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Synthesis of titanium silicalite-1 using ethyl silicate-40: a new silica source for zeolite synthesis

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Titanium silicalite-1 (TS-1) was synthesized using ethyl silicate-40 (ES-40) as a new silica source for zeolite synthesis. This procedure is advantageous because of the higher rate of crystallization, enhanced incorporation of Ti and the highly pure sub-micron sized crystalline product, which is highly active for phenol and anisole oxidation by aqueous H_2O_2, furthermore, ES-40 is cheaper compared to tetraethyl orthosilicate (TEOS). The product was characterized by XRD, IR, SEM, UV–VIS and XRF spectroscopy and adsorption studies. The nature of the silicate species in the intermediate stages of the synthesis was characterized by studying the ^{29}Si liquid NMR spectra. It was observed that if tetrabutyl orthotitanate (TBOT) was mixed with ES-40 before hydrolysis while preparing the reactive solution precursor, the Q^3 type of silicate species were predominantly formed, which resulted in faster crystallization of TS-1.

1 Introduction

In recent years, many researchers have studied titanium silicalite-1 (TS-1) because of its interesting catalytic properties in oxidation reactions using aqueous H_2O_2.[1–3] The catalytic properties of TS-1 are strongly affected by the Si/Ti ratio, crystallite size and the amount of framework and extra-framework titanium content. In the past, various silicon and titanium sources were used to incorporate large amounts of titanium in the TS-1 framework. Taramasso *et al.*[4] reported two methods for the hydrothermal synthesis of TS-1 using tetraethyl orthosilicate (TEOS) and colloidal silica (Ludox) as the silicon source, tetraethyl orthotitanate (TEOT) as the titanium source and tetrapropyl ammonium hydroxide (TPAOH) as the organic template. The maximum mole fraction of titanium that could be incorporated, according to this report, was 0.025 (corresponding to $Si/Ti = 39$). However, Thangaraj *et al.*[5] reported a modified synthesis procedure and claimed a higher amount of titanium incorporation ($Si/Ti < 20$). They used TEOS and TBOT as the silicon and titanium sources, respectively. In their procedure, TEOS was first hydrolyzed with aqueous TPAOH, to which TBOT in dry isopropyl alcohol (IPA) was added in order to avoid the precipitation of titanium dioxide. It is generally believed that the silicon source plays an important role in controlling the crystallization rate of the MFI-type zeolites. Tuel and Ben Taarit[6] reported the influence of the nature of the silicon and titanium sources on the rate of crystallization and the incorporation of titanium in TS-1. Various silicon alkoxides, such as silicon tetraethoxide (TEOS), tetramethoxide (TMOS), tetrapropoxide (TPOS) and tetrabutoxide (TBOS), were used for the synthesis. They did not recommend TPOS and TBOT because of their low rate of hydrolysis, which yielded materials with low crystallinity containing extra-framework TiO_2. The largest amount of titanium was incorporated using TMOS, which was attributed to a very high rate of hydrolysis of the silicon source. Until now, TEOS was thought to be the most preferred silicon source for the synthesis of TS-1 because of its monomeric nature and moderate rate of hydrolysis. But the high cost of TEOS makes TS-1 very costly and it is desirable to find an alternative cheaper silicon source to prepare pure TS-1 for industrial use. Ethyl silicate-40[7] (ES-40, CAS Registry No. 18954-71-7) is a mixture of linear, branched and cyclic ethoxysiloxanes and gives 40 wt% silica after hydrolysis. It is a partially hydrolyzed product of TEOS which is manufactured from industrial alcohol containing 7–10% water, whereas TEOS is manufactured using absolute alcohol and gives only 28 wt% silica on hydrolysis. Therefore, ES-40 is a cheaper silicon source compared to TEOS. We have successfully prepared highly pure TS-1 samples using ES-40 and the influence of synthesis parameters like temperature, SiO_2/TiO_2 and $TPAOH/SiO_2$ ratios were studied in detail. The results are presented in this paper.

2 Experimental

2.1 Synthesis

Two different methods for the synthesis of TS-1 were followed, as shown schematically in Fig. 1. In a typical synthesis *via* the first method, 1.98 g of TBOT (Aldrich) in 20 g of dry IPA (SD fine) was mixed with 30 g of ES-40 (Chemplast, India) at 25 °C and stirred for 10 minutes. A clear solution was obtained. Then 56 g of TPAOH (22.2 wt% in water prepared at NCL) was added slowly to the above solution while stirring. The resulting solution still remained clear. In the second method, the quantities of all the reactants were the same, but the order of their addition was different. The ES-40 was first hydrolyzed with TPAOH solution and then TBOT in IPA was added. The solutions obtained in both the methods were further stirred at 60–70 °C for about two hours to partially remove the alcohol. Then the required amount of water (80 g) was added. The solution still remained clear, it was further stirred for one hour. The chemical composition of these reactive solutions was $SiO_2 : 0.03\ TiO_2 : 0.33\ TPA : 35\ H_2O$. This solution was placed in several identical autoclaves (Parr). The autoclaves were stirred while heating at temperatures of 130, 150, 160 and 170 °C for hydrothermal crystallization. The synthesis was interrupted at various stages at different time intervals up to 60 h to isolate intermediate phases. The solids were recovered by centrifugation, washed with doubly distilled water and dried overnight at 100 °C in an air oven. The samples with different Si/Ti ratios were prepared by varying the amount of TBOT. For comparison, TS-1 was also prepared using TEOS as per the reported procedure.[5]

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2.2 Characterization

The ^{29}Si liquid NMR spectra were recorded at 59.6 MHz using a Bruker MSL 300 NMR spectrometer. In order to avoid the signal arising from the glass background, the measurements were carried out in a conventional wide line probe using a 10 mm o.d. plastic tube with a tight fitting cap. The free induction decays (FIDs) were collected with a 30° flip angle. The ^{29}Si signals during the hydrolysis reaction were monitored with a one second recycle delay. The crystallized samples were characterized by XRD (Rigaku, D-Max III VC model, nickel filtered Cu-Kα radiation) and FTIR spectroscopy (KBr pellet technique, Nicolet 60 SXB). FTIR spectra were recorded after preheating the samples at 100 °C for 4 h to remove water. The chemical composition of the sample was determined by XRF (Rigaku, 3700) and energy dispersive X-ray (EDX) attached to SEM (JEOL JSM 500). The adsorption measurements were carried out at 25 °C using all-glass gravimetric apparatus with a McBain–Baker type silica spring connected to a high vacuum system.[8] Adsorption of water, n-hexane and cyclohexane was carried out at a relative pressure $P/P_0 = 0.5$. The surface area was determined by N_2 adsorption (Coulter 100CX, Omnisorb) at 77 K and the catalytic reactions were carried out in the liquid phase in a batch reactor. The products were analyzed by GC (HP 5880A) equipped with a capillary column (50 m × 0.25 mm, cross-linked methylsilicon gum).

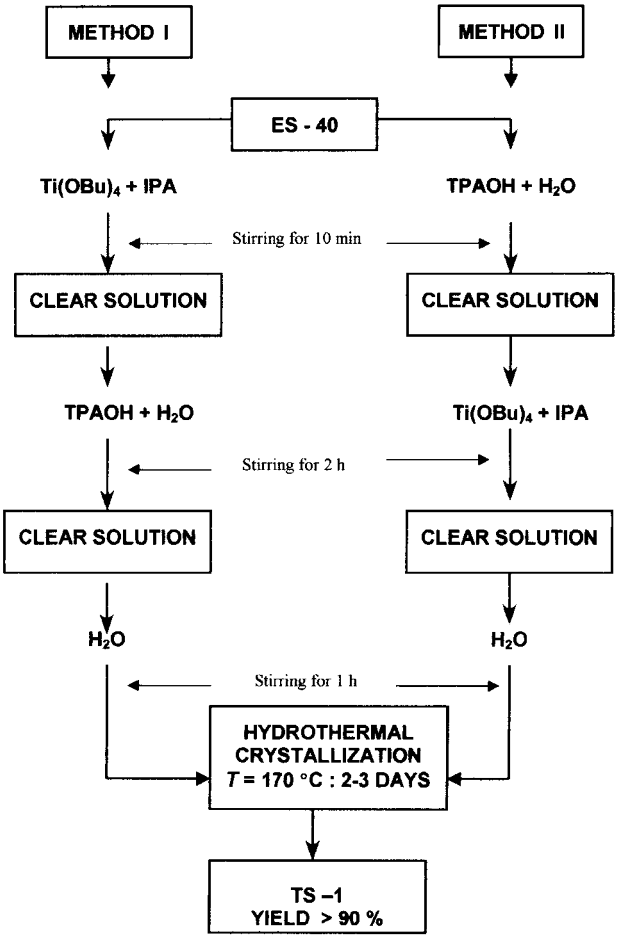

Fig. 1 Schematic representation of two different methods for TS-1 synthesis. ES-40: Ethyl Silicate-40, $Ti(OBu)_4$: titanium tetrabutoxide, IPA: isopropyl alcohol and TPAOH: tetrapropyl ammonium hydroxide.

3 Results and discussion

3.1 ^{29}Si liquid NMR studies

In order to characterize the nature and the amount of silicate species in precursor reactive solutions, high resolution liquid ^{29}Si NMR spectroscopy[9–11] was used. In Fig. 2, ^{29}Si liquid NMR spectra of the samples obtained *via* method I are shown. A typical spectrum of ES-40 is shown in Fig. 2a. The chemical shifts relative to that of TMS are −82.1, −89.1, −96.5 and −104.2 ppm, suggesting that ES-40 contains a variety of silicate species, assigned to Q^1, Q^2, Q^3 and Q^4 units, respectively. The addition of IPA to ES-40 did not change the nature of the spectrum (Fig. 2b) and the relative concentrations of Q^1, Q^2, Q^3, and Q^4 species also remained unchanged. In Fig. 2c, which was obtained after the addition of TBOT in IPA to the above solution, the concentrations of Q^3 and Q^4 species still remained unchanged, indicating the absence of any significant interactions in the solution. When aq. TPAOH was added to the same solution, the spectrum was obtained as shown in Fig. 2d. The Q^1, Q^2, Q^3 and Q^4 species now show broader bands around −80, −89, −98.3 and −108.3 ppm, respectively. In addition, the relative concentration of Q^3 species increased significantly. These changes are due to the hydrolysis and interactions in the solution when TPAOH was added to the mixture of ES-40 and TBOT in IPA. The rates of hydrolysis of different metal alkoxides $M(OR)_n$ are different and depend on the type of metal ion and alkyl group associated with it.[6] It was reported that the rate of hydrolysis of titanium tetraethoxide (TEOT) is very high compared to those of TBOT and TEOS. In our own experiments it was observed that TBOT hydrolyses faster than ES-40. When TPAOH solution was added to the mixture of ES-40 and TBOT in IPA, both alkoxides were partially hydrolyzed to form $(EtO)_nSi–OH$ and $(BuO)_3Ti–OH$ species, respectively, hydrolysis of TBOT being

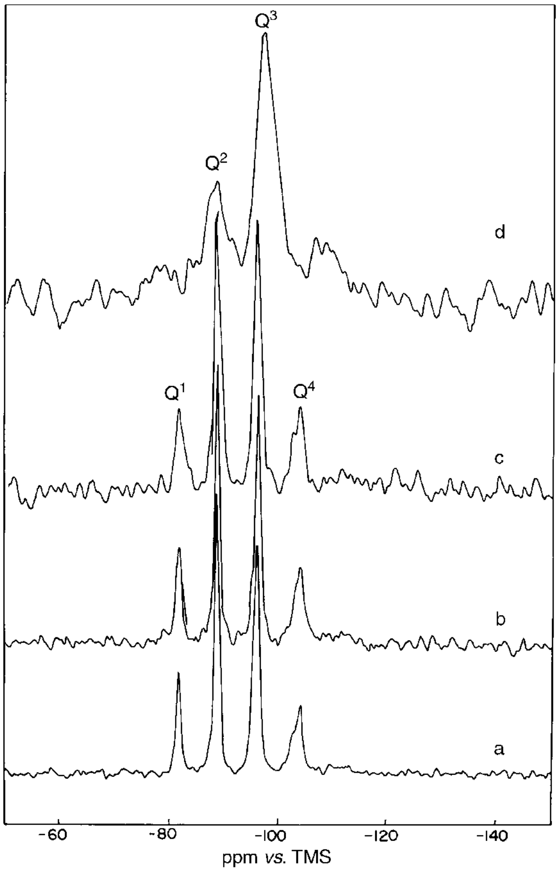

Fig. 2 ^{29}Si liquid NMR spectra of solutions in method I. (a) ES-40, (b) a + IPA, (c) b + $Ti(OBu)_4$ and (d) c + TPAOH + H_2O.

faster than that of ES-40. This results in the reaction between them forming metallosiloxanes through the following possible reactions, where ES-40 is represented as $Si(OEt)_n$.

$$\begin{aligned}&(BuO)_3Ti-OH+Si(OEt)_n\rightarrow\\&(BuO)_3Ti-O-Si(OEt)_{n-1}+EtOH\end{aligned}\qquad(1)$$

$$\begin{aligned}&(EtO)_{n-1}Si-OH+Ti(OBu)_4\rightarrow\\&(EtO)_{n-1}Si-O-Ti(OBu)_3+BuOH\end{aligned}\qquad(2)$$

These types of reactions are very well described in the literature.[12] In this way, Si–O–Ti linkages can form more efficiently. Tuel[13] observed that the formation of such linkages promotes the incorporation of Ti in the lattice, preventing the formation of extra-lattice TiO_2 species. The liquid ^{29}Si NMR spectra of solutions obtained *via* method II are presented in Fig. 3. In this method, ES-40 was first hydrolyzed by aq. TPAOH. The spectrum of the resulting solution (Fig. 3a) consists of four peaks at −80.0, −89.3, −96.8 and −104.5 ppm, which are attributed to four different silicate species Q^1, Q^2, Q^3 and Q^4, respectively. Though the positions of these peaks do not differ greatly from those of pure ES-40 given in Fig. 2a, all the peaks are significantly broadened and the intensity of the Q^3 peak is increased significantly. This is due to the hydrolysis of ES-40 with aqueous TPAOH and subsequent reorganization in this highly alkaline solution. The addition of TBOT in IPA to this highly alkaline solution also leads to the rapid hydrolysis of TBOT, which condenses and rearranges, with silicate species. The spectrum at this stage is depicted in Fig. 3b wherein the relative increase in the concentration of Q^3 species is clearly observed. Booxhorn *et al.*[14] and Thangaraj *et al.*[5] also made similar observations. In this spectrum, the peaks due to Q^1, Q^2, Q^3 and Q^4 species were observed at −79.7, −89.4, −97.6, −107.2 ppm, respectively. The nature of this spectrum is similar to the corresponding spectrum in method I, as shown in Fig. 2d, but the chemical shifts for Q^3 and Q^4 species are relatively shifted to lower field. Although very clear precursor solutions were obtained by both the methods, after the hydrothermal crystallization, the sample obtained by method II was contaminated with extra-lattice TiO_2 species. This is attributed to the uncontrolled hydrolysis of both ES-40 and TBOT separately in the highly alkaline TPAOH solution. Under such conditions, the possibility of the formation of –Ti–O–Ti– linkages increases, which is responsible for the formation of dense phase TiO_2 species in the product.

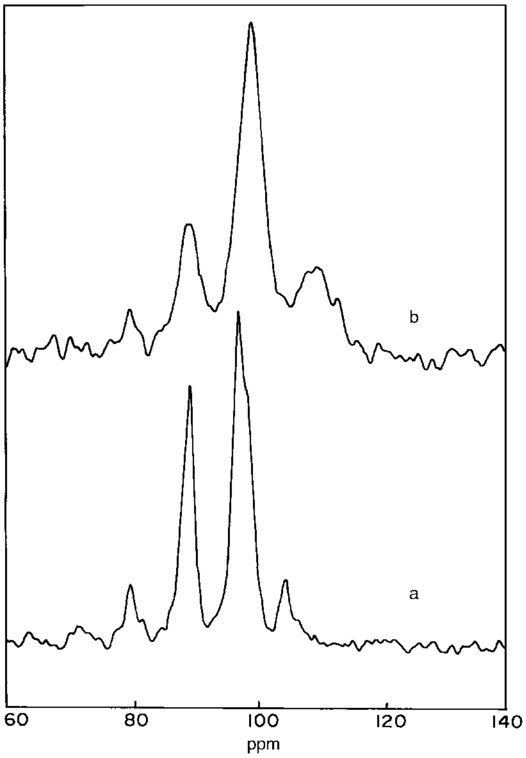

Fig. 3 ^{29}Si liquid NMR spectra of solutions in method II. (a) ES-40+aq. TPAOH and (b) a+$Ti(OBu)_4$+IPA.

It should be noted that these experiments were carried out on reactive solutions containing relatively large amounts of Ti. But in the case of the solutions containing low Ti content (Table 1), both methods I and II gave highly pure TS-1 samples. Tuel and Ben Taarit[6] studied the influence of the nature of silicon and titanium alkoxides on the titanium incorporation in TS-1 and concluded that TEOS is the silicon alkoxide of choice for higher incorporation of titanium in the lattice. But according to our observations for higher Ti incorporation, ES-40 is a better silica source than TEOS for TS-1 synthesis.

3.2 Crystallization kinetics

In order to study the influence of the temperature and SiO_2/TiO_2 and SiO_2/TPAOH ratios on the rate of crystallization, the reactant composition used was kept as SiO_2 : 0.03 TiO_2 : 0.33 TPA : 35 H_2O, which was identical to that in method I. The crystallinity of the samples was determined[15] by comparing the total area under all the peaks appearing in the 2θ range of 22–25° with that of the standard sample prepared by the same method and confirmed by adsorption of probe molecules.

3.2.1 Influence of Temperature. In Fig. 4, curves a–d, the XRD crystallinity of the samples prepared using ES-40 are plotted against the time of crystallization at 130, 150, 160 and 170 °C. Increasing the temperature of crystallization decreased the nucleation time and increased the rate of crystallization. The rate of crystallization of TS-1 at 160 °C and above was very high and fully crystalline TS-1 samples were obtained within 3–4 h. The rate of crystallization at 160 °C (curve b) using ES-40 was considerably higher than that using TEOS, as reported by Thangaraj *et al.*[5] (curve e). Fully crystalline samples were obtained at all the temperatures higher than 150 °C. The yield of the product was above 90% at all the temperatures, which was also more than that obtained[5] using TEOS. Derouane *et al.*[16] suggested that a silica source initially containing large amounts of silica monomer, like TEOS, which rapidly hydrolyses to give $Si(OH)_4$ on addition of alkali, gives a faster rate of zeolite crystallization compared to polymeric silica, like silica sol, which has to de-polymerize to $Si(OH)_4$

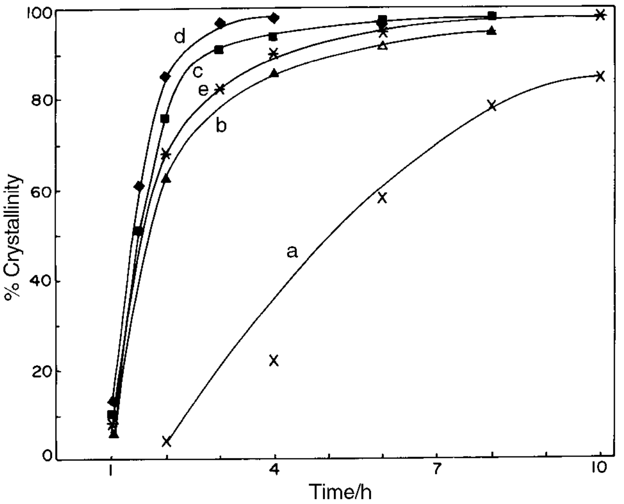

Fig. 4 Variation of XRD crystallinity with time of crystallization of TS-1 (Si/Ti = 33) at (a) 130, (b) 150, (c) 160, (d) 170 and (e) 160 °C [ref. 5].

Table 1 Physicochemical properties of TS-1 samples

	Ti/(Si+Ti) molar ratio			Sorption properties (wt%)			
No.	Gel	Product	BET surface area/m^2 g^{-1}	Water	n-Hexane	Cyclohexane	Unit cell volume/Å^3
1	—^{a}	—	384	5.2	12.4	4.8	5344
2	0.0079	0.0089	456	7.5	13.6	7.4	5347
3	0.0128	0.0147	434	7.9	13.9	7.7	5350
4	0.0163^b	0.0192	465	7.8	13.2	7.5	5353
5	0.0196	0.0232	489	7.6	13.7	8.2	5359
6	0.0196^b	0.0205	410	7.4	11.9	7.8	5352
7	0.0222	0.0243	449	7.2	13.4	7.8	5364
8	0.0277	0.0294	428	7.3	12.9	7.6	5368

^{a}Silicalite-1. ^{b}TS-1 prepared using method II.

before rearrangement. But ES-40, which already contains the silica in a limited range of polymerization, was able to produce TS-1 faster than TEOS. Even in the case of the highest extent of Ti incorporation (Si/Ti = 33), there is a need for insertion of only one Ti atom in 33 Si atoms. So it may not be necessary to completely de-polymerize ES-40 for Ti incorporation in the resulting product. Therefore, the rate of crystallization was faster when ES-40 was used as the silica source.

3.2.2 Influence of template concentration. Fig. 5 (curves a–d) shows the influence of the template (TPAOH) concentration on the rate of crystallization of TS-1, whereas all other parameters remained unchanged. The TPAOH/SiO$_2$ ratio of 0.33 (curve c) was found to be the ideal, as it resulted in the most crystalline material without any impurity phase. When the template concentration was decreased in the initial solution mixture (TPAOH/SiO$_2$ = 0.1, curve a), the crystallization of the sample was not complete, even after 72 h. When it was increased to 0.5, the crystallization was faster but the yield of the product was only 60–70%. Similar results were also observed by Kraushaar[17] The pH of the initial reaction mixture was found to be high (*ca.* 11.7), which increased to *ca.* 12.5 on completion of the crystallization.

3.2.3 Influence of SiO$_2$/TiO$_2$ ratio. In Fig. 6 curves a–c, the influence of SiO$_2$/TiO$_2$ ratio on the rate of crystallization is presented while all other parameters remain unchanged. The rate of crystallization decreased with increasing Ti content, as expected. The effect was not significant beyond an Si/Ti ratio of 40. The results are in good agreement with the published literature on metal substituted zeolites.[18,19]

3.3 Characterization

The chemical composition of the product was determined using EDX and XRF and is shown in Table 1. It was observed that the Si/Ti ratio (obtained by XRF only) in the product was lower than that in the precursor solution. Such enrichment of titanium in the product has also been observed by many authors.[5,20] The XRD patterns of crystalline TS-1 samples prepared in this study are compared with the reported patterns. The XRD patterns of calcined TS-1 prepared by both methods I and II (Fig. 7) are identical to that for ZSM-5 and show orthorhombic symmetry, whereas calcined silicalite shows monoclinic symmetry. This indicates the incorporation of Ti in the silicalite framework. The unit cell volumes are tabulated in Table 1. It is observed that the volume expands regularly with increasing titanium incorporation within the range studied. The SEM photographs of the samples prepared using ES-40 by both methods I and II are presented in Fig. 8a and b, respectively. The crystallites in the product obtained using ES-40 by both the methods are cuboids of 0.1 to 0.2 µm, which are smaller than those of the sample (0.4 µm) prepared using TEOS.[6] The polymeric silicate species in ES-40 react with TBOT forming smaller clusters of double metal alkoxide, then rapidly hydrolyze, rearrange and crystallize in the form of smaller crystallites. TEOS completely hydrolyzes to Si(OH)$_4$ and rearranges with Ti(OH)$_4$ species facilitating the formation of bulkier moieties. This leads to the formation of crystallites of larger size. The BET surface area (*ca.* 425 m^2 g^{-1}) and water, n-hexane and cyclohexane adsorption values (Table 1) *ca.* 7.5, 13.5 and 7.5 wt%, respectively indicate that the products are highly crystalline and free from occluded impurities. UV–VIS diffuse reflectance spectroscopy can be considered as the most widely applied technique to determine the quality of Ti-containing molecular sieves, since the presence of extra-lattice TiO$_2$ can be detected by the observation of an absorption band at 330 nm.[21] The TS-1 samples prepared by method I show (Fig. 9a) an intense band in the range 205–

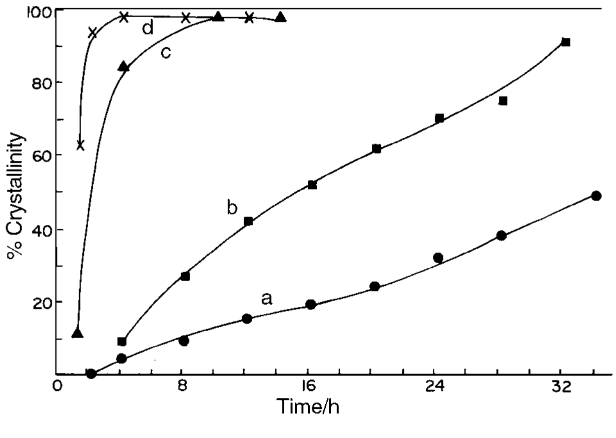

Fig. 5 Influence of TPAOH/SiO$_2$ ratio on the kinetics of crystallization of TS-1 (Si/Ti = 33) at 170 °C: ratio (a) 0.1, (b) 0.2, (c) 0.33 and (d) 0.5.

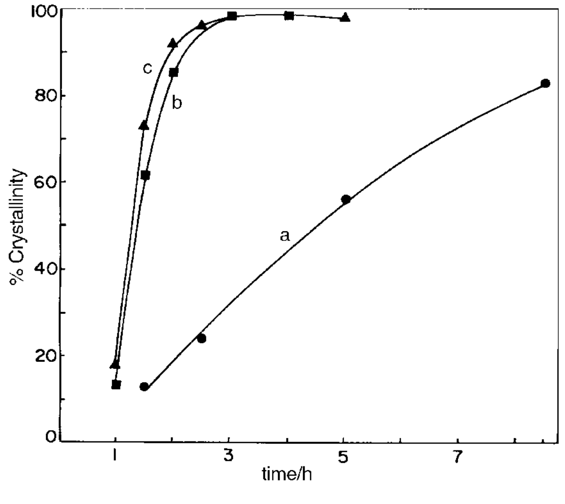

Fig. 6 Influence of SiO$_2$/TiO$_2$ ratio on the kinetics of crystallization of TS-1 at 170 °C: ratio (a) 20, (b) 33 and (c) 60.

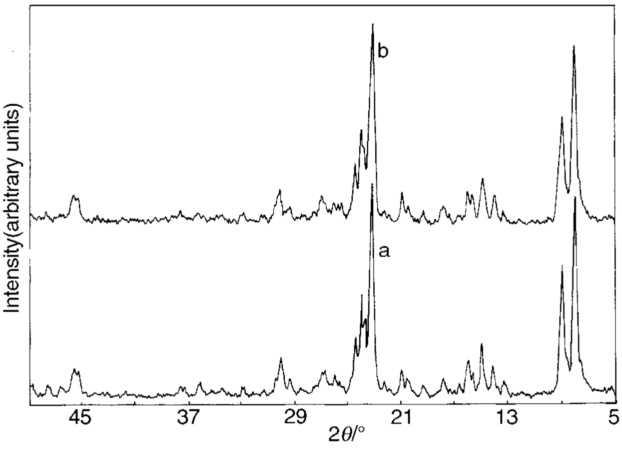

Fig. 7 XRD patterns of crystalline TS-1 samples (Si/Ti = 33) prepared by method I and method II (a and b, respectively) at 170 °C. (a) Sample 5: Table 1, (b) sample 6: Table 2.

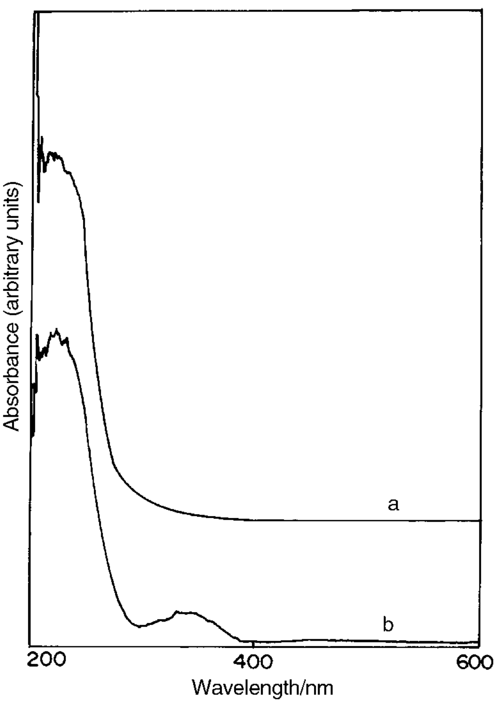

Fig. 9 UV–VIS diffuse reflectance spectra of TS-1 samples: (a) method I (sample 5: Table 1) and (b) method II (sample 6: Table 1).

215 nm; this is considered as evidence of Ti in the tetrahedral position. This band is attributed to the charge transfer character involving Ti(IV) in the [TiO_4] or [TiO_3OH] sites,[22] whereas the sample prepared by method II shows an additional small absorption band at around 330 nm, indicating the presence of extra-lattice TiO_2 species. The FTIR spectra of the samples in the framework vibration region are presented in Fig. 10. Though the FTIR spectrum does not give concrete evidence for the presence of Ti^{4+} ions in the TS-1 lattice, it is characterized by an absorption band[23] at 960 cm^{-1}. The FTIR spectra of the TS-1 samples prepared by method I and method II are almost identical to that of standard TS-1 reported previously, having characteristic bands at 968 and 963 cm^{-1}, respectively. In the FTIR spectra, the 960 cm^{-1} band is believed to be due to stretching vibrations of SiO_4 tetrahedra bound to Ti atoms as Si–O–Ti linkages. We have observed the systematic increase in the intensity of this band with increasing Ti content in the sample. However, we have also observed this band in a Ti-free silicalite sample, but it is very weak; this band is assigned to Si–O stretching vibrations of Si–O–H linkages[24] and such bands occur prominently only in zeolite samples with a lot of defect sites, like zeolite beta.[25] Various possible assignments are given for this band in the literature.[26] It may be due to the stretching mode (ν_3) of a [SiO_4] unit, more IR active due to the presence of adjacent Ti, the local stretching mode of a [TiO_4] and/or (O_3TiOH) unit in the silicate framework,

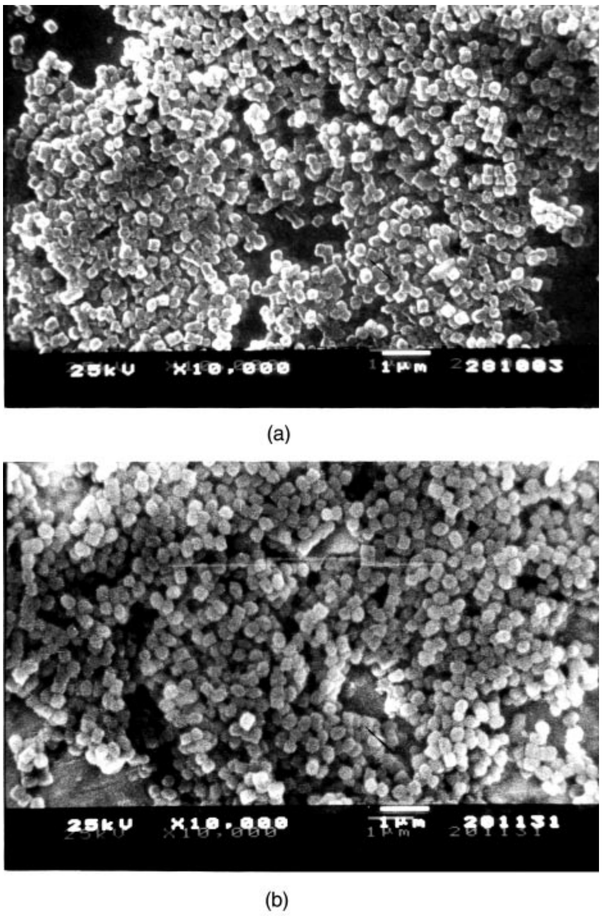

Fig. 8 SEM photographs of calcined TS-1: (a) method I (sample 5: Table 1) and (b) method II (sample 6: Table 1).

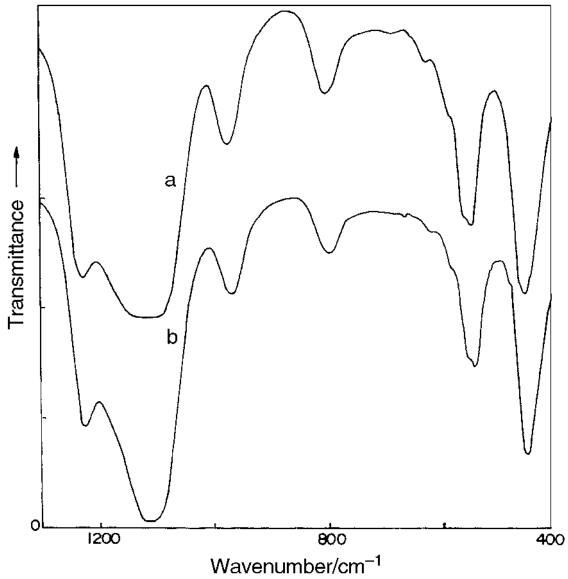

Fig. 10 FTIR spectra of TS-1 samples: (a) method I (sample 5: Table 1) and (b) method II (sample 6: Table 1).

Table 2 Hydroxylation of aromatics with aq. H_2O_2 [reaction conditions: $T = 80$ °C, phenol (anisole) : hydrogen peroxide = 5 : 1; reaction time = 5 h; solvent = water; water : phenol (anisole) = 10 : 1]

				Phenol hydroxylation			Anisole oxidation		
				S_{DHB}[c](%)			S_{HA}[d](%)		
No.	Sample	Crystal size/μm	Conv. H_2O_2 (%)[b]	Phenol	H_2O_2	*p*/*o*[e]	Anisole	H_2O_2	*p*/*o*[e]
1	TS-1 (TEOS)	0.4	99 (82)	93	89	1.41	61	76	2.8
2	TS-1 (method I)	0.1–0.2	95 (78)	92	87	1.57	58	72	3.1
3	TS-1 (method II)[a]	0.2	100 (30)	87	72	0.85	27	25	1.4

[a]Entry 6 of Table 1. [b]H_2O_2 Conversion; numbers in parentheses indicate H_2O_2 conversion for anisole oxidation. [c]Selectivity in dihydroxybenzenes (DHB) based on H_2O_2 (phenol): {(moles of dihydroxybenzenes formed)/[moles of H_2O_2 (phenol) consumed]} × 100. [d]Selectivity in hydroxyanisoles (HA) based on H_2O_2 (anisole): {(moles of hydroxyanisoles formed)/[moles of H_2O_2 (anisole) consumed]} × 100. [e]*para*/*ortho* ratio.

terminal Si–OH··· (HO–Ti) "defective sites" or contributions from some or all of these factors.

4 Hydroxylation of aromatics

The samples were tested further for catalytic activity in phenol and anisole oxidation using aq. H_2O_2. The results are summarized in Table 2. The activities of the samples prepared by methods I and II are compared with that of TS-1 prepared using TEOS. It is interesting to note that in both of these oxidations, the selectivity for the *p*-isomer was higher with the samples prepared using ES-40 than using TEOS. Although the conversion with respect to H_2O_2 is almost the same for all samples (95–100%) in phenol hydroxylation, the product distribution varies significantly. The sample prepared following method II in which extra-lattice TiO_2 was detected gave rise to some *p*-benzoquinone and less selectivity to hydroquinone.

5 Conclusions

It was found for the first time that TS-1 could be prepared using ES-40, a new silicon source for zeolite preparation. If silicon alkoxide and Ti alkoxide were mixed together and then hydrolyzed to form a double metal alkoxide, instead of hydrolyzing the individual alkoxides before mixing, the isomorphous substitution of Ti in to the lattice of silicalite was more efficient. It is advantageous to use ES-40 compared to TEOS as the silicon source because (i) the rate of crystallization was faster, (ii) the isomorphous substitution of Ti was more and (iii) smaller crystallites were formed. TS-1 prepared using ES-40 showed very high phenol oxidation activity using aq. H_2O_2, as good as that prepared using TEOS. Therefore, ES-40 is a better source of silicon for TS-1 preparation. It may also be a better source of silica compared to TEOS for other zeolite preparations as well.

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