Studies on the synthesis of ETS-10
I. Influence of synthesis parameters and seed content

Tapan Kr. Das, A.J. Chandwadkar, A.P. Budhkar, A.A. Belhekar, S. Sivasanker *

National Chemical Laboratory, Catalysis Division, Pune 411 008, India

Received 5 September 1994; accepted 18 December 1994

Abstract

The influence of various parameters such as temperature, concentration of the ingredients and amount of seed used on the kinetics of the synthesis of the large-pore molecular sieve ETS-10 is reported in the paper. Detailed physicochemical characterizations of the samples have been carried out with instrumental techniques such as X-ray diffraction (XRD), scanning-electron microscopy (SEM), ultraviolet–visible (UV–VIS) spectroscopy, infrared (IR) spectroscopy nuclear magnetic resonance (NMR) and sorption of water, *n*-hexane and mesitylene.

Keywords: ETS-10; Titanosilicates; ETS-10, physicochemical properties of; ETS-10, synthesis of; ETS-4

1. Introduction

A new family of titanium silicate molecular sieves was recently discovered by Engelhard [1,2]. These materials, called ETS-4 and ETS-10, have a unique molecular architecture due to octahedrally coordinated titanium framework ions. ETS-10 has an open three-dimensional structure consisting of Ti^{4+} octahedral chains linked to classical tetrahedral silica rings [3]. A three-dimensional network of the interconnecting channels intersect a central pore (8 Å diameter).

Though the synthesis of ETS-10 has been reported in the literature, a detailed kinetic study of its synthesis has so far not been reported. In the present paper, we report such a detailed kinetic study in the presence and absence of seeds of ETS-4. The influence of various factors on the nucleation and crystallization of the molecular sieve, as well as on the size and shape of the molecular sieve crystals, is reported.

* Corresponding author.

2. Experimental

Two synthesis procedures, one using ETS-4 as seed and the other without any seed, were studied. The patents [1,2] report the synthesis using ETS-4 as seed. Preliminary experiments revealed that ETS-10 itself could be used as the seed. However, as we did not find any improvement in the product crystallinity or reduction in the synthesis time on using ETS-10 as the seed, we have carried out the present investigation with the more easily obtained ETS-4 as the seed. Synthesis of the titanosilicate [ETS-10(S)] using seeds of ETS-4 was carried out hydrothermally using sodium silicate, titanium trichloride solution (15% solution in HCl, Loba Chemie, Bombay, India), sodium hydroxide, potassium fluoride dihydrate (G.R., Loba Chemie) and seeds of ETS-4 (titanosilicate having a small pore size of 4 Å prepared as reported previously [1,2]).

The molar composition of the gel in terms of oxides was as follows: 4.42 Na_2O:0.95 K_2O:TiO_2:5.71 SiO_2:81.88 H_2O for ETS-4 and 3.70 Na_2O:0.95 K_2O:TiO_2:5.71 SiO_2:171 H_2O for ETS-10(S).

Synthesis of the titanosilicate [ETS-10(D)] in the absence of seeds of ETS-4 was carried out using sodium chloride in addition to the above. The molar composition of the gel in terms of oxides was as follows: 4.95 Na_2O:0.95 K_2O:TiO_2:5.71 SiO_2:342.85 H_2O.

A typical synthesis of ETS-10 is given below.

2.1. Synthesis of ETS-4 (seed)

Solution A comprising 63.0 g of sodium silicate (28.6% SiO_2, 8.82% Na_2O, 62.58% H_2O) was stirred vigorously. NaOH pellets (11.4 g) were added to the above solution (A) and the gel was stirred for a further 10 min. A 54.4-g amount of titanium trichloride ($TiCl_3$, 15% solution in HCl) was added dropwise to this solution, and the mixture was stirred for 0.5 h to get a blackish paste (solution B). Finally, 9.4 g of potassium fluoride dihydrate ($KF·2H_2O$) were added to solution B and the mixture was stirred for 1 h at room temperature to get a homogeneous gel (pH ~ 11.0). This gel was transferred to a stainless-steel autoclave; it was then capped tightly, and crystallization was carried out at 423 K for seven days. The pH of the mother liquor was 10.7 at the end of the synthesis. The solid material was filtered off and washed with deionized water. The product was then dried and identified as the crystalline small-pore titanosilicate (ETS-4) with the XRD pattern presented in Fig. 1A.

2.2. Synthesis of ETS-10 using seeds of ETS-4

Solution A comprising 63 g of sodium silicate (28.6% SiO_2, 8.82% Na_2O, 62.58% H_2O) and 20 g of distilled water was stirred vigorously. Solution B was prepared by dissolving 8.4 g of NaOH pellets in 58.8 g of distilled water and added slowly to the above solution (A) under stirring. The gel was stirred for 15–20 min and 54.4 g of $TiCl_3$ (15% solution in HCl) were added dropwise taking care to avoid sputtering of the above stirred gel. The paste-like blackish material (paste C) was stirred for 0.5 h. A 9.4-g amount of $KF·2H_2O$ was added to paste C and the mixture was stirred for 1 h to get paste D. Finally 1.3 g of titanosilicate seeds of ETS-4 were added to paste D very slowly and
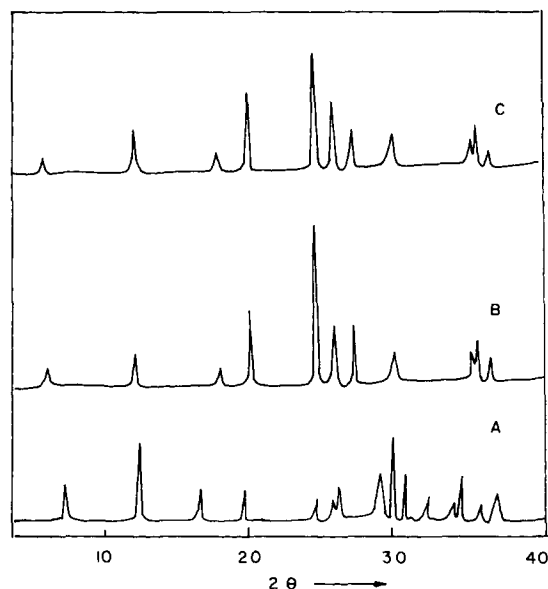

Fig. 1. XRD patterns of the as-synthesized titanosilicates. (A) ETS-4; (B) ETS-10(S) (seed = 7.0%); (C) ETS-10(D).

stirred vigorously for 1 h until the combination became homogeneous (pH 10.8–11.0) at room temperature. It was then transferred to a stainless-steel autoclave. The autoclave was capped tightly, and crystallization was carried out at 443 K for ten days. The pH of the mother liquor was 10.6 at the end of the crystallization. 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) with the XRD pattern presented in Fig. 1B.

Titanosilicates [ETS-10(S)] were also prepared with SiO_2/TiO_2 = 3, 4 and 7.5 (input ratios) using seeds of ETS-4 (7.0%) by the above procedure. The X-ray diffraction patterns showed mixed phases (ETS-4 + ETS-10) and less crystalline products in the case of SiO_2/TiO_2 = 3 and 4 and less crystalline ETS-10 in the case of SiO_2/TiO_2 = 7.5 (input ratio) as compared to ETS-10(S) using seeds of ETS-4 (7.0%) having SiO_2/TiO_2 = 5.7 (input ratio).

2.3. Synthesis of ETS-10 without seeds of ETS-4

Solution A comprising 63 g of sodium silicate (28.6% SiO_2, 8.82% Na_2O, 62.58% H_2O) and 60 g

of distilled water was stirred vigorously. Solution B was prepared by dissolving 9.9 g of NaOH pellets in 77.7 g of distilled water and added slowly to the above solution (A) under stirring. The gel was stirred for 15–20 min. A 54.4-g amount of $TiCl_3$ (15% solution in HCl) was added dropwise to the above stirred gel. The paste-like blackish material (paste C) was stirred for 0.5 h. A 9.4-g amount of $KF·2H_2O$ was added to paste C, and the mixture was stirred for 1 h to get paste D. Finally 5.5 g of NaCl dissolved in 20 g of deionized water were added to paste D. The mixture was stirred for 1 h until it became homogeneous (pH 11–11.5) at room temperature and then it was transferred to a stainless-steel autoclave. The autoclave was capped tightly, and crystallization was carried out at 473 K for ten days. When crystallization was complete, the pH of the mother liquor was found to be 11.0. The solid material was filtered off and washed with deionized water. The product was then dried and identified as ETS-10. Its XRD pattern is presented in Fig. 1C.

The crystalline phase identification and phase purity of the sample was verified by XRD (Rigaku, Model D-max III). The chemical composition of the samples was determined by a combination of wet chemical methods and atomic adsorption spectroscopy (Hitachi, Model Z-8000). Their average particle size and morphology were determined by SEM (JEOL, JSM 5200). The UV–VIS diffuse reflectance spectra of the samples were obtained using a Shimadzu (Model UV-2101PC) spectrometer. 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 and ^{23}Na were recorded at 295 K using a Bruker MSL-300 FT NMR spectrometer. Bloch decays were averaged 2400 times before Fourier transformation to obtain spectra with a sufficient signal-to-noise ratio. While acquiring the ^{29}Si spectra, a recycle time of 4 s was found to be sufficient to give fully relaxed spectra. ^{29}Si spectra were recorded at $\gamma = 59.6$ MHz using tetramethylsilane (TMS) as the primary reference. An excitation pulse (t pulse) of 2 µs was used with 2000 numbers of scans (NS). While acquiring the ^{23}Na spectra, a recycle time of 1 s was found to be sufficient to give fully relaxed spectra. ^{23}Na spectra were measured using sodium chloride as the primary reference. ^{23}Na spectra were recorded at 79.39 MHz. An excitation pulse of 2 µs was used with 200 NS.

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

3. Results and discussion

Chemical analysis of the titanosilicate samples used in this investigation revealed the following: $0.78\ Na_2O:0.28\ K_2O:TiO_2:3.11\ SiO_2:3.18\ H_2O$ for ETS-4; $0.82\ Na_2O:0.38\ K_2O:TiO_2:5.72\ SiO_2:3.11\ H_2O$ for ETS-10(S) and $0.88\ Na_2O:0.12\ K_2O:TiO_2:5.68\ SiO_2:7.28\ H_2O$ for ETS-10(D).

The chemical composition is not significantly influenced by variations of the seed concentration (0.9–14.0%, input SiO_2 basis).

The XRD patterns of the titanosilicates ETS-4, ETS-10(S) and ETS-10(D) shown in Fig. 1 match very closely with those published earlier [1–3]. The relative crystallinity of the sample was calculated by comparing the peak areas in the range $2\theta = 24.65–27.5°$ to that of the most crystalline reference material (ETS-10) obtained from the same batch composition. Variation of the seed concentration from 0.9 to 14.0% (input SiO_2 basis) did not affect the relative crystallinity of the titanosilicate [(ETS-10(S)]. However, when no seed was used, the crystallinity of the product, ETS-10(D), was only 75% of ETS-10(S). The lowered crystallinity could be due to the presence of amorphous matter. The presence of such extra lattice material is inferred from the lower adsorption for hydrocarbons (see the discussions on IR and adsorption). However, amorphous materials are not seen clearly in SEM pictures.

3.1. Influence of temperature on crystallization

To study the effect of temperature on the formation of the titanosilicate, the kinetics of crystallization were studied in the range 423–473 K by

comparing the extent of crystallization of the gel mixture at different intervals of synthesis time. The extent of crystallization is conventionally evaluated either by sorption of water vapor/nitrogen at fixed relative pressure on a completely dehydrated zeolite or by the ratio of the sum of the areas of the intense XRD peaks of the sample under consideration to that of the most crystalline sample obtained during the study [4–6]. The curves (based on XRD estimation of crystallinity) for the crystallization kinetics of ETS-10 for the gel composition mentioned earlier are presented in Fig. 2. The curves typically exhibit a sharp continuous rise of crystallization. The intercept made by the curve on the time axis (abscissa) is defined as the induction period (the time needed to form crystallization centers or nuclei). In accordance with thermodynamic expectations, it is found from Fig. 2 that the induction period is inversely proportional to the temperature. The rate of nucleation may be assumed to be proportional to the reciprocal of the induction period; hence, it varies directly with the crystallization temperature. The induction period is followed by the formation of crystalline material, the rate of crystallization increasing with time up to about 60–70% crystallinity and then slowing down. Nearly, 100% crystallization occurs after about seven days. The phase purity (ETS-10) or crystallinity was not affected even after autoclaving for twenty-five days.
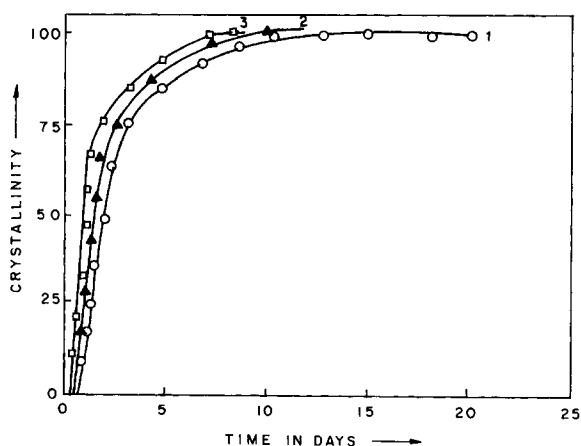

Fig. 2. Effect of temperature on the kinetics of crystallization of ETS-10(S) (seed = 7.0%). Curves 1–3 correspond to 423, 443 and 473 K, respectively.

Linear plots were obtained when the data were fitted into the Avrami-Erofeev equation [7]. Applying the Arrhenius equation, we found the activation energy values for nucleation (E_n) and crystallization (E_c) to be 76.5 and 38.3 kJ mol^{-1}, respectively. Thompson [8] has recently pointed out the shortcomings of the applicability of the above equation to zeolite crystallization data. He proposed that these Avrami-Erofeev transformation kinetics should be viewed as providing only a qualitative interpretation of zeolite crystallizations. Similarly, Den Ouden and Thompson [9] have pointed that the assumptions made to arrive at the rate of nucleation and crystal growth in order to apply the Arrhenius equation to evaluate the apparent E_n and E_c may not be realistic.

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 overall synthesis gel. Only the water content was changed and the relative ratios of the other components remained the same in all the batches. For convenience, we will be expressing the water content with respect to SiO$_2$ as H$_2$O/SiO$_2$ ratio. The influence of water concentration in the gel in the crystallization is presented in Fig. 3A and B, respectively, for the titanosilicate prepared by the seed method [ETS-10(S)] (seed content = 7.0%) at 423 K and that prepared directly [ETS-10(D)] at 443 K. The dilution of the gel affects the rate of nucleation only marginally but influences the rate of crystallization appreciably. Fig. 3A shows that the crystallization rate is enhanced when the water content is lower (H$_2$O/SiO$_2$ = 15) (curve 1). When the H$_2$O/SiO$_2$ ratio is increased from 15 to 40 (curves 1–3), the crystallization period increases from seven to ten days. On increasing the H$_2$O/SiO$_2$ ratio further up to 60 (curves 4 and 5), the crystallization period increases to twelve days and it takes twenty days to obtain fully crystalline material. For H$_2$O/SiO$_2$ = 15, we observed two impurity peaks (2θ = 7.6 and 9.1) in the XRD pattern. When the H$_2$O/SiO$_2$ ratio was lower than 15, the water content was found to be too low to obtain a homogeneous gel and hence crystalliza-
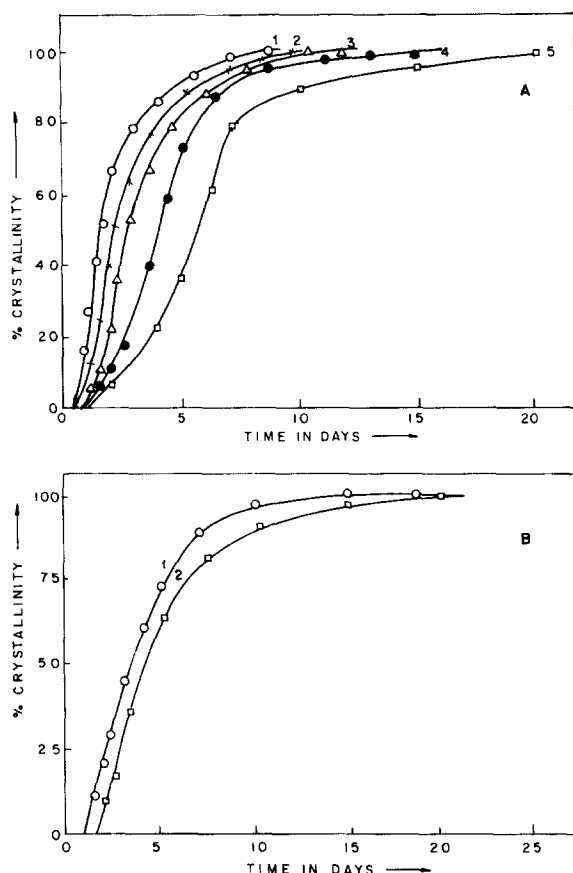
Fig. 3. Influence of H_2O/SiO_2 ratio on the kinetics of crystallization of ETS-10. (A) ETS-10(S) (seed = 7.0%). Curves 1–5 correspond to H_2O/SiO_2 values of 15, 30, 40, 50 and 60, respectively. (B) ETS-10(D). Curves 1 and 2 correspond to H_2O/SiO_2 values of 30 and 60, respectively.

tion was not attempted. An increase in the rate of crystallization at lower water content is also observed (Fig. 3B) for the titanosilicates [ETS-10(D)] prepared in the absence of seeds. Curves 1 and 2 correspond to $H_2O/SiO_2 = 30$ and 60, respectively. A fully crystalline sample is obtained between eighteen and twenty days. These studies show that crystallization rate increases with decreasing H_2O/SiO_2 ratio whether or not seeds are present.

The water content of the synthesis gel has the most influence on the size and morphology of the ETS-10 crystals (Figs. 4 and 5). In the case of ETS-10(S), as the dilution is increased from

$H_2O/SiO_2 = 30$ to 50, the size of the cuboid crystals increases (Fig. 5C for $H_2O/SiO_2 = 30$ and Fig. 4A for $H_2O/SiO_2 = 50$). However, on further dilution to $H_2O/SiO_2 = 60$, the crystal morphology changes and elongated crystals of 4–8 μm are obtained (Fig. 4B). The higher rates of crystallization found in the more concentrated systems (see above) and larger crystal sizes in dilute solutions are commonly observed in zeolite synthesis [10].

In the case of the titanosilicate synthesized in the absence of seed [ETS-10(D)] using $H_2O/SiO_2 = 30$, very prominent, cuboidal layered particles of 5–7 μm are observed (Fig. 4C). But when the water content is increased ($H_2O/SiO_2 = 60$), mixtures of sheaf-like bundles of narrow strips (~ 8 μm long) and large cuboids (6–8 μm) are seen (Fig. 4D).

3.3. Influence of seed concentration

SEM photographs show that the small-pore titanosilicate (ETS-4) used as seed in the present study has very irregular undefined particles ranging in size from 1 to 8 μm (Fig. 5A). On the other hand, ETS-10 synthesized (with $H_2O/SiO_2 = 30$) using ETS-4 seeds (14.0 wt.-% based on SiO_2 input) crystallizes as sharp, twinned cuboids in the size range 1–4 μm (Fig. 5B). On decrease of seed concentration to 7.0, 3.5, 1.7 and 0.9%, individual cuboids tend to form clusters with increasing size (Figs. 5C and 5D for 7.0 and 0.9 wt.-% seeds, respectively). The crystallinity (XRD) of the samples was not influenced by variation in the quantity of seed used.

3.4. IR studies

The framework IR spectra (in the region 450–1300 cm^{-1}) of ETS-4, ETS-10(D), ETS-10(S) (7.0% seed), ETS-10(S) (0.9% seed) and dried precursor gel are shown in Fig. 6 (curves A, B, C, D and E, respectively). ETS-4 shows a prominent band at 1000 cm^{-1} and two weak absorptions at 1100 and 920 cm^{-1}. The positions of the major absorption bands and shoulders corresponding to the different symmetric and asymmetric stretching vibrations [11] remained almost unchanged (± 5 cm^{-1}) for all the titanosilicates prepared using

A

C
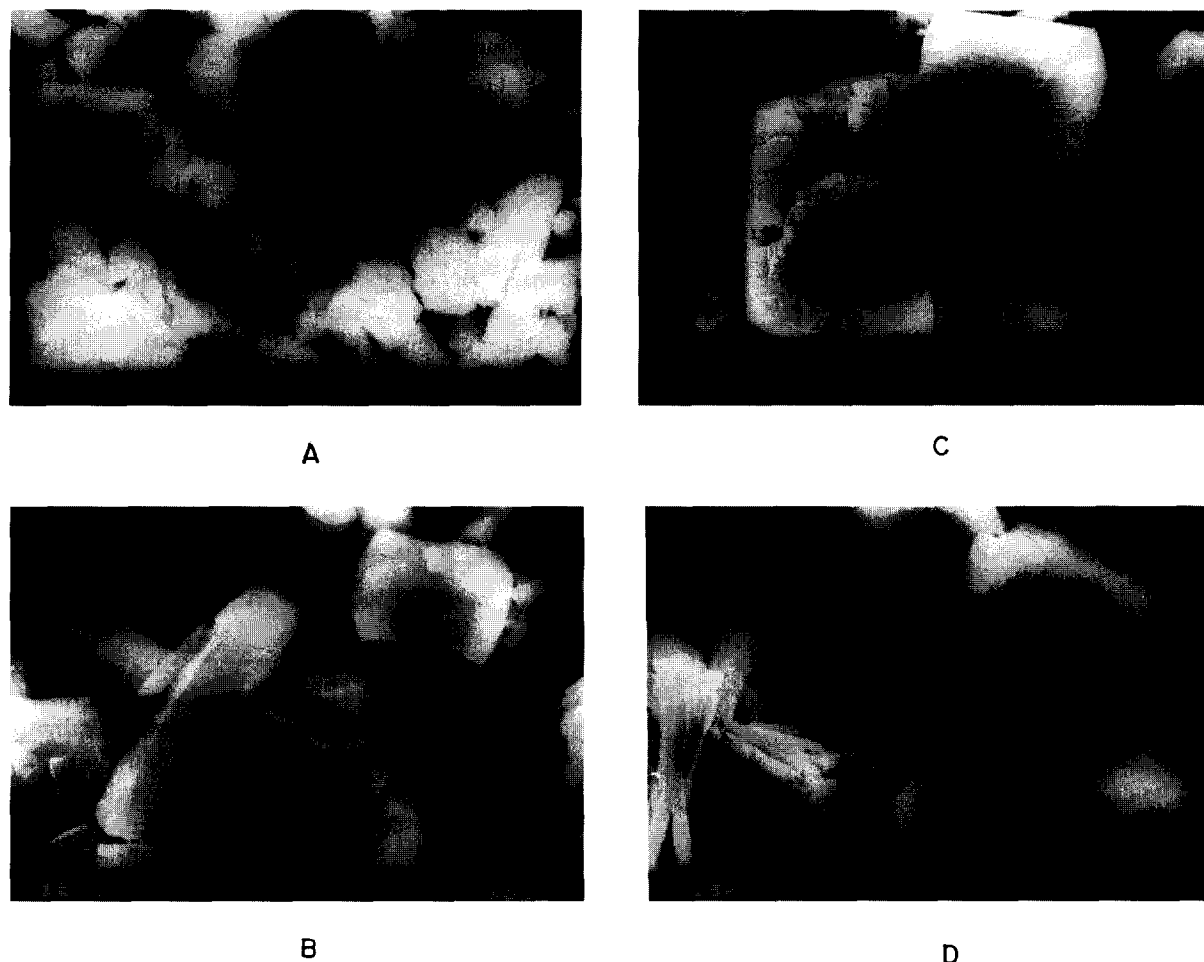

B

D

Fig. 4. Influence of water content, H_2O/SiO_2 (X), of gel on morphology of ETS-10 crystals. (A) ETS-10(S) (seed = 7.0%), $X = 50$; (B) ETS-10(S) (seed = 7.0%), $X = 60$; (C) ETS-10(D), $X = 30$; (D) ETS-10(D), $X = 60$.

seeds. However, the spectral bands for ETS-10(D) are not sharp, though the major bands occur at the same positions as those for ETS-10(S). The lack of sharpness may be due to contributions from amorphous material (see the discussion on XRD). No distinct sharp bands are observed in the IR spectrum of the precursor gel (amorphous material) except for a weak peak at 775 cm^{-1}. This peak is also present as a very weak absorption in the spectrum of the sample prepared without seeds. The FTIR spectra of surface hydroxyl groups in dehydrated ETS-10(S) is shown in Fig. 7. The peak around 3735 cm^{-1} is due to isolated terminal silanol groups [12]. The sharp

peak at 3700 cm^{-1} observed on ETS-10 is probably due to isolated Ti-OH groups. The broad band around 3200–3600 cm^{-1} is probably due to H-bonded surface hydroxyl groups of both Si and Ti.

3.5. UV–VIS (diffuse reflectance spectra)

The diffuse reflectance spectra in the UV–VIS region of ETS-10(S), ETS-4, ETS-10(D) and dried precursor gel are presented in Fig. 8 (curves a, b, c and d, respectively). The broad absorption in the region 250–320 nm suggests the presence of Ti^{4+} in O_h coordination [13].
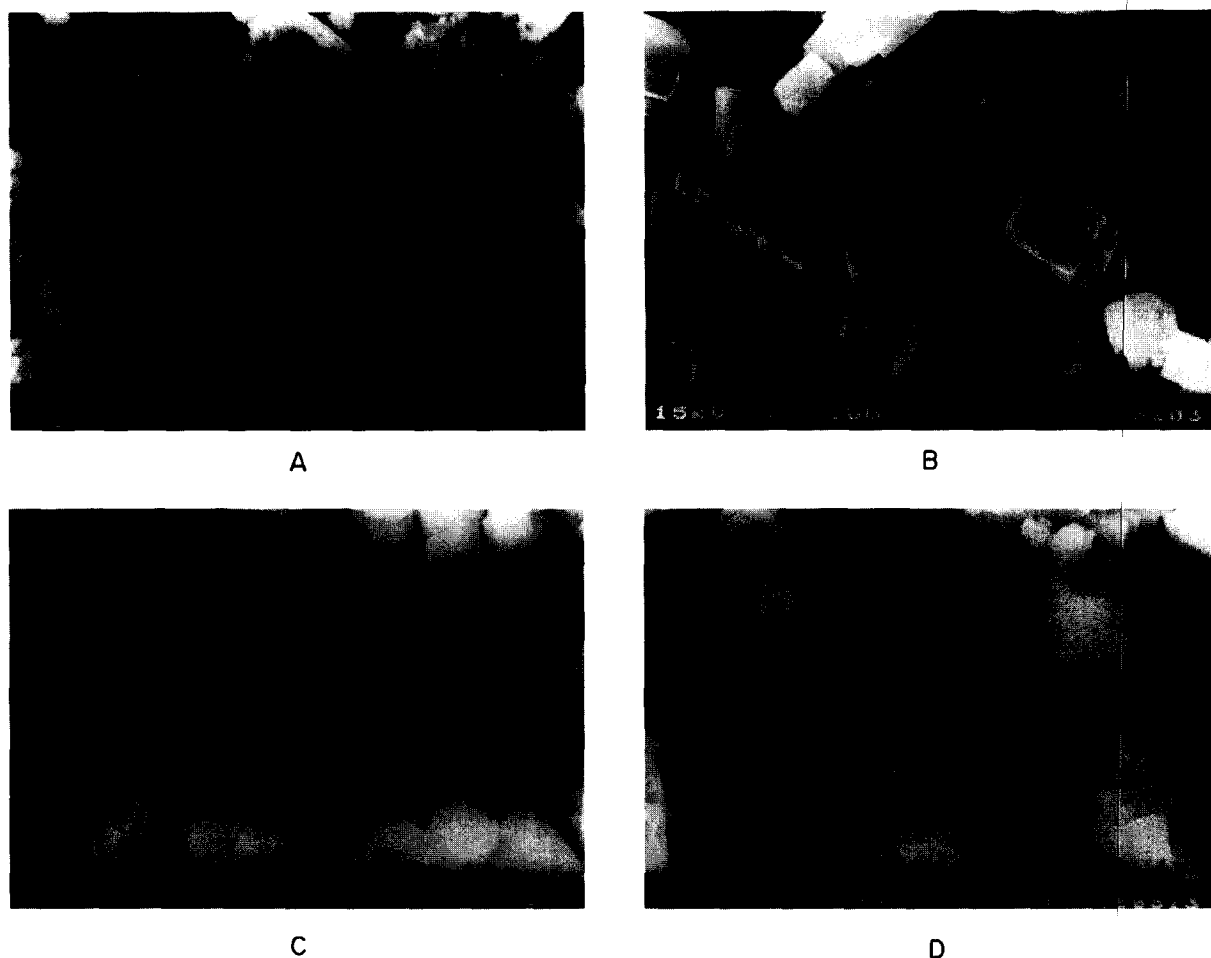
Fig. 5. SEM photographs of the titanosilicates. Influence of seed content on morphology of crystals. (A) ETS-4 (seed); (B) ETS-10(S) (14.0% seed); (C) ETS-10(S) (7.0% seed); (D) ETS-10(S) (0.9% seed).

3.6. MAS NMR

The ^{29}Si NMR spectra of ETS-10(S) (Fig. 9A) shows three sharp bands at $\delta = -94.4$ (1), -96.8 (2) and -103.8 (3) ppm, indicating the presence of at least three different Si environments in ETS-10. The weak band at $\delta = -90.74$ ppm (marked by an arrow) is probably due to ETS-4 present as an impurity in the sample, as this band was prominent in the case of pure ETS-4. Further, this band disappeared after calcination at 623 K.

^{23}Na NMR spectra (Fig. 9B) show the presence of two resonance bands at $\delta = 9.17$ (1) and -9.90

(2) ppm corresponding to their presence in two different environments [14].

3.7. Sorption studies

The sorption isotherms for water, n-hexane and 1,3,5-trimethylbenzene obtained at 298 K at a $P/P_0 = 0.5$ are presented in Fig. 10. ETS-10(S) (Fig. 10A) sorbs larger amounts of all the gases than ETS-10(D) (Fig. 10B). Besides, the rate of adsorption is also higher over ETS-10(S). The observed values for adsorption of water and n-hexane did not change when the adsorption
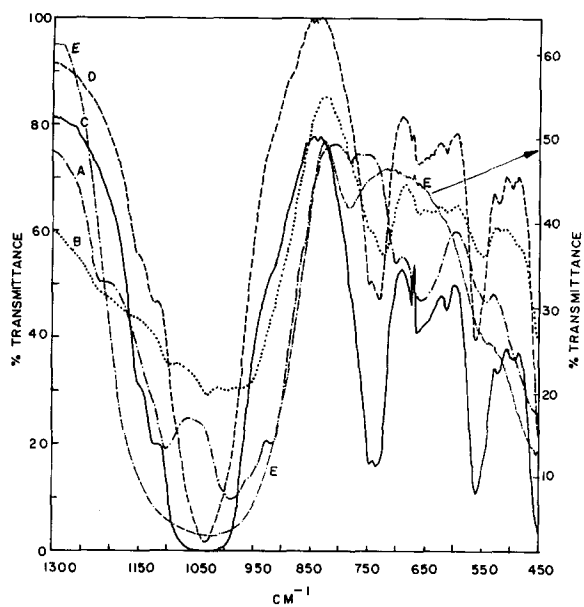
Fig. 6. IR framework vibration spectra of the titanosilicates. (A) ETS-4; (B) ETS-10(D); (C) ETS-10(S) (14.0% seed); (D) ETS-10(S) (7.0% seed); (E) precursor gel of ETS-10.
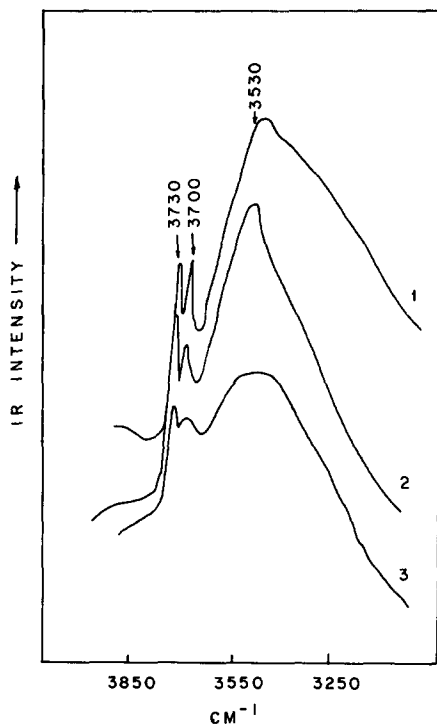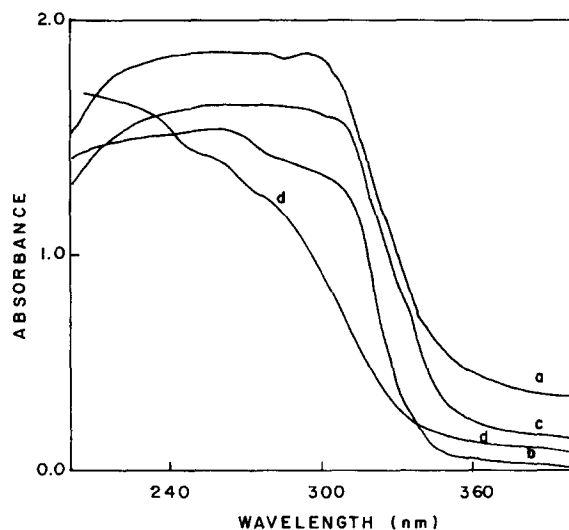

Fig. 8. UV–VIS diffuse reflectance spectra of titanosilicate samples.   (a)   ETS-10(S)   (seed = 7.0%);   (b)   ETS-4; (c) ETS-10(D); (d) precursor gel of ETS-10.
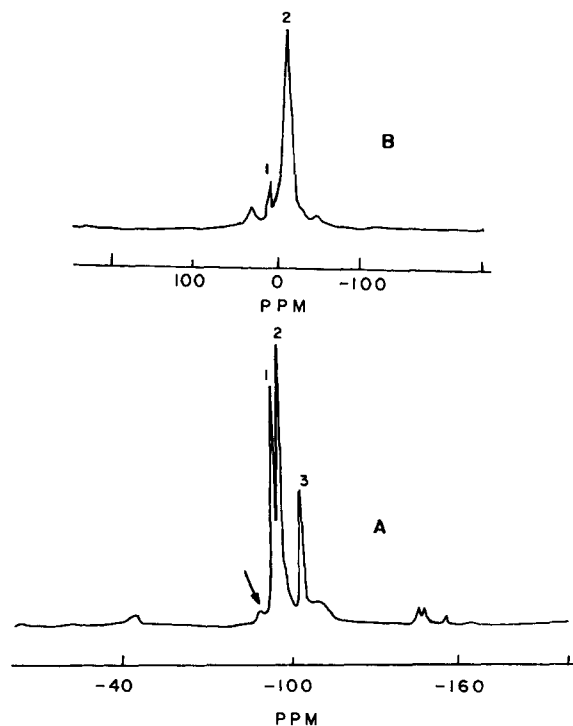

Fig. 7. FTIR spectra of ETS-10(S) (seed = 7.0%) recorded at 313, 373 and 473 K (curves 1–3, respectively).

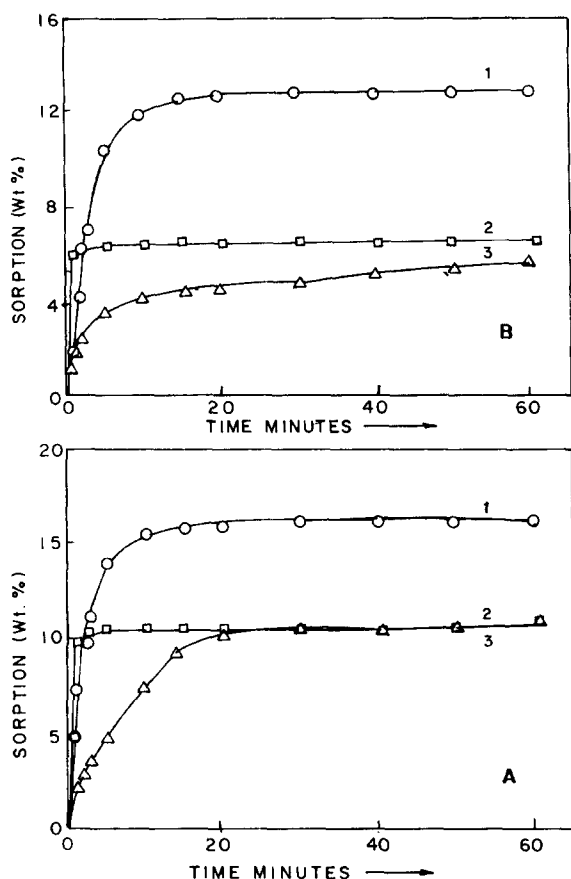Fig. 9. ^{29}Si and ^{23}Na MAS-NMR (curves A and B, respectively) of ETS-10(S) (seed = 7.0%).

Fig. 10. Sorption isotherms of H_2O, *n*-hexane and 1,3,5-trimethylbenzene (curves 1, 2 and 3, respectively) of the titanosilicates. (A) ETS-10(S) (seed = 7.0%), (B) ETS-10(D).

experiment was prolonged to 24 h in the case of both samples. However, the adsorption of mesitylene did increase by about 20% (more than the 60-min value) in the case of ETS-10(D). The adsorption data suggest that ETS-10(D) is not pure and that its pores are partially blocked.

4. Conclusions

The results show that ETS-10 synthesized in the absence of seeds of ETS-4 is not pure. The amount of seed used influences the crystallite size of ETS-10. Similarly, the H_2O/SiO_2 ratio of the synthesis gel influences the nature of the product.

Acknowledgements

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. Phillippou, S.P. Mackay, A. Ferreira, J. Rochca and S. Lidin, *Nature*, 367 (1994) 347.
[4] G.V. Tsitsishvilli, A.Yu. Krupenikov, M.V. Mamulashvili and M.V. Urushadze, *Russ. J. Phys. Chem.*, 53 (1979) 975.
[5] D. Domine and J. Quobex, *J. Mol. Sieves, Soc. Chem. Ind. London*, (1968) 78.
[6] K.J. Chao, T.C. Tasi, M.S. Chen and I. Wang, *J. Chem. Soc. Faraday Trans.*, 77 (1981) 547.
[7] S.B. Kulkarni, V.P. Shiralkar, A.N. Kotasthane, R.B. Borade and P. Ratnasamy, *Zeolites*, 2 (1982) 313.
[8] R.W. Thompson, *Zeolites*, 12 (1992) 680.
[9] C.J.J. Den Ouden and R.W. Thompson, *Ind. Eng. Chem. Res.*, 31 (1992) 369.
[10] S. Ernst, P.A. Jacobs, J.A. Martens and J. Weitkamp, *Zeolites*, 7 (1987) 46.
[11] E.M. Flanigen and H. Katami, *Molecular Sieve Zeolites. I. Adv. Chem. Ser.*, 101 (1971) 201.
[12] A.J. Chandwadkar, R.A. Abdulla, S.G. Hegde and J.B. Nagy, *Zeolites*, 13 (1993) 470.
[13] P.A. Jacobs, *DGMK Tagenbericht*, 171 (1992) 9204.
[14] G. Engelhardt and D. Michel, *High Resolution Solid State NMR of Silicates and Zeolites*, John Wiley and Sons, Chichester, 1987.