

# Studies on the synthesis, characterization and catalytic properties of the large pore titanosilicate, ETS-10

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## Abstract

The titanosilicate ETS-10 has been synthesized from titanosilicate gels in the presence and absence of seeds of ETS-4 and in the presence of an organic templating agent. The templates used were choline chloride [ $\text{HOCH}_2\text{CH}_2(\text{CH}_3)_3\text{N}^+\text{Cl}^-$ ] 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 influence of some synthesis parameters on the crystallization of ETS-10 in the presence and absence of seeds and templates has been investigated. The physico-chemical characterization of these synthesized materials has been carried out by XRD, SEM, IR, DTA/TGA and sorption of different probe molecules. The activities of the H-forms of the ETS-10 samples prepared by the different routes in catalyzing the dehydration of n-butanol, isomerization of *m*-xylene and 1,3,5-trimethyl benzene are reported.

**Keywords:** ETS-10 synthesis; Templates for ETS-10; Characterization of ETS-10; Activity of ETS-10; Titanosilicate (ETS) molecular sieves

## 1. Introduction

The synthesis of the titanosilicate ETS-10 in the absence and presence of seeds of ETS-4 has been reported earlier [1–3]. Valtchev and Mintova [4] have reported the use of tetramethyl ammonium chloride (TMACl) as a templating agent during the synthesis of ETS-10. Recently, we have reported the use of two new templates, viz., choline chloride and hexaethyl diquat-5 in the synthesis of ETS-10 [5]. In the present paper, we are comparing the kinetics of crystallization of ETS-10 in the absence and presence seeds and organic templates. Physico-chemical characterization and evaluation of the catalytic

activities of the ETS-10 samples in n-butanol dehydration, isomerization of *m*-xylene and 1,3,5-trimethyl benzene have been carried out.

## 2. Experimental

The synthesis of ETS-10(NS) in the absence of seeds, ETS-10(S) in presence of seeds (7% input on  $\text{SiO}_2$  basis), ETS-10(C) using choline chloride and ETS-10(D) using hexaethyl diquat-5 were carried out hydrothermally using sodium silicate (28.6%  $\text{SiO}_2$ , 8.82%  $\text{Na}_2\text{O}$ , 62.58%  $\text{H}_2\text{O}$ ), titanium trichloride solution (15% solution in HCl, Loba, Bombay), sodium hydroxide and potassium fluoride dihydrate (G.R., Loba, Bombay). Choline chloride (2-hydroxy ethyl trimethyl ammonium chloride, purity 99%) was

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obtained from Aldrich, USA and the bromide salt of hexaethyl diquat-5 was synthesized in the laboratory (purity 99% by chemical analysis).

The molar composition of the titanosilicate gels in terms of oxides was as follows:

1. 4.42 Na<sub>2</sub>O:0.95 K<sub>2</sub>O:TiO<sub>2</sub>:5.71 SiO<sub>2</sub>:81.81 H<sub>2</sub>O [ETS-4]
2. 4.95 Na<sub>2</sub>O:0.95 K<sub>2</sub>O:TiO<sub>2</sub>:5.71 SiO<sub>2</sub>:342.85 H<sub>2</sub>O [ETS-10(NS)]
3. 3.70 Na<sub>2</sub>O:0.95 K<sub>2</sub>O:TiO<sub>2</sub>:5.71 SiO<sub>2</sub>:171.4 H<sub>2</sub>O [ETS-10(S)]
4. 1.14 R<sub>2</sub>O:3.7 Na<sub>2</sub>O:0.95 K<sub>2</sub>O:TiO<sub>2</sub>:5.71 SiO<sub>2</sub>:256.9 H<sub>2</sub>O [ETS-10(C)]
5. 1.14 R<sub>2</sub>O:3.7 Na<sub>2</sub>O:0.95 K<sub>2</sub>O:TiO<sub>2</sub>:5.71 SiO<sub>2</sub>:171.4 H<sub>2</sub>O [ETS-10(D)]

where R = choline chloride or hexaethyl diquat-5.

The synthesis of ETS-4, and ETS-10 with and without seeds (ETS-10(S) and ETS-10(NS), respectively) was carried out according to the procedure described earlier [3,5]. XRD patterns of ETS-10(NS) and ETS-10(S) are presented in Fig. 1 (NS) and (S).

### 2.1. Synthesis of ETS-10 using templates

Solution (A) comprising 63 g sodium silicate (28% SiO<sub>2</sub>, 8.82% Na<sub>2</sub>O, 62.58% H<sub>2</sub>O) and 20 g distilled water was stirred vigorously. Solution (B) was prepared by dissolving 8.4 g NaOH

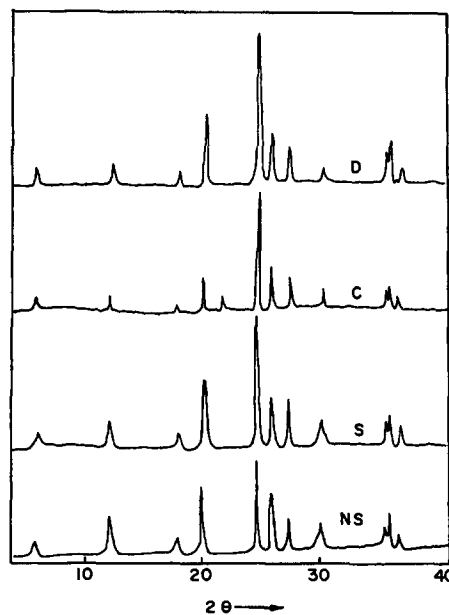


Fig. 1. XRD patterns of the as-synthesized titanosilicates. NS, S, C and D correspond to: ETS-10 prepared in the absence of seed, ETS-10(NS), presence of seed, ETS-10(S), presence of choline chloride, ETS-10(C) and presence of hexaethyl diquat-5, ETS-10(D).

pellets in 58.8 g distilled water and added slowly to the above solution (A) with continuous stirring. The gel was stirred for a further 15 min and 16.3 g choline chloride dissolved in 52.6 g of deionized water (or 51.8 g of the hexaethyl diquat-5 in 20.8 g of water) was added slowly while stirring the mixture continuously. Next,

Table 1  
Chemical composition, adsorption and catalytic properties

Sample	Chemical composition	Adsorption <sup>a</sup> (%)			Catalytic activities <sup>c</sup>			
		Water	n-Hexane	TMB <sup>b</sup>	n-Butanol conv. (%)	m-Xylene	1,3,5-TMB	
					Conv. (%)	D/I <sup>d</sup>	Conv. (%)	D/I <sup>d</sup>
ETS-4	Na <sub>50</sub> K <sub>18</sub> Ti <sub>32.1</sub> Si <sub>100</sub> O <sub>298</sub> · 102H <sub>2</sub> O	11.1	0.6	Nil	–	–	–	–
ETS-10(NS)	Na <sub>31</sub> K <sub>4.2</sub> Ti <sub>17.6</sub> Si <sub>100</sub> O <sub>252.8</sub> · 128H <sub>2</sub> O	13.1	7.3	6.2	82.0	15.0	2.0	35.9
ETS-10(S)	Na <sub>28.6</sub> K <sub>13.3</sub> Ti <sub>17.5</sub> Si <sub>100</sub> O <sub>256</sub> · 54H <sub>2</sub> O	16.1	10.6	10.6	88.0	16.4	2.1	44.3
ETS-10(C)	Na <sub>24.8</sub> K <sub>5.5</sub> Ti <sub>15.3</sub> Si <sub>100</sub> O <sub>246</sub> · 24H <sub>2</sub> O	15.2	9.4	9.0	88.3	19.9	2.0	45.3
ETS-10(D)	Na <sub>25.7</sub> K <sub>4</sub> Ti <sub>15.7</sub> Si <sub>100</sub> O <sub>246</sub> · 22H <sub>2</sub> O	16.2	11.8	10.4	93.8	23.3	2.0	50.2

<sup>a</sup>  $p/p_0 = 0.5$ ; temperature = 298 K.

<sup>b</sup> 1,3,5-Trimethylbenzene.

<sup>c</sup> Reaction conditions: temperature = 573 K; WHSV (h<sup>-1</sup>) = 2.0 (n-butanol); 1.0 (m-xylene and 1,3,5-TMB); data at TOS = 1 h.

<sup>d</sup> D/I based on no. of moles of disproportionation and isomerization products in the catalysate.

54 g of  $\text{TiCl}_3$  (15% solution in HCl) was added dropwise taking care to avoid sputtering of the above stirred gel. The dark coloured material (C) was stirred for 30 min and 9.4 g  $\text{KF} \cdot \text{H}_2\text{O}$  was added to it. The mixture was stirred further (1 h) to get paste (D) which had a pH of 11.3–11.5. The mixture was transferred to a stainless steel autoclave, capped tightly and kept in an oven preheated to the desired temperature. The crystallization was carried out under static conditions at 473 K for 7 days in the case of choline chloride and 5 days in the case of the hexaethyl diquat-5 salt. At the end of the desired period, the autoclave was cooled rapidly and the crystalline solid separated by filtration from the mother liquor which had a pH of 10.7–10.8. The crystalline material was washed well with deionized water, dried at 383 K for 12 h and calcined at 723 K (12 h) in a flow of dry air to obtain the template free ETS-10(C or D).

The various experimental methods such as XRD, IR, NMR, SEM and sorption studies used in characterizing the samples have been described elsewhere [3]

### 3. Results and discussion

The chemical composition of the titanosilicates used in this investigation are presented in Table 1. The Si:Ti ratio is nearly the same as the input ratio for ETS-10(NS) and ETS-10(S), whereas slightly siliceous titanosilicates are formed when templates are used in the synthesis (ETS-10(C) and ETS-10(D)). A similar behaviour was also observed by us [6] during the synthesis of large pore mordenite in the absence and presence of the organic template. Interestingly, the proportion of charge balancing  $\text{K}^+$  ions are more when the synthesis is carried out in the presence of seeds (Table 1).

The X-ray diffraction patterns of the titanosilicates shown in Fig. 1 match well with those published earlier [1–5]. The relative crystallinities of the samples were calculated by comparing the sums of the areas of the peaks in the  $2\theta$

range of 24.65 to 27.5° of the sample and the most crystalline material obtained from the same batch composition. Variation of the seed concentration from 0.9 to 14.0% (input  $\text{SiO}_2$  basis) did not affect the relative crystallinity of the ETS-10(S). However, when no seed was used, the crystallinity of ETS-10(NS) was only 75% of ETS-10(S) [3]. Similarly ca. 98% crystalline titanosilicate material could be obtained when choline chloride was used as the templating agent with an impurity peak at  $2\theta = 21.8^\circ$  (Fig. 1C). The presence of extra lattice material in the ETS-10(C) is also inferred from the decrease in absorption of hydrocarbons. However, amorphous material is not noticed clearly in the SEM pictures [5].

#### 3.1. Kinetics of crystallization of ETS-10

To study the effect of temperature and water content on the formation of the titanosilicate, the kinetics of crystallization were studied in the temperature range of 423–473 K (at  $\text{H}_2\text{O}/\text{SiO}_2 = 15$  to 60) by comparing the extent of crystallization of the gel mixture at different intervals of synthesis time [3,6]. Relative ratios of other starting materials were kept the same in all the batches. Isotherms for the best crystalline titanosilicate materials obtained during the study (473 K; molar compositions mentioned earlier)

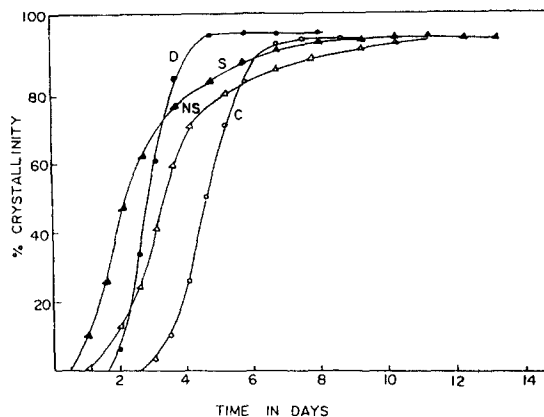


Fig. 2. Kinetics of crystallization of the titanosilicates. NS: ETS-10(NS); S: ETS-10(S); C: ETS-10(C) and D: ETS-10(D).

are shown in Fig. 2. Even though the induction period required for the ETS-10(D) and ETS-10(C) is higher than ETS-10(S) and ETS-10(NS), the time required to achieve  $\approx 100\%$  crystalline material is shorter when templates are used, 5 and 7 days, respectively, being required for ETS-10(D) and ETS-10(C) when

compared to 10 days required for ETS-10(S) and ETS-10(NS) (Fig. 2).

SEM photographs of the titanosilicates are shown in Fig. 3, seeds of ETS-4 (irregular shapes) are shown in Fig. 3A. ETS-10(NS) crystallizes as cuboidal layered particles of 5–7  $\mu\text{m}$  (Fig. 3B). When seeds of ETS-4 (7% input

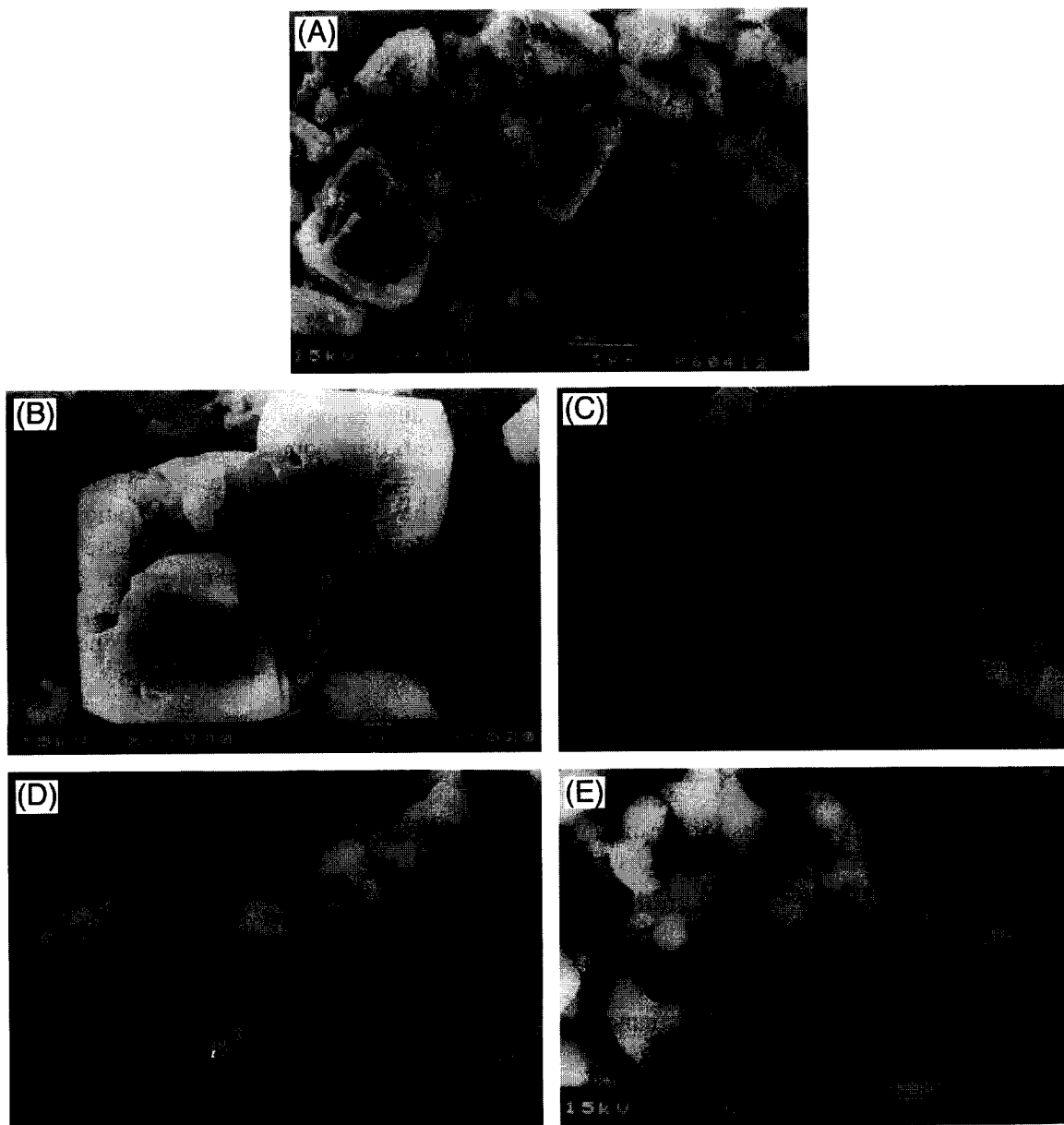


Fig. 3. SEM photographs of the titanosilicates. A: ETS-4; B: ETS-10(NS); C: ETS-10(S); D: ETS-10(C) and E: ETS-10(D).

SiO<sub>2</sub> basis) are used during synthesis, sharp, twinned cuboids in the size range of 1–4 μm are obtained (Fig. 3C). While ETS-10(C) crystallizes as aggregates of irregular crystals of < 0.5 μm (Fig. 3D), ETS-10(D) crystallizes as wheat shaped polycrystallites of 2–4 μm (Fig. 3E). This shows that the crystal morphology is affected by the presence and absence of seed and the nature of the organic template used.

### 3.2. IR studies

The framework IR spectra (in the region 450–1300 cm<sup>-1</sup>) of ETS-10(NS), ETS-10(S) and calcined ETS-10(C) and ETS-10(D) are shown in Fig. 4. The position of the major absorption bands corresponding to the different symmetric and asymmetric stretching vibrations [3,7] are nearly the same for all the titanosilicates. However, the spectral bands for ETS-10(NS) and ETS-10(C) (Fig. 4, curves NS and S, respectively) are not sharp, though the major bands occur at the same positions as those of ETS-10(S) and ETS-10(D). The lack of sharpness may be due to contributions from amorphous material. A weak shoulder at ca. 985

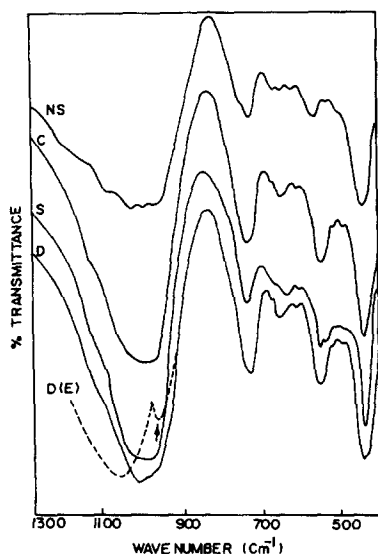


Fig. 4. IR framework vibration spectra of the titanosilicates. NS: ETS-10(NS); S: ETS-10(S); C: ETS-10(C); D: ETS-10(D) and D(E): ETS-10(D) after acid leaching.

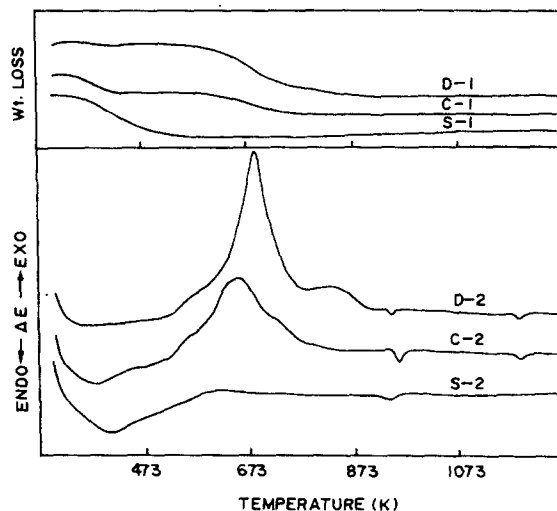


Fig. 5. Thermoanalytical curves of the titanosilicates. TGA curves; D-1: ETS-10(D); C-1: ETS-10(C) and S-1: ETS-10(S). DTA curves; D-2: ETS-10(D); C-2: ETS-10(C) and S-2: ETS-10(S).

cm<sup>-1</sup> is also seen (Fig. 4, curves NS and S) but it is relatively prominent for the titanosilicates synthesized with templates Fig. 4, curves C and D). The intensity of this band (970 cm<sup>-1</sup>) is enhanced after the calcined ETS-10(D) sample was leached with 0.5 M H<sub>2</sub>SO<sub>4</sub> [5]. This is similar to the observation of Khouw and Davis [8] who synthesized TS-1 in the presence of Na-ions. The above band has recently been attributed to Si–O<sup>-</sup> vibrations by Cambor et al. [9]. The occurrence of this band in acid washed ETS-10 is surprising.

### 3.3. TGA / DTA

The thermal behaviour of the as-synthesized ETS-10(S), ETS-10(C) and ETS-10(D) are shown in Fig. 5. The thermograms of ETS-10(C) and ETS-10(D) resemble the thermogram of the titanosilicate prepared by using TMACl [4]. Loss of water occurs upto 533 K and is found to be 13.2%, 4.78% and 0.521% in the case of ETS-10(S), ETS-10(C) and ETS-10(D), respectively (Fig. 5, curves S-1, C-1 and D-1, respectively). The oxidative decomposition of the templates in the range 533–843 K results in mass loss of 5.53% and 11.87% (Fig. 5, curves S-2, C-2 and

D-2, respectively). The sharp endotherm observed at 948 K (Fig. 5, curves S-2, C-2 and D-2) suggests the melting or phase transformation of these materials.

### 3.4. Sorption studies

The sorption capacity of the titanosilicates was measured using water (2.65 Å), n-hexane (4.3 Å) and 1,3,5-trimethyl benzene (8.1 Å) as probe molecules. The equilibrium sorption capacity of ETS-10(S) and ETS-10(D) for all the probe molecules is close to the earlier reported values [3]. The equilibrium sorption capacities observed for ETS-10(NS) and ETS-10(C), however, are lower. This is probably due to the presence of amorphous material and impurity phases (seen in XRD, Fig. 1C,  $2\theta = 21.8^\circ$ ).

### 3.5. Catalytic activities

The catalytic tests were carried out using the H-form of the samples (2 g) in a vertical flow fixed bed reactor (i.d. = 12 mm). Details of the preparation of the H-form of the samples, reaction and analysis methods are described elsewhere [5]. The catalytic performances of the samples presented are in Table 1.

#### 3.5.1. Dehydration of n-butanol

All the four H-ETS-10 samples were active in the dehydration of n-butanol. The activities of the samples increases in the order ETS-10(NS) < ETS-10(S) < ETS-10(C) < ETS-10(D). The products, as expected were mostly 1-butene and 2-butenes. Small amounts of i-butene were also produced. The ratio of i-butene/(1-butene + 2-butenes) is very small, being between 0.02 to 0.03 in all the cases. This value is far below the expected thermodynamic value of 1.3 suggesting that skeletal isomerization of olefins does not occur to any significant extent due to the relatively weak acidity of the materials. A *t*-butene-2/*c*-butene-2 ratio of ca. 1.3 is found in the products from all the samples. This value is also less than the thermodynamic value of 1.7 expected at the reaction temperature.

#### 3.5.2. *m*-Xylene isomerization

Again, the catalytic activity of the samples increases in the same order as in the case of n-butanol dehydration. Interestingly, the disproportionation activities of the samples is more than their isomerization activities. The disproportionation/isomerization (D/I) ratio is 0.98 in the case of ETS-10(NS) and 1.05–1.06 for the other three samples. The high disproportionation activity is a result of the large pores providing enough space for the bimolecular reaction. Besides, the high density of the acid sites arising from the need to charge compensate (doubly) the large number of  $\text{Ti}^{4+}$  octahedra should enable the adsorption of xylene molecules in close proximities favouring the bimolecular disproportionation reactions.

#### 3.5.3. 1,3,5-Trimethyl benzene isomerization

The catalytic activity of the samples increases in the same order as in the earlier reactions. The highest conversion of 50.2% is observed over ETS-10(D). Significant amounts of tetramethyl benzenes are also produced along with xylenes due to disproportionation reactions. The D/I ratios range between 0.46 and 0.60 and are smaller than the values obtained in the case of *m*-xylene isomerization as spatial requirements for bimolecular reactions involving two 1,3,5-trimethyl benzene molecules are more than for two *m*-xylene molecules.

## 4. Conclusions

ETS-10 can be synthesized in the presence and absence of seeds (ETS-4) or templates. Use of the bromide salt of hexaethyl diquat-5 leads to rapid synthesis and also purer material. Templates and seeds have a profound influence on the size and morphology of the ETS-10 crystallites. IR studies reveal the presence of a band at  $970\text{ cm}^{-1}$ , attributed by earlier workers to Si–O–Ti or Si–O<sup>−</sup> vibrations, in acid washed ETS-10 samples. The H-form of ETS-10 is active in catalyzing reactions such as dehydra-

tion of n-butanol and isomerization of *m*-xylene and 1,3,5-trimethylbenzene.

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