

Studies on the synthesis of titanium silicalite, TS-1

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A new procedure for the synthesis of titanium silicalite-1 (TS-1) with high Ti/(Si + Ti) ratios is being reported. The rationale for the method adopted and the reasons for the incorporation of more Ti (than reported by earlier workers) are discussed based on liquid-phase n.m.r. studies of the precursors and reaction mixture. The influence of various synthesis parameters like temperature, SiO₂/TiO₂, OH⁻/SiO₂, and H₂O/SiO₂ ratios, the silica source, and nature of organic additives on the synthesis of TS-1 is discussed. The TS-1 samples have been characterized by XRD, i.r. t.g./d.t.a., and SEM.

Keywords: TS-1 synthesis; ²⁹Si n.m.r. studies; kinetics of crystallization of TS-1; characterization of TS-1; titaniumsilicates

INTRODUCTION

Titanium silicalite-1 (TS-1) belongs to the MFI structure group.¹ It possesses interesting catalytic properties, especially in reactions involving the use of H₂O₂ as the oxidant² like the hydroxylation of phenol,³ benzene,⁴ alkanes,⁵ and ammoxidation of cyclohexanone.⁶ Taramasso et al.⁷ reported two methods for the hydrothermal synthesis of TS-1. A major problem often encountered during the synthesis of the TS-1 molecular sieve is the precipitation of the oxides of titanium outside the lattice framework. This gives rise to samples that, though they are highly crystalline, are inactive in oxidation reactions. Further, the maximum mole fraction of titanium that could be incorporated in TS-1 according to literature reports⁷⁻⁹ is 0.025 (corresponding to Si/Ti = 39), even though reactant mixtures with a Si/Ti ratio as low as 5 had been used⁷ in the synthesis.

This paper presents a modified synthesis procedure to incorporate larger amounts of Ti⁴⁺ in the MFI framework (Si/Ti lower than 20). It also identifies (by n.m.r.) the silicate species formed in the reaction mixture during synthesis. The kinetics of crystallization and the influence of various factors on the synthesis of TS-1 are also reported.

EXPERIMENTAL

A general procedure for the preparation of crystalline TS-1 is given below:

To a solution of tetraethyl orthosilicate (TEOS), an

appropriate amount (almost three-fourths of the required quantity) of aqueous tetrapropylammonium hydroxide (20%, aq. TPAOH solution, Aldrich) was added to hydrolyze the TEOS. To the resultant liquid mixture (pH 12.8), a solution of the required quantity of titanium tetrabutoxide [Ti(OBu)₄] in dry isopropyl alcohol was added dropwise under vigorous stirring. The clear liquid thus obtained was stirred for 15 min in order to complete the hydrolysis of TEOS and Ti(OBu)₄. Finally, the remaining TPAOH in double-distilled water was added slowly to the above mixture. The final mixture was stirred at 348–353 K for about 3 h to remove the alcohol. The chemical composition of the initial gel was:

$x\text{TiO}_2 \cdot \text{SiO}_2 : 0.36 \text{ TPA} : 35 \text{ H}_2\text{O}$ (where $x = 0.00-0.10$)

The crystallization was carried out at 443 K, typically for 1 d under static conditions. The solid obtained was filtered, washed with distilled water, and dried at 373 K for 5 h in static air.

N.m.r. measurements of the clear aqueous solutions were recorded using a Bruker MSL 300 FTn.m.r. spectrometer operated at 293 K. ²⁹Si n.m.r. spectra were collected using 90° pulse with 5 s recycle delay time. FIDs, 200–2000, were accumulated. A D₂O lock was used to improve the apparent resolution of the spectra. Chemical shifts were referred to external TMS.

The crystalline phase identification was carried out by XRD (Rigaku, Model D/MAX III VC). Chemical analyses were performed by wet chemical methods and ICP (Jobin Yuon-JY VHR) spectrometry. The TS-1 samples were further characterized by i.r. spectroscopy (Perkin-Elmer 221), t.g./d.t.a. (Netsch, Model STA 490), and scanning electron microscopy (Cambridge, Model 150).

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RESULTS AND DISCUSSION

Synthesis procedures

The synthesis of crystalline TS-1 from the alkoxides of Si and Ti in the presence of TPAOH involves the initial hydrolysis of the alkoxides. If there are differences in the relative rates of hydrolysis of the two alkoxides, then the precipitation of solid TiO_2 or SiO_2 can occur. Preliminary tests were carried out to examine the hydrolysis behavior of Si and Ti alkoxides. Table 1 presents the results.

The following conclusions are reached from the results of Table 1. These conclusions are also supported by n.m.r. data that are reported in a later section.

- (i) In the presence of TPAOH, SiO_2 is not precipitated from $\text{Si}(\text{OC}_2\text{H}_5)_4$. Monomeric SiO_4^{4-} species stabilized by TPA^+ ions are apparently formed (Exp. 1, Table 1) (n.m.r. data reported later).
- (ii) Ti-alkoxides hydrolyze to Ti-hydroxides (which transform to the oxide on calcination) in the presence of TPAOH (Exp. 2).
- (iii) The addition of $\text{Ti}(\text{OBu})_4$ to monomeric $\text{Si}(\text{OH})_4$ species (stabilized by TPA^+ ions) does not lead to Ti-hydroxide formation. The Ti^{4+} ions are probably stabilized by forming titanium silicate species (Exp. 7, Table 1).
- (iv) The addition of $\text{Ti}(\text{Oisopr})_4$ (instead of the butoxide) to monomeric $\text{Si}(\text{OH})_4$ species causes precipitation of Ti (Exp. 8, Table 1), presumably due to the more rapid hydrolysis¹⁰ of the isopropoxide compared to the butoxide.

Based on the above results, the following modified procedure was adopted for the synthesis of TS-1. This procedure leads to the formation of TS-1 with

Table 1 Hydrolysis of TEOS and tetraalkyltitanates

| | Reactants | Observation |
|------|---|-----------------------|
| (1) | 2 ml $\text{Si}(\text{OEt})_4$ + 2 ml TPAOH | Clear solution |
| (2) | 0.5 ml $\text{Ti}(\text{OR})_4^a$ + 2 ml TPAOH | Immediate precipitate |
| (3) | 0.5 ml $\text{Ti}(\text{OR})_4^a$ + 2 ml TPAOH (in 5 ml isopropyl alcohol) | Immediate precipitate |
| (4) | 5 ml $\text{Si}(\text{OEt})_4$ + 0.2 ml $\text{Ti}(\text{OBu})_4$ | Clear solution |
| (5) | 5 ml $\text{Si}(\text{OEt})_4$ + 0.2 ml $\text{Ti}(\text{OBu})_4$ (in isopropyl alcohol) | Clear solution |
| (6) | 5 ml $\text{Si}(\text{OEt})_4$ + 0.2 ml $\text{Ti}(\text{OBu})_4$ + 5 ml TPAOH | Turbid solution |
| (7) | 5 ml $\text{Si}(\text{OEt})_4$ + 5 ml TPAOH + 0.2 ml $\text{Ti}(\text{OBu})_4$ (in isopropyl alcohol) | Clear solution |
| (8) | 5 ml $\text{Si}(\text{OEt})_4$ + 5 ml TPAOH + 0.2 ml $\text{Ti}(\text{Oisopr})_4$ (isopropyl alcohol) | Turbid solution |
| (9) | 5 ml $\text{Si}(\text{OEt})_4$ + 0.2 ml $\text{Ti}(\text{OEt})_4$ + 5 ml TPAOH | Turbid solution |
| (10) | 5 ml $\text{Si}(\text{OEt})_4$ + 5 ml TPAOH + 0.2 ml $\text{Ti}(\text{OEt})_4$ (in isopropyl alcohol) | Turbid solution |

^a R = CH_3 , C_2H_5 , C_3H_7 , C_4H_9

TPAOH = 20% aqueous tetrapropylammonium hydroxide (Aldrich); All experiments were carried out at 300 K

higher Ti contents ($\text{Ti}/(\text{Si} + \text{Ti}) \approx 0.1$) when compared to the lower Ti contents [$\text{Ti}/(\text{Si} + \text{Ti}) \approx 0.03$] reported by earlier workers.⁷⁻⁹

Three modifications have been made: First, $\text{Ti}(\text{OBu})_4$ was used as the source of titanium instead of the conventional $\text{Ti}(\text{OC}_2\text{H}_5)_4$. Second, the $\text{Ti}(\text{OBu})_4$ was dissolved in **dry** isopropyl alcohol to avoid the instantaneous hydrolysis of $\text{Ti}(\text{OBu})_4$ to the hydroxide, which results in poor incorporation of Ti. Third, the sequence of addition of the reactants was modified as follows:

TPAOH was added first to $\text{Si}(\text{OC}_2\text{H}_5)_4$ under stirring to hydrolyze all $\text{Si}(\text{OC}_2\text{H}_5)_4$ into monomeric $\text{Si}(\text{OH})_4$ species. $\text{Ti}(\text{OBu})_4$ in isopropyl alcohol was then added soon after the addition of aqueous TPAOH [within 5–50 min to avoid the polymerization of $\text{Si}(\text{OH})_4$] to form a clear solution. In this modified procedure, the incorporation of titanium in the silicate network does not depend on the relative rates of hydrolysis of the two alkoxides. It depends mainly on the concentration of monomeric and dimeric silicate species encountered by titanium in solution. It may be mentioned here that while the silicon alkoxides are always present as monomers, the titanium alkoxides are present mostly as trimers.¹¹ During hydrolysis, the trimers are converted into monomeric species that combine with silica monomers, leading to the formation of $\text{Si}-\text{O}-\text{Ti}-\text{O}-\text{Si}$ bonds instead of $\text{Ti}-\text{O}-\text{Ti}$ bonds. The above method of synthesis, hence, provides TS-1 with higher Ti content in the silicate framework [$\text{Ti}/(\text{Si} + \text{Ti}) = 0.125$]. Further, the synthesis time was also reduced considerably (1 d at 433 K compared to 6–30 d⁷ at 448 K). The synthesis procedure described above is schematically represented as method A in Figure 1. For a typical synthesis of TS-1 (with $\text{Si}/\text{Ti} = 33$), the quantities of the reagents used were TEOS = 45 g; TPAOH (20% aq. solution) = 70 g; $\text{Ti}(\text{OBu})_4 = 2.2$ g in 10 g of isopropyl alcohol; and water 70 g (added to the mixture at the end, before autoclaving).

An alternate method of converting $\text{Si}(\text{OC}_2\text{H}_5)_4$ into monomeric silicate species is by acid (H^+) hydrolysis (method B in Figure 1). When $\text{Ti}(\text{OBu})_4$ (in isopropyl alcohol) is then added, no turbid solution is produced, suggesting the absence of TiO_2 or SiO_2 precipitates. A dense transparent titanium silicate gel was next formed by adding TPAOH to the solution containing Si and Ti. This gel slowly dissolved to give a slightly turbid solution (pH 12.5). The turbidity suggests the presence of the hydroxides of Ti/Si. The turbid solution was then crystallized as before. The total yield of the crystalline product (TS-1) obtained by method B was slightly higher (86% for a $\text{Si}/\text{Ti} = 33$) than that by method A (80% for a $\text{Si}/\text{Ti} = 33$, see Figure 1). However, Ti incorporation was slightly lower (confirmed from the 960 cm^{-1} i.r. band, ²⁹Si n.m.r., and catalytic tests¹²) than in the case of method A. During dissolution of the thick gel, the polymeric $\text{Si}-\text{O}-\text{Ti}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{Si}$ species break up into soluble titanium silicate and silicate oligomers and insoluble TiO_2 , resulting in the formation of a turbid solution. This leads to a lower incorporation of

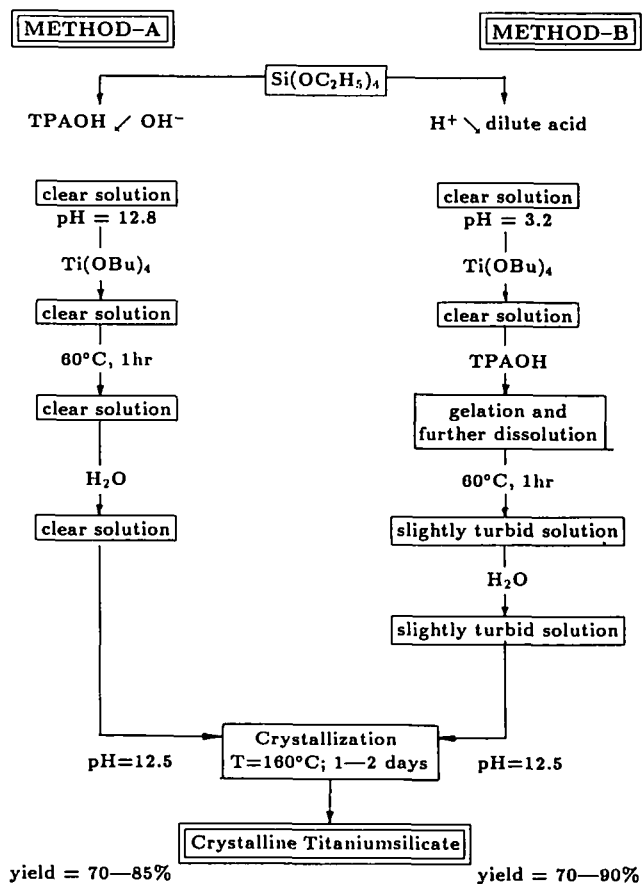


Figure 1 Schematic representation of TS-1 synthesis.

Ti^{4+} in the silicate framework since part of the Ti is lost as TiO_2 .

^{29}Si high-resolution liquid n.m.r. studies

In the case of (aluminum-containing) zeolites, Barer postulated¹³ that zeolite nuclei are formed from the precursors present as soluble aluminosilicate species in the synthesis solutions. High-resolution liquid ^{29}Si n.m.r. can provide information about the silicate species present in the solution phase during zeolite synthesis.¹⁴ Since titanium silicates can be synthesized from a clear solution medium,^{4,9,12} it was easy to study the species responsible for the Si–O–Ti bond formation. The synthesis procedure described in method A was systematically investigated by ^{29}Si n.m.r. The n.m.r. spectra are presented in Figure 2.

Figure 2a is the ^{29}Si liquid n.m.r. spectrum of $\text{Si}(\text{OEt})_4$. There is a sharp peak at $\delta = -82.5$ ppm. Addition of aqueous TPAOH to $\text{Si}(\text{OEt})_4$ solution causes immediate hydrolysis of the alkoxide to monomeric (Q^0) and a small amount of the dimeric $(\text{OH})_3\text{Si}-\text{O}-\text{Si}(\text{OH})_3$ (Q^1) species (Figure 2, spectrum b). At this stage, the mixture is still a clear solution. After about 200 min, the (Q^2), $(\text{OH})_2\text{Si}-[\text{O}-\text{Si}(\text{OH})_3]_2$ peak starts appearing at $\delta = -90$ ppm. The addition of $\text{Ti}(\text{OBu})_4$ to the solution containing $\text{Si}(\text{OEt})_4$, TPAOH, and water gives a clear solution again (see Table 1, Exp. 7) and leads to the immediate

shift of the Q^0 and Q^1 species into Q^2 and Q^3 [$\text{HO}-\text{Si}-\text{O}-(\text{M}-(\text{OH})_3)_3$] (where M = Si or Ti) silicate and titanium silicate species, (spectrum c, Figure 2), clearly indicating the formation of oligomers probably through Si–O–Ti–O–Si and Si–O–Si–O–Si bonds and not Ti–O–Ti–O–Ti bonds. If Ti–O–Ti bonds were formed, turbidity or precipitation due to TiO_2 would have been noticed. The broadness of the Q^2 and Q^3 titanium silicate and silicate species may originate from a wide distribution of similar, closely related species that exist in equilibrium with each other. Species Q^4 , $\text{Si}-[\text{O}-\text{M}-(\text{OH})_3]_4$, is also seen in the spectrum (curve c). These titanium silicate species are stable in solution even on further dilution with water. As the aging time increases, the concentration of monomer peaks decreases and the oligomers (Q^2 , Q^3 , and Q^4) become predominant. The relative amount of Q^3 increases with increasing aging time (spectrum d, Figure 2). A peak at $\delta = -98.5$ ppm assigned to D5R units¹³ is also found in spectrum d.

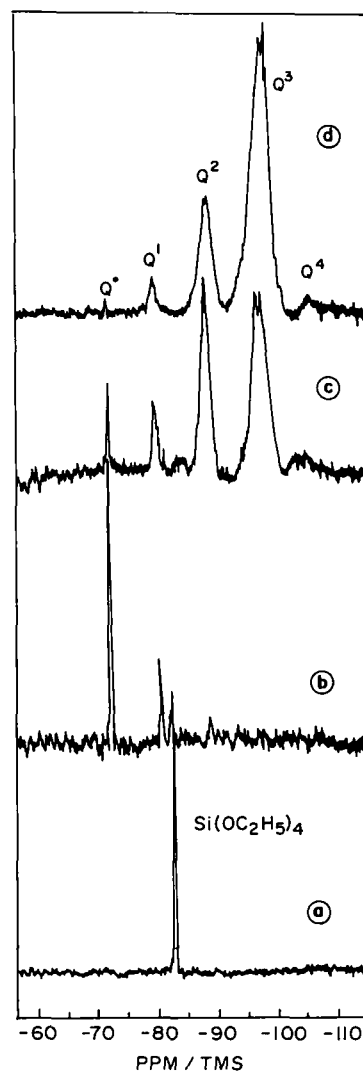


Figure 2 ^{29}Si n.m.r. spectra of silicate and titanium silicate species: (a) TEOS; (b) $\text{SiO}_2:0.34 \text{ TPA}^+:34 \text{ H}_2\text{O}$; (c) $\text{SiO}_2:0.027 \text{ TiO}_2:0.34 \text{ TPA}^+:0.40 \text{ IPA}:34 \text{ H}_2\text{O}$; (d) sample c, aged for 24 h at 298 K.

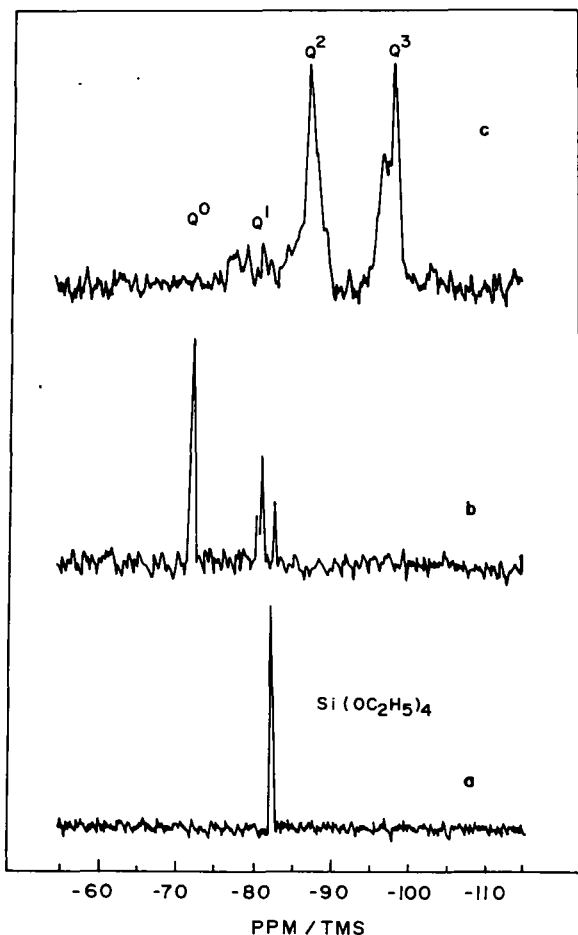


Figure 3 ^{29}Si n.m.r. spectra of silicate species: (a) TEOS; (b) $\text{SiO}_2\text{:}0.34 \text{ TPA}^+\text{:}34 \text{ H}_2\text{O}$; (c) $\text{SiO}_2\text{:}0.34 \text{ TPA}^+\text{:}0.76 \text{ IPA}\text{:}34 \text{ H}_2\text{O}$.

To examine whether the isopropyl alcohol that is present with $\text{Ti}(\text{OBU})_4$ causes the transformation of species Q^0 to Q^2 and Q^3 , isopropyl alcohol was added to the solution containing $\text{Si}(\text{OH})_4$. The ^{29}Si n.m.r. spectra (Figure 3) show that isopropyl alcohol also plays a key role in redistributing the silicate ions. Boxhoorn et al.¹⁵ also observed the immediate redistribution of silicate species to D5R by the addition of solvents including alcohols. Addition of $\text{Ti}(\text{OBU})_4$ to the solution containing Q^2 and Q^3 silicate species (after the polymerization of Q^0) caused formation of a turbid solution due to the precipitation of TiO_2 [the availability of free $\text{Si}(\text{OH})_4$ groups being insufficient to form a bond with Ti], leading to a limited amount of Ti^{4+} incorporation into TS-1. The n.m.r. spectrum of this mixture (not shown in Figure 3) showed a broad band and no distinct species could be observed.

Hence, it is concluded that the addition of $\text{Ti}(\text{OBU})_4$ to the monomeric silicate species leads to better incorporation of Ti in the lattice (method A). Further, gelation and redissolution of the titanium silicate gel, a procedure generally adopted in the preparation of metallosilicates, leads to poor incorporation of titanium in the MFI framework.

KINETICS OF CRYSTALLIZATION

Effect of temperature on the kinetics of crystallization

Based on some preliminary experiments, the following molar composition of the reaction mixture was chosen for studies on the crystallization kinetics:

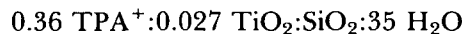


Figure 4 shows the influence of temperature on the nucleation and crystallization of TS-1. The curves a, b, and c and point d have been obtained at 393, 413, 433, and 453 K, respectively, for the above batch composition. Increasing the temperature of crystallization decreased the nucleation period and increased crystallization rates considerably. At all temperatures, fully crystalline TS-1 was obtained. The calculated apparent activation energies (from the Arrhenius equation) of nucleation (E_n) and crystallization (E_c) are 34.86 and 38.19 kJ mole^{-1} , respectively. The apparent activation energies of E_n and E_c for MFI-zeolites depends on the reaction parameters, namely, the nature and amount of the template, silica source, Si/M ($\text{M} = \text{Al}^{3+}$, Fe^{3+} , or Ti^{4+}) ratio, and the nature of the metal ions. Crystallization of zeolites from organic hydroxides involves lower activation energies than from the corresponding bromides. Using organic hydroxides as templates, Chao et al.¹⁶ reported values of $E_n = 25 \text{ kJ mole}^{-1}$ and $E_c = 81.5 \text{ kJ mole}^{-1}$. Higher values of $E_n = 107.5$ and $E_c = 81.5 \text{ kJ mole}^{-1}$ were reported by Erdem and Sand¹⁷ for bromide templates.

Effect of $\text{SiO}_2/\text{TiO}_2$ ratio

TS-1 was synthesized as a crystalline phase over the temperature range 393–453 K with varying batch compositions ($\text{SiO}_2/\text{TiO}_2 = 17\text{--}160$). Figure 5 shows the typical crystallization curves at 433 K for different reactant compositions. As the titanium content increases, the rates of nucleation and crystal growth decrease. However, the effect is not significant above a $\text{SiO}_2/\text{TiO}_2$ ratio of 33. These results are consistent

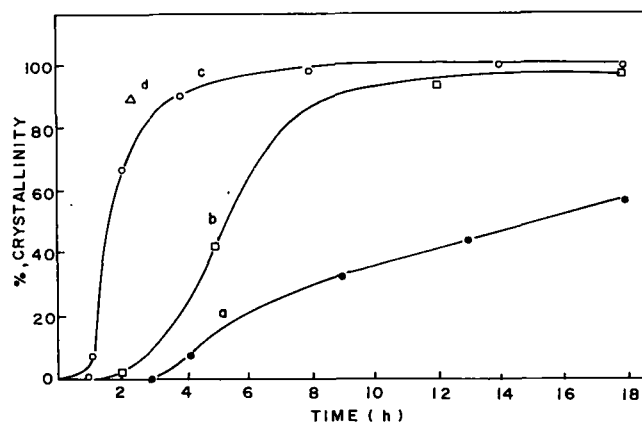


Figure 4 Kinetics of crystallization of TS-1 at (a) 393 K, (b) 413 K, (c) 433 K, and (d) 453 K.

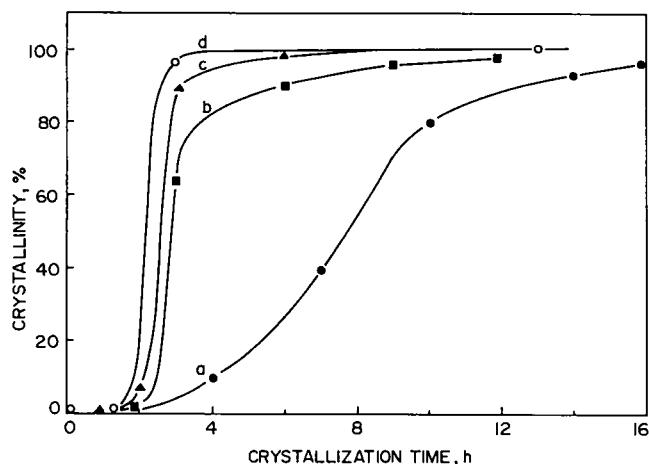


Figure 5 Kinetics of crystallization: influence of $\text{SiO}_2/\text{TiO}_2$ ratio at 433 K. Curves a–d refer to $\text{SiO}_2/\text{TiO}_2$ molar ratios of 17, 33, and 99 and silicalite-1.

with those reported in the case of other metal-substituted zeolites.^{16,18,19} Table 2 compares the $\text{SiO}_2/\text{TiO}_2$ molar ratios and the chemical compositions of the crystalline solids. The synthesis method A described in this paper always produced crystalline TS-1 with larger amounts of Ti incorporation compared to the Si/Ti ratio in the starting reaction mixture. The lower incorporation of Si during crystallization of TS-1 is supported by the following observations:

- (i) No Ti was detected in the mother liquor after filtration, but significant amounts of Si were detected in all cases.
- (ii) The yield of the crystalline product decreased with decreasing Ti content in the starting mixture.

Effect of template OH^-/SiO_2 ratio

Figure 6 shows the crystallization curves for TS-1 systems with varying amounts of TPAOH, other parameters being kept constant. At very low ratios of OH^-/SiO_2 (0.1), the rates of nucleation and crystallization are very low (Figure 6, curve a). As the concentration of TPAOH increases, the rate increases, indicating the formation of more nuclei responsible for nucleation and subsequent crystallization. Beyond an OH^-/SiO_2 ratio of 0.36, however, the

Table 2 Chemical composition and yield of crystalline TS-1

| Sample | $\text{SiO}_2/\text{TiO}_2$ (molar) | Chemical composition of the crystalline products (wt%) ^a | | | | Yield (wt%) crystalline product) |
|---------------------|--|---|----------------|------|-------|--|
| | | SiO_2 | TiO_2 | C | N | |
| a(S-1) ^b | — | 82.54 | — | 7.3 | 0.711 | 20 |
| b | 99 | 78.43 | 1.06 | 7.1 | 0.692 | 65 |
| c | 47 | 78.24 | 2.18 | 7.9 | 0.769 | 75 |
| d | 22 | 74.43 | 4.47 | 8.29 | 0.807 | 80 |
| e | 17 | 73.52 | 5.89 | 8.41 | 0.818 | 80 |
| f | 10 | 70.34 | 8.98 | 8.52 | 0.830 | 80 |
| g | 07 | 62.80 | 12.22 | 8.60 | 0.838 | 85 |

^a Na^+/K^+ impurities less than 3 ppm; rest is hydrogen and water
^bSilicalite-1

total yield of the crystallized product decreases to 60% (compared to ~80% at $\text{OH}^-/\text{SiO}_2 = 0.36$). The total yield of silicalite at $\text{OH}^-/\text{SiO}_2 = 0.36$ (in the absence of Ti) is < 20%. The amount of titanium incorporation in the MFI framework was inferred from the proportional increase in the intensity of the 960 cm^{-1} band.^{12,20} Similar results have also been reported by Kraushaar.⁹

Effect of $\text{H}_2\text{O}/\text{SiO}_2$ ratio

The dilution of the gel mixture with water in the TS-1 synthesis is found to have little influence on the rate of crystallization. It is well known that MFI-type zeolites can be crystallized using a wide range of $\text{H}_2\text{O}/\text{SiO}_2$ ratios.^{21,22} In the case of ZSM-5, Rollmann and Valyocsik²² also reported that the $\text{H}_2\text{O}/\text{SiO}_2$ ratio had little effect on the rate of crystallization. Since TS-1 is synthesized from the solution phase, the concentration of the active nuclei does not change significantly on further dilution with water.

The nature of the silica source

The source of silica also plays an important factor in controlling the crystallization rates of MFI-type zeolites. Silica sources containing large amounts of the silica monomer crystallize faster than gels in which silica is present in a highly polymeric form.²³ Although the crystallization rates are significantly affected by the nature of the silica source, almost all the silica sources (in our experiments) crystallize the MFI type of zeolites. Crystalline TS-1 is successfully synthesized from silicon alkoxides, because the latter can be hydrolyzed to monomeric or lower-branched silicate species by aqueous TPAOH. Further, they are also free of alkali or alkaline earth metal ions. TS-1 was also synthesized using silica sol. The polymeric silica species present in the silica sol are depolymerized into monomeric and lower-branched silicate (Q^0 and Q^1) species in the presence of TPAOH. The presence of a small amount of Na^+ (0.8 wt% Na_2O) in silica sol does not cause the precipitation of TiO_2 . However, the TS-1 prepared from silica sol is less active in oxidation reactions compared to TS-1 prepared using silicon alkoxide.²⁰

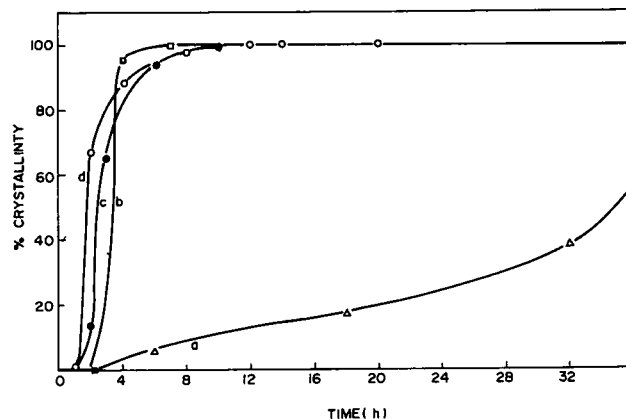


Figure 6 Kinetics of crystallization: influence of OH^-/SiO_2 ratio at 433 K. Curves a–d refer to $\text{OH}^-/\text{SiO}_2 = 0.1, 0.17, 0.36,$ and 0.72 .

Table 3 Influence of organic additives on the crystallization of TS-1^a

| Organic additive | Temp. (K) | Crystallization time (h) | Crystal Phase | % Crystallization | Catalytic activity (theo. phenol conv., %) ^b |
|-----------------------------|-----------|--------------------------|---------------|-------------------|---|
| TPAOH | 433 | 12 | MFI | > 95 | > 90 |
| TBAOH | 433 | 12 | MEL | > 95 | > 80 |
| TEAOH | 433 | 120 | MFI | 70 | — |
| TMAOH | 433 | 500 | — | — | — |
| TEBABr + NH ₄ OH | 433 | 72 | MFI | > 95 | — |
| TPABr + NH ₄ OH | 433 | 60 | MFI | > 95 | — |
| TPA | 433 | 200 | — | — | — |
| TPA + NH ₄ OH | 433 | 600 | MFI | > 60 | — |

^a0.36 R:0.027 TiO₂:SiO₂:35 H₂O; R = organic additive

^bTheoretical phenol conv. = Experimental phenol conversion/Expected phenol conversion × 100. (Experimental details of phenol hydroxylation are reported in ref. 25.)

The nature of the organic additive

Although MFI-type zeolites can be synthesized using a large number of organic additives (Table 3), only TPAOH could crystallize TS-1 with an efficient incorporation of Ti in the MFI-type framework. A titanium silicalite with MEL-type structure (TS-2) has also been synthesized using tetrabutylammonium hydroxide (TBAOH) under similar synthesis conditions.²⁴ A mixture of tripropylamine and ammonia solution also crystallizes TS-1 (MFI structure), but the crystallization takes more than 35 d at 453 K. Tripropylamine, triethylamine, trimethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, and their mixtures did not form any crystalline phase even after 60 d. TS-1 synthesized using TPAOH is highly active in the hydroxylation of phenol with H₂O₂ (Table 3).

Mechanism for silicalite and titanium silicalite crystallization

The following conclusions have been drawn from our results of n.m.r. spectroscopy and crystallization kinetics:

1. Tetraethyl orthosilicate (TEOS) is hydrolyzed by aqueous TPAOH into monomeric and lower-branched silicate ions (Q⁰ and Q¹).
2. The silicate monomers then oligomerize into Q² and Q³ units when titanium tetrabutoxide and isopropyl alcohol are added. The titanium tetrabutoxide hydrolyzes rapidly but does not precipitate as TiO₂. Titanium is probably incorporated into the silicate species during the oligomerization process.
3. As the aging time increases, the Q³ silicate/titanium silicate species (mainly D5R units) are predominant, indicating that the most favored titanium silicate and silicate species to form an active nuclei are the Q³ species.

Since silicalite and titanium silicalite are crystallized directly from a clear aqueous medium, soluble silicate

ions are the reactive species responsible for nuclei formation. Van Santen et al.²⁶ proposed that the D5R species are the precursors of ZSM-5 zeolites via ring opening and polymerization of the D5R silicate anions.

CHARACTERIZATION

X-ray diffraction

Figure 7 presents the X-ray powder diffraction patterns for crystalline TS-1 and silicalite-1. The XRD patterns for the as-synthesized TS-1 (a) and silicalite-1 (b) are characteristic of the MFI-type structure with an orthorhombic symmetry. Upon calcination at 823 K in air (to remove TPA⁺), silicalite-1 is transformed into a material with monoclinic symmetry, while TS-1 retains its orthorhombic symmetry.

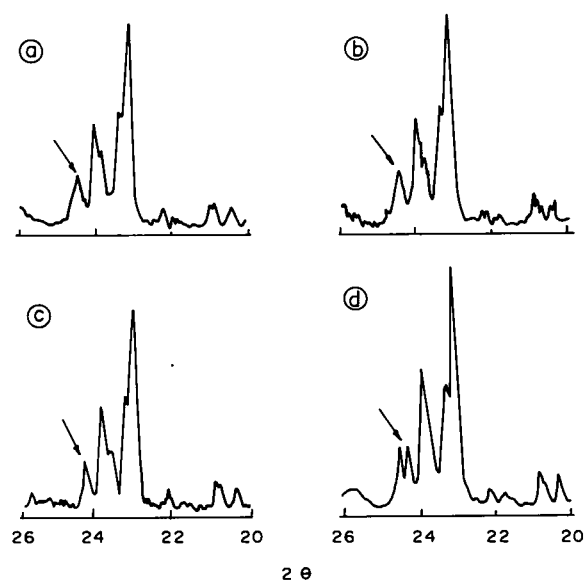


Figure 7 X-ray powder diffraction patterns of silicalite-1 and TS-1; as-synthesized samples: (a) silicalite-1, (b) TS-1; calcined samples: (c) TS-1, (d) silicalite-1.

The incorporation of Ti^{4+} in the MFI-type framework causes an increase in its unit cell dimensions, the increase being proportional to the titanium content.^{8,9,12}

Infrared spectroscopy

The lattice vibrational bands ($200\text{--}1300\text{ cm}^{-1}$) for the amorphous and crystalline samples revealed (i) the presence of a band at 550 cm^{-1} in addition to one at 450 cm^{-1} , (ii) that the intensity of the band at 550 cm^{-1} increased with increasing crystallinity, and (iii) the appearance of a band around $950\text{--}970\text{ cm}^{-1}$ on titanium incorporation.

Figure 8 presents the infrared spectra for the amorphous titanium silicate (curve a) and the crystalline TS-1 (curve b). Both the samples show a strong absorption band at 1100 cm^{-1} assigned to internal vibration of TO_4 tetrahedra. A band at around 960 cm^{-1} is observed in both crystalline and amorphous materials. After calcination at 823 K in air, an increase in the intensity of the 960 cm^{-1} band was observed only in the case of the crystalline TS-1, while

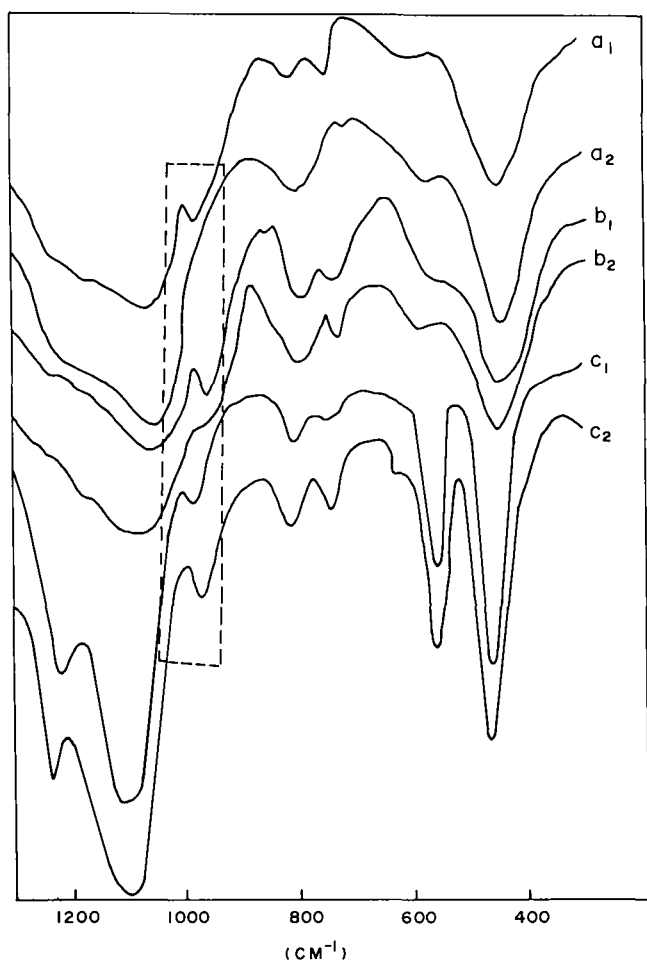


Figure 8 Framework i.r. spectra: curves a1 and b1 refer to the amorphous gels of silicalite-1 and TS-1 ($Si/Ti = 33$), respectively. Curves a2 and b2 refer to the samples after calcination at 823 K in air. The spectra of crystalline TS-1 in the as-synthesized and calcined forms are shown in c1 and c2, respectively.

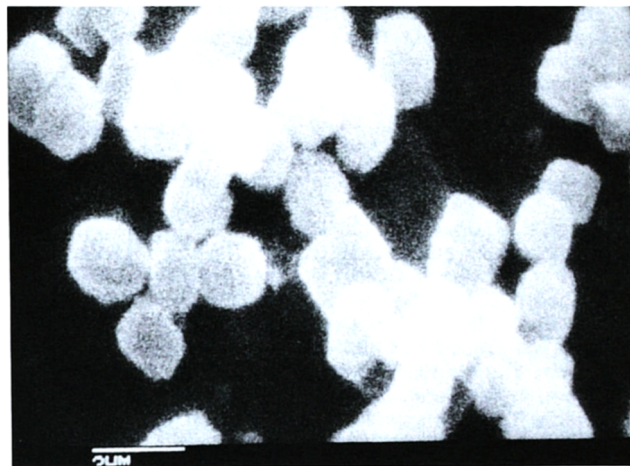


Figure 9 SEM photograph of crystalline TS-1 ($SiO_2/TiO_2 = 23$).

the intensity decreases in the case of the amorphous sample. Amorphous silica also exhibited absorption in this region, which disappeared after calcination. Further, a linear increase in the intensity of the band at 960 cm^{-1} with increase in titanium content was also observed.¹²

The incorporation of titanium in the MFI framework was also confirmed by ^{29}Si MAS n.m.r. With increasing titanium content of the samples, the band (at $\delta = -116$) assigned to the distorted environment of Si bonded with titanium¹² increases in intensity.

Scanning electron microscopy

The scanning electron micrograph of a TS-1 sample ($Si/Ti = 23$) is presented in Figure 9. The sample consists of crystals of uniform size ($< 1\text{ }\mu\text{m}$) and shape (cuboid).

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