}\text{O}_{192}$	5348	O
C	48	$\text{Si}_{94.04}\text{Ti}_{1.96}\text{O}_{192}$	5349	O
D	23	$\text{Si}_{91.86}\text{Ti}_{4.14}\text{O}_{192}$	5352	O
E	17	$\text{Si}_{90.55}\text{Ti}_{5.45}\text{O}_{192}$	5378	O
F	10	$\text{Si}_{87.67}\text{Ti}_{8.33}\text{O}_{192}$	5396	O
G	7	$\text{Si}_{84.15}\text{Ti}_{11.85}\text{O}_{192}$	5395	O

^a Molar composition of gel (excluding alcohol): 0.36 TPAOH : 0.00–0.10 TiO_2 : SiO_2 : 35 H_2O . The chemical compositions of the samples were obtained from both wet chemical analytical methods and ICP-analysis (Jobin Yvon JYU-38 VHR). (In addition, the presence of Ti in the framework was confirmed by IR spectroscopic studies in the zeolite-framework region. The line observed at 960 cm^{-1} (attributed to Si–O–Ti linkages^{3,5} in the zeolite framework) was found to be proportional to the titanium content of the samples B to F). ^b From powder XRD patterns (Philips, PW-1710, Cu-K α) using PDP-11 software (Dept. of Chemical Sciences, University of Trieste, Italy). ^c Silicalite-1 (Si : Al > 2000). ^d M = monoclinic, O = orthorhombic.

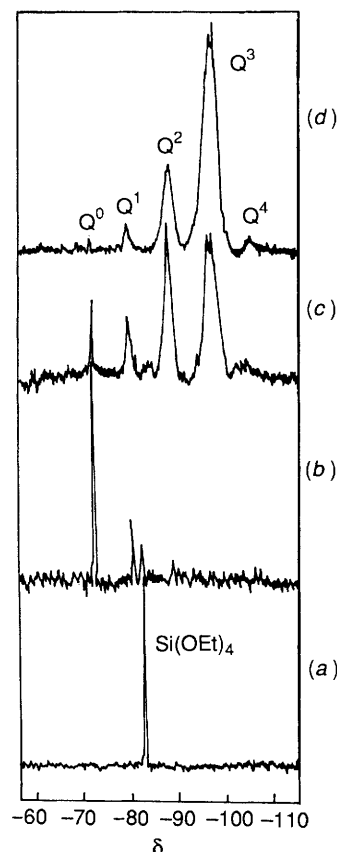


Fig. 1 ^{29}Si NMR spectra of silicate and titanium silicate species: (a) $\text{Si}(\text{OEt})_4$. (b) SiO_2 : 0.34 TPAOH : 34 H_2O ; (TPAOH = tetrapropyl ammonium hydroxide). (c) SiO_2 : 0.027 TiO_2 : 0.34 TPAOH : 0.40 IPA : 34 H_2O (IPA = isopropyl alcohol). (d) sample c, aged for 24 h at 298 K.

^{29}Si NMR spectra were recorded using Bruker MSL 300 FT-NMR spectrometer operated at 293 K. Spectra were collected using 90° pulse with 5 s recycle delay time. 200–2000 FID were accumulated. D_2O external lock was used to improve the resolution of the spectra. Chemical shifts were referenced to SiMe_4 .

synthesis provides TS-1 with larger amounts of Ti in the framework.

In a typical synthesis experiment, 70 g TPAOH (20% aqueous solution) was added to 50 g Si(OEt)₄. To the resultant clear solution, a solution of 2.3 g Ti(OBu)₄ in isopropyl alcohol (15 g) was added. Finally, H₂O (60 g) was added to the above clear solution. The mixture was then crystallized at 433 K for 12 h under autogeneous pressure. All the chemicals used were from Aldrich, USA.

Table 1 presents the results of the characterization of the TS-1 samples with different Si:Ti ratios. The samples (A-F) were highly crystalline and free from amorphous non-framework TiO₂, but sample G had some amorphous TiO₂. We conclude that the maximum number of Ti ions that can be incorporated in the MFI framework is eight Ti ions per unit cell (sample F), which is similar to that reported in the case of Al-incorporation (ZSM-5).¹⁰

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