

Studies on the synthesis of ETS-10 II. Use of organic templates

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Abstract

ETS-10 has been synthesized using titanosilicate gels and organic templating agents such as choline chloride $[\text{OHCH}_2\text{CH}_2(\text{CH}_3)_3\text{N}^+\text{Cl}^-]$ and the bromide salt of hexaethyl diquat-5 $[\text{Br}^-(\text{C}_2\text{H}_5)_3\text{N}^+(\text{CH}_2)_5\text{N}^+(\text{C}_2\text{H}_5)_3\text{Br}^-]$. The influences of temperature and concentration of the ingredients on the kinetics of synthesis are reported. Physicochemical characterizations of the samples have been carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and differential thermogravimetric analysis (DTA)/thermogravimetric analysis (TGA), and adsorption of water, *n*-hexane and mesitylene. The catalytic activities of H-ETS-10 in the dehydration of *n*-butanol and in the isomerization of *m*-xylene and 1,3,5-trimethylbenzene are reported.

Keywords: ETS-10; Titanosilicate; ETS-10, synthesis of, ETS-10, synthesis using templates; Choline chloride; Hexaethyl diquat-5

1. Introduction

The synthesis of ETS-10 in the absence of templates was reported by Engelhard [1–3]. We have reported in an earlier paper some studies on the synthesis of the above material, both in the presence and in the absence of seeds of ETS-4 [4]. The use of tetramethylammonium chloride (TMACl) in the crystallization of ETS-10 was reported recently by Valtchev and Mintova [5]. We have found that templates other than TMACl also result in the successful synthesis of ETS-10.

In this paper, we report our studies on the use of choline chloride and hexaethyl diquat-5 as

templates in the synthesis of ETS-10. The two templates used by us are structurally different from TMACl used by the earlier workers. We report the influence of temperature and compositional variations on the nucleation and crystallization of the molecular sieve, as well as on the size and shape of the molecular sieve crystals. The catalytic properties of ETS-10 samples prepared in the presence of templates are also reported.

2. Experimental

Synthesis of ETS-10(C) and ETS-10(D) using choline chloride and the bromide salt of hexaethyl diquat-5, respectively, was carried out hydrother-

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mally using sodium silicate, titanium trichloride (15% solution in HCl, Loba Chemie, Bombay, India), sodium hydroxide and potassium fluoride dihydrate (G.R. Loba Chemie). Choline chloride [(2-hydroxyethyl)trimethylammonium chloride; purity=99%] was obtained from Aldrich (Milwaukee, WI, USA) and the bromide salt of hexaethyl diquat-5 was synthesized in the laboratory (purity >99% by elemental analysis).

The molar compositions of the gels of ETS-10(C) and ETS-10(D) in terms of oxides were, respectively, 1.14 R₂O:3.7 Na₂O:0.95 K₂O:TiO₂:5.71 SiO₂:256.9 H₂O and 1.14 R₂O:3.7 Na₂O:0.95 K₂O:TiO₂:5.71 SiO₂:171.4 H₂O where R = organic template.

2.1. Synthesis of ETS-10(C) using choline chloride

Solution A comprising of 63 g of sodium silicate (28% SiO₂, 8.82% Na₂O, 62.58 H₂O) and 35 g of distilled water was stirred vigorously. Solution B was prepared by dissolving 8.4 g of NaOH pellets in 70 g of distilled water and was added slowly to solution A under stirring. The gel was stirred for 15 min and then 16.3 g of choline chloride dissolved in 52.6 g of deionized water were added slowly. The mixture was stirred for 0.5 h (solution C). A 54.4-g amount of TiCl₃ (15% solution in HCl) was added dropwise to the above gel under stirring, followed by the addition of 9.4 g of KF·2H₂O in small amounts. The final sticky grey gel (pH=11.3–11.5) was stirred for 1 h at room temperature and then transferred to a stainless-steel autoclave. The autoclave was capped tightly and crystallization was carried out at 473 K for seven days. When the crystallization was over (pH of the mother liquor=10.7–10.8), the solid material was filtered off and washed with deionized water. The product was then dried and identified as the crystalline large-pore titanosilicate ETS-10 [1–5] with the XRD pattern presented in Fig. 1C.

2.2. Synthesis of ETS-10(D) using the bromide salt of hexaethyl diquat-5

Solution A, which included 63 g of sodium silicate (28% SiO₂, 8.82% Na₂O, 62.58% H₂O) and 10 g of distilled water, was stirred vigorously.

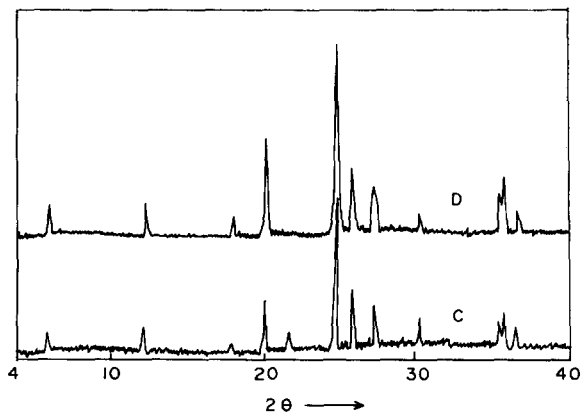


Fig. 1. XRD patterns of the as-synthesized titanosilicates (C) ETS-10(C) and (D) ETS-10(D).

Solution B was prepared by dissolving 8.4-g NaOH pellets in 48 g of distilled water and was added slowly to solution A. The gel was stirred for 15 min; then 51.8 g of hexaethyl diquat-5 (bromide salt) dissolved in 20.8 g of deionized water were added slowly and next the mixture was stirred for 0.5 h (solution C). A 54.4-g amount of TiCl₃ (15% solution in HCl) was added dropwise to the above stirred gel, followed by the addition of 9.4 g of KF·2H₂O. The final sticky grey gel (pH = 11.3–11.5) was stirred for 1 h at room temperature and then the stirred gel was transferred to a stainless-steel autoclave. The autoclave was capped tightly and crystallization was carried out at 473 K for five days. When the crystallization was over (pH of the mother liquor=10.7–10.8), the solid material was filtered off and washed with deionized water. The product was then dried and identified as the crystalline large-pore titanosilicate with the XRD pattern presented in Fig. 1D.

The end-products obtained as described in Sections 2.1 and 2.2 were calcined at 723 K (12 h) in flowing air to remove the organic templates. Acid-washed samples were prepared by treating with 0.5 M H₂SO₄ solution (zeolite/solution = 1:10) at ambient temperature overnight.

Studies on the influence of compositional variations were carried out following the general synthesis procedures described above, but by using different quantities of the reactants (TiCl₃, H₂O and template).

Crystalline phase identification and examination of the phase purity of the samples were carried out by XRD (Rigaku, Model D-max III). The chemical composition of the samples was determined by a combination of wet chemical methods and atomic absorption spectroscopy (Hitachi, Model Z-8000). Average particle size and morphology of the crystals were determined by SEM (JEOL, JSM 5200). Fourier transform infrared (FTIR) spectra were recorded with a Nicolet FTIR spectrometer (Model 60 X B). The solid-state magic-angle spinning (MAS) NMR spectra of ^{29}Si were recorded at 295 K using a Bruker MSL-300 FT NMR spectrometer as described earlier [4].

The zeolite samples were also further characterized by the sorption of different probe molecules using a vacuum (Cahn) electrobalance. Prior to sorption measurements, about 200 mg of the sample were degassed at 573 K under vacuum.

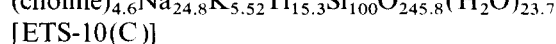
Catalytic activities of the ETS-10 samples were determined using partially exchanged H forms. These were obtained by three exchanges (of the calcined samples) with aqueous NH_4NO_3 (5% solution: molecular sieve/solution = 1:10, w/w) at $80 \pm 5^\circ\text{C}$ for 6 h, drying at 383 K for 8 h and calcination at 623 K for 12 h in a flow of dry air. The above treatment resulted (on the average) in the exchange of about 70% of the Na ions and about 94% of the K ions.

The catalytic activity tests were carried out at atmospheric pressure in a fixed-bed reactor (12 mm I.D.) using 2 g of the sample compacted in a hydraulic press and crushed into small pieces (10–14 mesh). Prior to the catalytic runs, the samples were pretreated in situ in flowing N_2 at 623 K for 2 h. The reactant was introduced using a syringe pump (Braun Melsungen, Germany). The products were analyzed by gas chromatography (HP 5880A; Shimadzu GC-15A) using capillary (HP1, 50 m \times 0.5 mm I.D.) and packed (Bentone-34, 2 m \times 3 mm I.D.) columns.

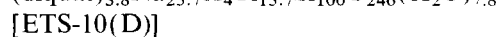
3. Results and discussion

ETS-10 samples were prepared in the presence of seeds of ETS-4 [4] or the templates, choline chloride and hexaethyl diquat-5. The influences of the various synthesis parameters on the crystalliza-

tion of ETS-10 in the presence of the two templates were examined (Figs. 2–4 and 6). The samples synthesized using ETS-4 seeds are designated as ETS-10(S); those synthesized using the templates are designated as ETS-10(C) (choline chloride) and ETS-10(D) (hexaethyl diquat-5). The most crystalline (XRD) samples obtained during the syntheses using seeds [4] or templates have been used in the characterization studies (XRD, Fig. 1; SEM, Fig. 5; IR, Fig. 7; TGA/DTA, Fig. 8; NMR, Figs. 9 and 10; sorption, Fig. 11; catalytic activities, Table 1). The chemical compositions (molar) of the samples used in these studies are as follows:



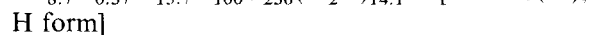
[ETS-10(C)]



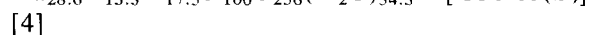
[ETS-10(D)]



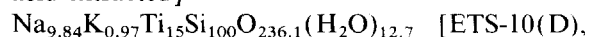
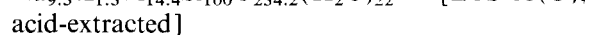
[ETS-10(C), H form]



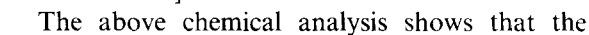
[ETS-10(D), H form]



[ETS-10(S)]



[ETS-10(C), acid-extracted]



[ETS-10(D), acid-extracted]

The above chemical analysis shows that the $\text{SiO}_2/\text{TiO}_2$ ratio is enhanced by the templating agent. The chemical analysis also indicates that choline chloride or hexaethyl diquat-5 ions replace the hydrated potassium ions in the ETS-10 structure, while TMA ions were reported to replace mainly the hydrated sodium ions [5]. When the $\text{SiO}_2/\text{TiO}_2$ molar ratio of the synthesis gel (standard) was 5.71, the $\text{SiO}_2/\text{TiO}_2$ ratio of the crystalline product was 6.55 for ETS-10(C) and 6.37 for ETS-10(D). Changing the $\text{SiO}_2/\text{TiO}_2$ ratio of the gel to 3.0 and 9.0 resulted in products with ratios of 3.62 and 9.52, respectively, in the case of choline chloride and 3.21 and 9.34, respectively, in the case of hexaethyl diquat-5.

The XRD patterns of the titanosilicates ETS-10(C) and ETS-10(D) shown in Fig. 1 match well with those published earlier [1–5]. The XRD patterns of ETS-10 prepared using different $\text{SiO}_2/\text{TiO}_2$ ratios (not shown in the figure) also match with the above.

3.1. Influence of temperature on crystallization

To study the effect of temperature on the formation of the titanasilicate, the kinetics of crystallization were studied in the range 413–473 K by comparing the extent of crystallization of the gel mixture at different intervals of synthesis time. The extent of crystallization was evaluated by comparing the ratio of the sums of the areas of the most intense XRD peaks ($2\theta=24.65\text{--}27.5^\circ$) of the sample under study with that of the most crystalline sample obtained during the study. The curves for the crystallization kinetics of ETS-10 for the gel composition mentioned earlier are presented in Fig. 2. The curves typically exhibit a continuous increase of crystallization with respect to time. The rate of crystallization is lower for ETS-10(C) ($\text{H}_2\text{O}/\text{SiO}_2=45$, Section 2.1) when compared to ETS-10(D) ($\text{H}_2\text{O}/\text{SiO}_2=30$, Section 2.2) (Fig. 2, curves 3C and 3D for ETS-10(C) and ETS-10(D), respectively). Also, the induction period for ETS-10(C) is larger, suggesting that the formation of the nuclei is slower when choline chloride is used as the template. As a result, 70–75% crystalline material of ETS-10(C) and ETS-10(D) are obtained after five and three days, respectively; seven and five days (respectively) are required to get $\sim 100\%$ crystalline material at 473 K (Fig. 2, curves 3C and 3D for ETS-10(C) and ETS-10(D),

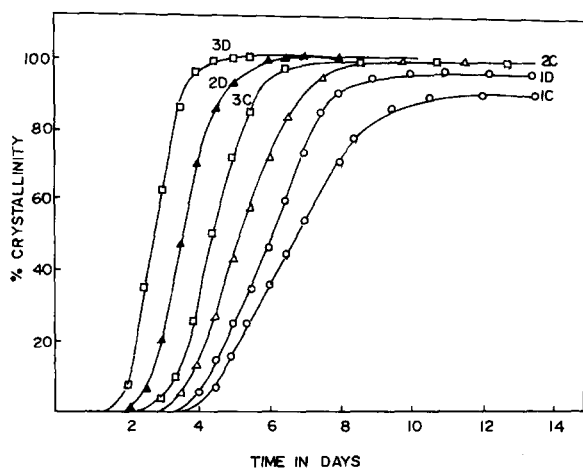


Fig. 2. Effect of temperature on the kinetics of crystallization of ETS-10(C) and ETS-10(D). Curves 1–3 correspond to 423, 443 and 473 K, respectively.

respectively). Fully crystalline (100%) titanasilicate could not be obtained at 413 K (Fig. 2, curves 1C and 1D) even on prolonging the period of crystallization to thirty days. Applying the Arrhenius equation, we found the activation energies for nucleation (E_n) and crystallization (E_c) to be 17.4 and 13.1 kJ/mol for ETS-10(C) and 22.7 and 20.1 kJ/mol for ETS-10(D). These values are lower than the values reported for ETS-10 synthesized in the absence of templates [4].

3.2. Influence of water content of the gel

Water plays an important role in the hydrothermal synthesis of molecular sieves. Studies were carried out by changing the water content in the synthesis mixture. Only the water content was changed and the relative ratios of the other components were kept the same (as in Sections 2.1 and 2.2) in all the batches. For convenience, we will express the water content with respect to SiO_2 as $\text{H}_2\text{O}/\text{SiO}_2$ ratio. The influence of water concentration of the gel on the crystallization is presented in Fig. 3 for ETS-10(C) and ETS-10(D) at 473 K. Dilution of the gel influences the rate of nucleation and also the rate of crystallization appreciably. Fig. 3 shows that the crystallization rate is enhanced when the water content is lowered (curves 1C and

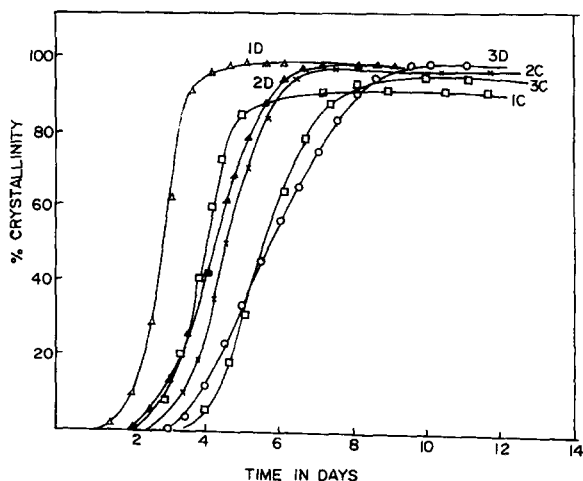


Fig. 3. Influence of $\text{H}_2\text{O}/\text{SiO}_2$ ratio on the kinetics of crystallization of ETS-10(C) and ETS-10(D). Curves 1–3 correspond to $\text{H}_2\text{O}/\text{SiO}_2$ values of 30, 45 and 60, respectively.

1D). However, only 92% crystalline material is obtained (Fig. 3, curve 1C) even on prolonged heating up to twenty days at 473 K, when choline chloride is used as the template. Besides, an impurity peak (XRD) at $2\theta=21.8^\circ$ is also observed. When the $\text{H}_2\text{O}/\text{SiO}_2$ ratio is increased from 30 to 45, the crystallization improves and 98% crystallinity is observed in about seven days (Fig. 3, curve 2C). Further increase in crystallinity could not, however, be noticed even after thirty days. The magnitude of the impurity peak at $2\theta=21.8^\circ$ is smaller when $\text{H}_2\text{O}/\text{SiO}_2=45$. Thus, good ETS-10(C) can be obtained only when the $\text{H}_2\text{O}/\text{SiO}_2$ ratio is 45 or 60 (Fig. 3, curves 2C and 3C, respectively). An increase in the crystallization rate at lower water contents is also observed (Fig. 3) in the case of ETS-10(D). Curves 1D, 2D and 3D in Fig. 3 correspond to $\text{H}_2\text{O}/\text{SiO}_2$ ratios of 30, 45 and 60, respectively. 100% crystalline material is obtained in five, seven and ten days when the $\text{H}_2\text{O}/\text{SiO}_2$ ratios are 30, 45 and 60, respectively.

3.3. Influence of template concentration

Studies were carried out by changing the concentrations of choline chloride and the bromide salt of hexaethyl diquat-5 in the synthesis gel, keeping the relative ratios of the other components as required for obtaining the most crystalline material. For convenience, we will be expressing the template content (with respect to SiO_2) as R/SiO_2 ratio. The influence of the template concentration of the gel on the crystallization rate is presented in Fig. 4 for ETS-10(C) and ETS-10(D) at 473 K and $\text{H}_2\text{O}/\text{SiO}_2=45$ and 30. The rate of nucleation and crystallization were both influenced appreciably by changes in the template concentration. 98% crystalline material was obtained in seven days for ETS-10(C) at 473 K and $\text{H}_2\text{O}/\text{SiO}_2=45$ when $\text{R}/\text{SiO}_2=0.4$ (Fig. 4, curve 1C). On increasing R/SiO_2 from 0.4 to 0.6, the crystallinity of the material obtained even after thirty days was only 90% (Fig. 4, curve 2C). Fig. 4 also shows that crystallization is faster when the template (hexaethyl diquat-5) content is lower, i.e., $\text{R}/\text{SiO}_2=0.4$ (Fig. 4, curve 1D). When R/SiO_2 is 0.6 (Fig. 4, curve 2D), 100% crystallinity is achieved in six days at 473 K. On the other hand, when R/SiO_2 was decreased to 0.2, neither ETS-10(C) nor

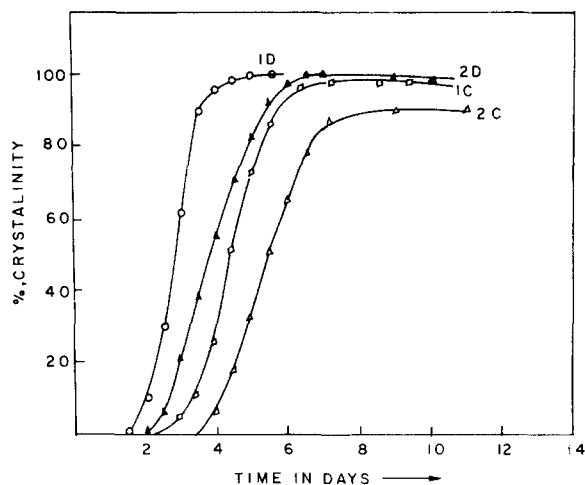


Fig. 4. Influence of R/SiO_2 ratio on the kinetics of crystallization of ETS-10(C) and ETS-10(D) at 473 K. Curves 1 and 2 correspond to R/SiO_2 values of 0.4 and 0.6, respectively.

ETS-10(D) crystallized at all. This suggests that the above templates play a positive role in the synthesis of ETS-10.

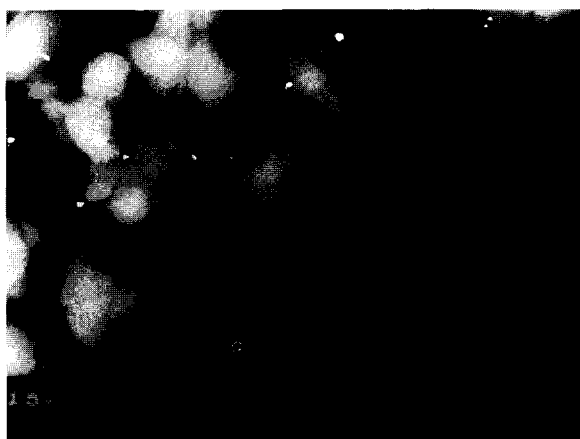
SEM photographs of the titanosilicates [ETS-10(C) and ETS-10(D)] crystallized in the presence of choline chloride and hexaethyl diquat-5 are shown in Fig. 5A and B, respectively. Agglomerates of cuboidal crystals ($\leq 0.5 \mu\text{m}$) with a few cuboidal growing clusters (2–4 μm) are seen in Fig. 5A and wheat-shaped polycrystallites (2–4 μm) are seen in Fig. 5B. This shows that the nature of the organic template used during the crystallization of the titanosilicate has a significant influence on the morphology of the ETS-10 crystals.

3.4. Influence of titanium content of the gel

Studies were carried out by changing the titanium content in the synthesis gel, keeping the other components the same as in Sections 2.1 and 2.2. The influence of titanium concentration ($\text{SiO}_2/\text{TiO}_2$) in the gel on crystallization (at 473 K) is presented in Fig. 6 for ETS-10(C) and ETS-10(D). As noted earlier in the case of the other parameters, both the rate of nucleation and crystallization are affected significantly when the $\text{SiO}_2/\text{TiO}_2$ ratio is changed; 98% crystalline titanosilicate material is obtained in seven and eight



A



B

Fig. 5. SEM photographs of the titanosilicates ETS-10(C)(A) and ETS-10(D)(B).

days for $\text{SiO}_2/\text{TiO}_2$ ratios of 5.71 and 9, respectively [ETS-10(C); curves 2C and 3C, respectively], whereas 90% crystallinity is the upper limit when $\text{SiO}_2/\text{TiO}_2=3$ [ETS-10(C); curve 1C]. On the other hand, five and seven days are sufficient to get good crystalline material for $\text{SiO}_2/\text{TiO}_2$ ratios of 5.71 and 9, respectively, for ETS-10(D) (curves 2D and 3D, respectively), and almost 95% crystalline material for $\text{SiO}_2/\text{TiO}_2=3$ (curve 1D). When the titanium content was increased further (i.e., $\text{SiO}_2/\text{TiO}_2 < 3$), the material did not crystallize at all.

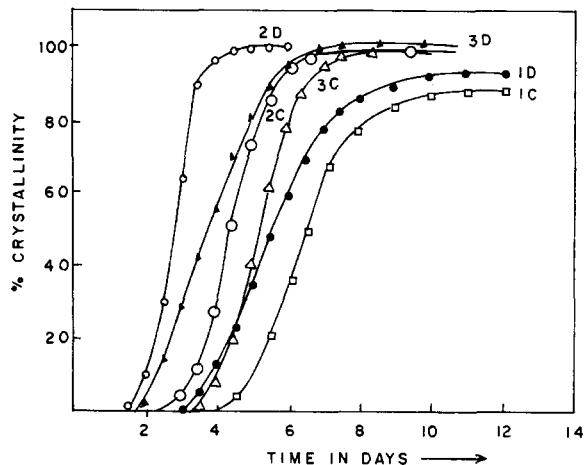


Fig. 6. Influence of $\text{SiO}_2/\text{TiO}_2$ ratio on the kinetics of crystallization of ETS-10(C) and ETS-10(D) at 473 K. Curves 1–3 correspond to $\text{SiO}_2/\text{TiO}_2$ values of 3, 6 and 9, respectively.

3.5. Physicochemical characterization of ETS-10(C) and ETS-10(D)

IR studies

The framework IR spectra (in the region $450\text{--}1300\text{ cm}^{-1}$) of calcined ETS-10(C) and ETS-10(D) are shown in Fig. 7. The positions of the major absorption bands corresponding to the different symmetric and asymmetric stretching vibrations [4,6] are nearly the same ($\pm 5\text{ cm}^{-1}$) for these titanosilicates. However, the spectral bands for ETS-10(C) (spectrum 1C) are not sharp, though the major bands occur at the same positions as those of ETS-10(D) (spectrum 1D). A weak shoulder at $\sim 985\text{ cm}^{-1}$ is also seen (Fig. 7, curves 1C and 1D, respectively) in the case of the calcined samples of these titanosilicates [Na and K forms of ETS-10(C) and ETS-10(D)]. The calcined samples were extracted with 0.5 M H_2SO_4 solution (zeolite/acid solution ratio of 1:10) at ambient temperature overnight, filtered, washed and dried and their IR spectra were obtained. An IR absorption band appears at $\sim 970\text{ cm}^{-1}$ [Fig. 7, curves 2C and 2D for ETS-10(C) and ETS-10(D), respectively] in the leached samples. A similar observation was made by Khouw and Davis [7] in the case of TS-1 samples synthesized in the presence of Na. Though the occurrence of this band in acid-washed samples is surprising, it could

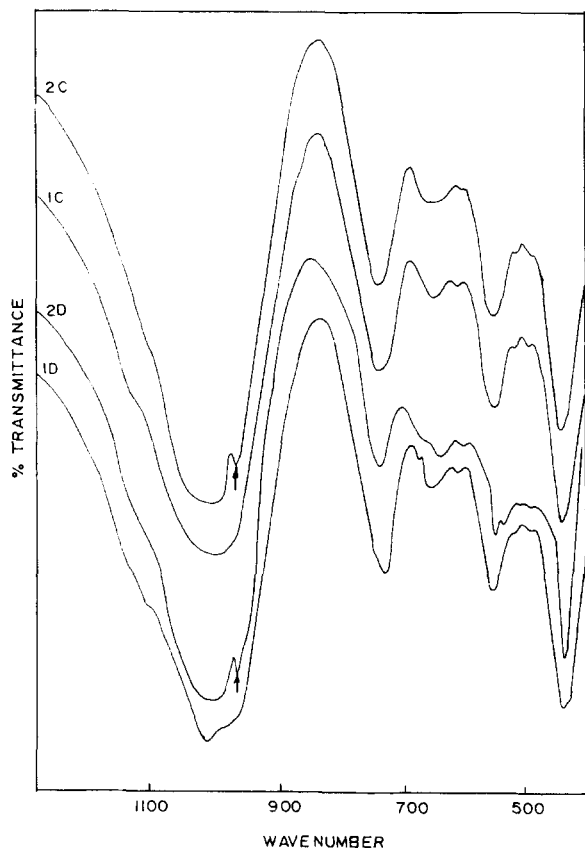


Fig. 7. IR spectra of the titanositicates. Curves 1C and 1D refer to the calcined samples of ETS-10(C) and ETS-10(D), respectively. Curves 2C and 2D refer to the acid-extracted samples of ETS-10(C) and ETS-10(D), respectively.

be due to $-\text{Si}-\text{O}^{-1}$ vibrations as suggested by Cambor et al. [8] in the case of TS-1 and Ti- β .

TGA/DTA

The thermal behavior of as-synthesized ETS-10(C) and ETS-10(D) are shown in Fig. 8A and B, respectively. The thermograms resemble the thermogram of the titanositicate prepared using TMAcl [5]. Loss of water occurs up to 533 K and is found to be 4.78% in the case of ETS-10(C), while it is 0.52% in the case of ETS-10(D). The oxidative decomposition of the templates in the range 533–843 K results in a mass loss of 5.53 and 11.87%, respectively, for ETS-10(C) and ETS-10(D) (Fig. 8AC and 8AD). The sharp endotherm observed at 948 K (Fig. 8BC and 8BD) for

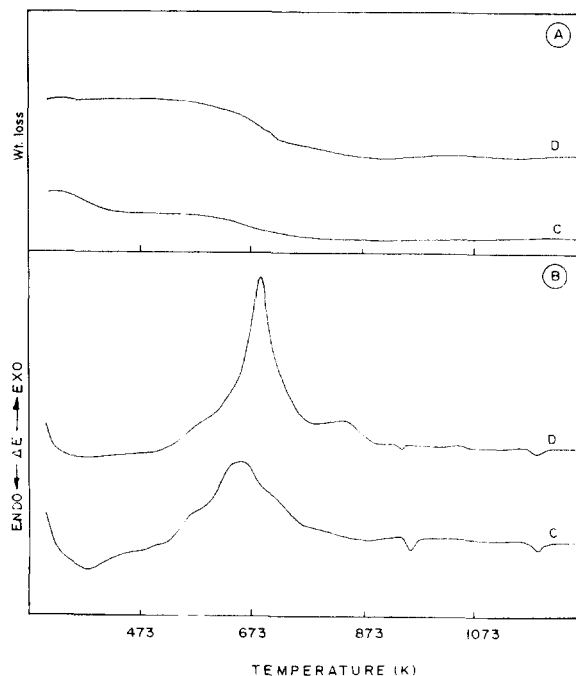


Fig. 8. Thermoanalytical curves of the as-synthesized titanositicates. (A) Curves C and D, TGA of ETS-10(C) and ETS-10(D), respectively. (B) Curves C and D, DTA of ETS-10(C) and ETS-10(D), respectively.

both ETS-10(C) and ETS-10(D) suggests the melting or phase transformation of these materials.

MAS NMR

The ^{29}Si NMR spectra of ETS-10(C) and ETS-10(D) before and after calcination are shown in Fig. 9A and B and Fig. 10A and B, respectively. Three sharp bands at $\delta = -95.01(1)$, $-98.08(2)$ and $-104.41(3)$ ppm are observed in the spectrum obtained using a 300-MHz instrument (Fig. 9A). These bands are slightly shifted to $\delta = -95.33(1)$, $-97.50(2)$ and $-104.99(3)$ ppm (Fig. 9B) when the titanositicate sample is calcined at 723 K to remove the organic template. Similarly, three sharp bands at $\delta = -94.69(1)$, $-97.73(2)$ and $-104.01(3)$ ppm are also observed in ETS-10(D) (Fig. 10A). These bands are marginally shifted to $\delta = -95.06(1)$, $-97.74(2)$ and $-105.43(3)$ ppm on calcination (Fig. 10B). The nature of the spectra is similar to the one reported earlier [4] except for the absence of the weak band reported at $\delta = -90.74$ ppm, which probably was due to

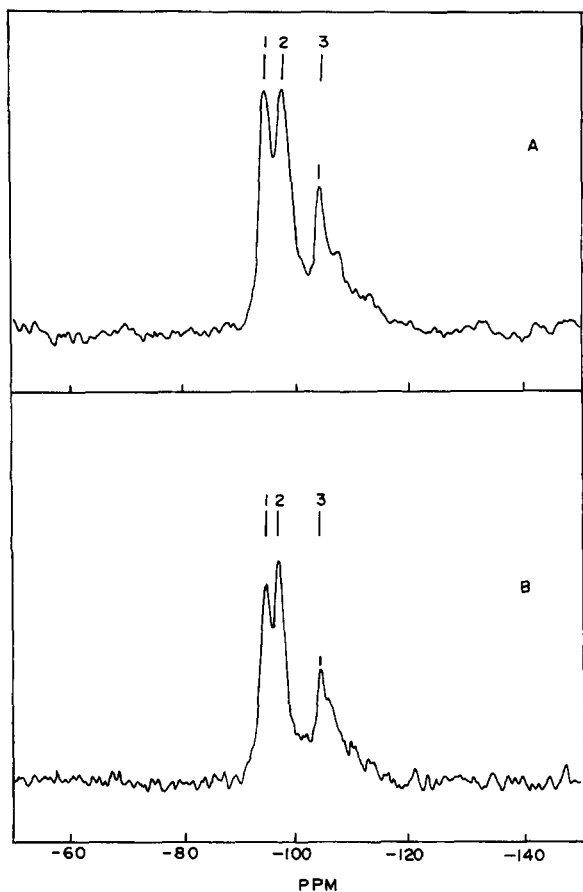


Fig. 9. ^{29}Si MAS NMR spectra of ETS-10(C) before (curve A) and after (curve B) calcination.

ETS-4 impurities. Anderson et al. [3] have reported a four-line spectrum for ETS-10 using an instrument with a higher resolution (400 MHz) and have assigned the lines observed by them at $\delta = -94.1$, -95.8 and -96.5 ppm to Si(3Si, 1Ti) and the line at $\delta = -103.3$ ppm to Si(4Si, 0Ti). Our lines at $\delta = -95.01$ and -98.08 ppm are assigned to Si(3Si, 1Ti) while the line at $\delta = -104.41$ ppm is assigned to Si(4Si, 0Ti).

Sorption studies

The sorption capacity of the titanosilicates was measured using H_2O (kinetic diameter = 2.65 \AA), *n*-hexane (4.3 \AA) and 1,3,5-trimethylbenzene (8.1 \AA). The time courses of adsorption of the above molecules obtained at 298 K at $p/p_0 = 0.5$

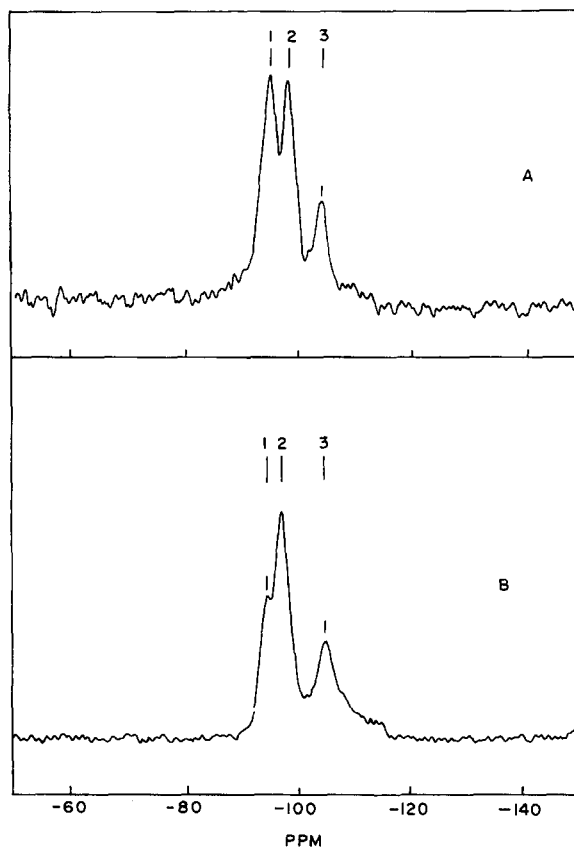


Fig. 10. ^{29}Si MAS NMR spectra of ETS-10(D) before (curve A) and after (curve B) calcination.

are presented in Fig. 11. The equilibrium sorption capacities of ETS-10(D) for all the probe molecules are close to the earlier reported values [4]. The equilibrium sorption capacities observed for ETS-10(C), however, are lower. This is probably due to the presence of impurity phases (seen in XRD; Fig. 1C, $2\theta = 21.8^\circ$). The broad IR bands (Fig. 9, curves 1C and 2C) also confirm the poorer crystallinity of ETS-10(C).

Catalytic activities

The results of the catalytic tests performed on ETS-10(C) and ETS-10(D) are presented in Table 1.

Dehydration of n-butanol. The samples were highly active in the dehydration reaction, though less than H-Y (Linde, LZ-Y62 calcined at 773 K

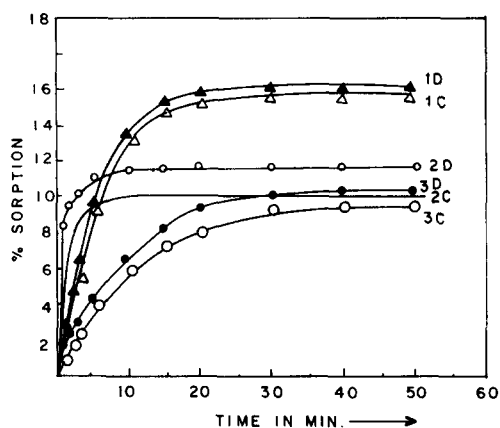


Fig. 11. Sorption kinetics of H_2O , *n*-hexane and 1,3,5-trimethylbenzene (curves 1, 2 and 3, respectively) of ETS-10(C) and ETS-10(D), respectively.

for 6 h). H-Y gave a conversion of 98.2% at 523 K, while ETS-10(D) gave a conversion of 93.8% at 573 K. The products, as expected, were mostly 1- and 2-butenes. Besides, small amounts (<3%) of isobutene and other components (C_1 – C_3 and C_4^+ ; <5% in all) were also obtained. The 1-butene/2-butenes ratio in the products from the ETS-10 samples was 0.28 ± 0.01 , compared to the thermodynamic equilibrium value of 0.20. The *trans*-butene-2/*cis*-butene-2 ratio in the products from both samples was 1.3. This value is only slightly smaller than the expected equilibrium value, 1.5. In the case of H-Y, the observed values are 0.2 and 1.6 compared to the expected equilibrium values of 0.14 and 1.6 (523 K)

for the 1-butene/2-butenes and *trans*-butene-2/*cis*-butene-2 ratios, respectively. These differences suggest that thermodynamic equilibrium is not fully obtained at the reaction conditions. Besides, the product pattern could have also been affected by the formation of side-products. The ratio of isobutene/(1-butene + 2-butenes) is very small (about 0.03) for both ETS-10 and H-Y, being far below the equilibrium values of 1.4 (573 K) and 1.5 (523 K). All the above observations can be explained based on the minimum strength of acid sites required to catalyze the different reactions. The acidity requirement increases in the order dehydration \approx *cis*–*trans* isomerization < double bond isomerization < skeletal isomerization. Apparently, the acid strengths in ETS-10 and H-Y at the temperatures investigated are such that skeletal isomerization is not possible, while the *cis*–*trans* and double bond isomerizations and dehydration reactions take place to different extents. Besides, the water produced in the reaction might also poison/weaken the acid centres.

m-Xylene isomerization. The ETS-10 catalysts are found to be active in the isomerization of *m*-xylene, though the conversion levels are below the equilibrium value (equilibrium conversion \sim 46% [9]). Disproportionation reactions generally accompany the isomerization of xylenes. These reactions are bimolecular in nature and involve bulky intermediates [10]. As a result, zeolites with high acid site densities enabling the adsorption of two xylene molecules at adjacent sites are more

Table 1
Comparison of the catalytic activities of ETS-10 samples with H-Y

Sample	Catalytic activity ^a					
	<i>n</i> -Butanol		<i>m</i> -Xylene		1,3,5-Trimethylbenzene	
	Conversion (%)	1-Butene/2-butene	Conversion (%)	I/D ^c	Conversion (%)	I/D ^c
ETS-10(C)	88.3	0.27	19.9	0.50	45.3	0.78
ETS-10(D)	93.8	0.29	23.3	0.50	50.2	0.75
H-Y	98.2 ^b	0.20 ^b	25.0	0.65	52.4	0.73

^a Reaction conditions: temperature, 573 K; WHSV, 2.0 h^{-1} (*n*-butanol), 1.0 h^{-1} (*m*-xylene and 1,3,5-trimethylbenzene); N_2 diluent, 5 ml/min STP; data reported at 1 h on stream.

^b Reaction temperature, 523 K.

^c I/D values based on the number of moles of isomerization and disproportionation products in the catalysate.

likely to catalyze the disproportionation reaction [11]. Again, zeolites with pore sizes large enough to accommodate the bulky transition states involved in disproportionation reactions tend to have higher disproportionation activities [12]. Hence, the isomerization/disproportionation (I/D) activity ratios during *m*-xylene conversion can be used as a measure of acid site density and/or pore dimensions in molecular sieves. The I/D activity ratios of both the ETS-10 catalysts are 0.5. Earlier workers [12] have reported an I/D ratio of about 4 for H- β and of 8 for H-mordenite at about 25% conversion. The very low I/D ratio obtained over ETS-10 is mainly due to the high acid site density and a larger pore dimension (than β and mordenite). The high acid site density arises from the large number of Ti^{4+} (O_h) ions with two unbalanced (negative) charges on each ion [3]. Under identical conditions, the conversion over H-Y is 25% and the I/D activity ratio is 0.65.

1,3,5-Trimethylbenzene isomerization. The conversion of 1,3,5-trimethylbenzene is 45.3% over ETS-10(C) and 50.2% over ETS-10(D), compared to the expected equilibrium conversion of 71%. The I/D ratios (0.78 and 0.75; Table 1) are larger than those observed in the case of *m*-xylene isomerization, because spatial requirements for the bimolecular disproportionation reactions involving two 1,3,5-trimethylbenzene molecules are more than for two *m*-xylene molecules. At the same reaction conditions, the conversion of 1,3,5-trimethylbenzene over a commercial H-Y sample (Linde, LZ-Y62, calcined at 773 K for 6 h) was 52.4%, the I/D ratio being 0.73. The performance of ETS-10 in the above reaction is similar to that of H-Y.

In all the reactions studied above, ETS-10(C) is found to be slightly less active than ETS-10(D). This could be due to the presence of catalytically non-active amorphous material occluded in the pores of the molecular sieve in the case of ETS-10(C). This is also suggested by the reduced sorption of hydrocarbons and water by ETS-10(C) (Fig. 11). As XRD does not reveal any TiO_2 phases, it is possible that the occluded material is SiO_2 . This is a likely possibility as the Si/Ti ratio in

ETS-10(C) is slightly more than that in ETS-10(D) (see previous section).

4. Conclusions

ETS-10 can be synthesized in the presence of the organic templates, choline chloride and bromide salt of hexaethyl diquat-5 without using ETS-4 seeds. The templates reduce the synthesis time required for obtaining well crystallized samples. The size and morphology of the crystals are altered by the templates. Use of hexaethyl diquat-5 leads to a purer material than choline chloride. Partially exchanged H forms of ETS-10 are active in the reactions normally catalyzed by acid catalysts. Disproportionation reactions occur to a considerable extent during the isomerization of *m*-xylene and 1,3,5-trimethylbenzene.

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References

- [1] S.M. Kuznicki, U.S. Pat., 4 938 939 (1990).
- [2] S.M. Kuznicki, U.S. Pat., 4 853 202 (1989).
- [3] M.W. Anderson, O. Terasaki, T. Ohsuna, A. Philippou, S.P. Mackay, A. Ferreira, J. Rocha and S. Lidin, *Nature*, 367 (1994) 347.
- [4] T.Kr. Das, A.J. Chandwadkar, A.P. Budhkar, A.A. Belhekar and S. Sivasanker, *Microporous Mater.*, 4 (1995) 195.
- [5] V. Valtchev and S. Mintova, *Zeolites*, 14 (1994) 697.
- [6] E.M. Flanigen and H. Katami, *Adv. Chem. Ser.*, 101 (1971) 201.
- [7] C.B. Khouw and M.E. Davis, *J. Catal.*, 151 (1995) 77.
- [8] M.A. Camblor, A. Corma and J. Perez-Pariente, *J. Chem. Soc. Chem. Commun.*, (1993) 1557.
- [9] D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, New York, 1969.
- [10] J.A. Martens, J. Perez-Pariente, E. Sastre, A. Corma and P.A. Jacobs, *Appl. Catal.*, 45 (1988) 85.
- [11] E. Van Broekhoven and H. Wijngaards, *Proceedings of the AKZO Catalysts Symposium*, Scheveningen, CIP Data Koninklijke Bibliotheek, Den Haag, 1988, p. F-8.
- [12] R. Kumar and K.R. Reddy, *Microporous Mater.*, 3 (1994) 195.