A rapid method of synthesizing the titanium silicate ETS-10

Tapan Kr. Das, A. J. Chandwadkar and S. Sivasanker*

National Chemical Laboratory, Pune 411 008, India

The use of $TiCl_4$ as the source of Ti produces highly crystalline and pure ETS-10 samples within 16 h.

The synthesis of ETS-10, a novel large-pore titanosilicate molecular sieve was first reported by Kuznicki.[1] In ETS-10, the Ti^{4+} ions are present in an octahedral arrangement[2] of O^{2-} ions, linked to the Si^{4+} (T_d) ions through corner-sharing of O^{2-} ions. As a result of the O_h coordination of the Ti^{4+} ions, there is a net negative charge of two units associated with each Ti^{4+} ion, the charge being compensated by alkali-metal ions (Na^+/K^+). The double negative charge on each Ti^{4+} octahedron makes ETS-10 a highly hydrophilic molecular sieve with a large sorption capacity for polar molecules making it eminently suitable as an adsorbant.

In the original patent of Kuznicki,[3] $TiCl_3$ was used as the source of Ti along with seeds of ETS-4 (a small-pore titanosilicate) in the examples cited by him. Besides, other workers[2,4–7] have also used $TiCl_3$, either along with seeds of ETS-4 or with templates. Valtchev and Mintova[8,9] have used $TiCl_4$ for synthesis, but along with tetramethylammonium chloride (TMACl) as the template. All the above workers reported that 4–10 days are necessary for the crystallization of ETS-10. Even so, in many of the syntheses, ETS-4 impurities were found in the product.[4,8] We now report the synthesis of ETS-10 over very short reaction times (< 16 h) using $TiCl_4$ and in the absence of seeds or templates. The use of $TiCl_4$, a much cheaper raw material than $TiCl_3$, should reduce the cost of manufacture of ETS-10. Besides, the samples synthesized by us using $TiCl_4$ (as described below) were purer, contained no ETS-4 impurities and had better thermal stability.

The hydrothermal synthesis of ETS-10(A) using $TiCl_4$ was carried out with a gel of the following molar composition: $3.70\ Na_2O : 0.95\ K_2O : TiO_2 : 5.71\ SiO_2 : 171\ H_2O$.

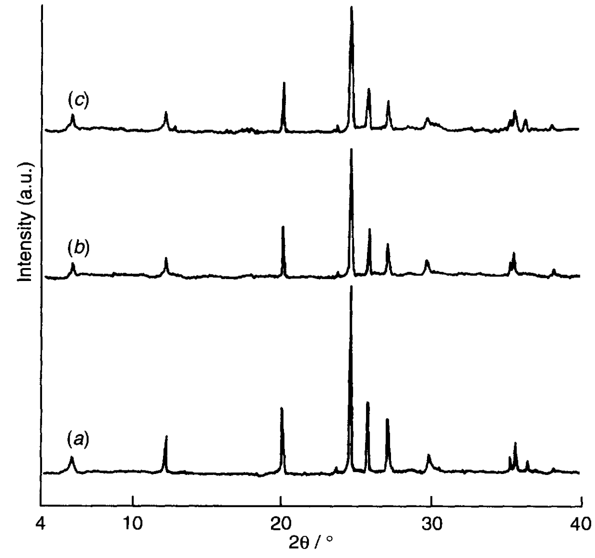

Fig. 1 XRD patterns of as-synthesized ETS-10 samples: (*a*) ETS-10(A), (*b*) ETS-10(S) and (*c*) ETS-10(D)

In a typical synthesis, a solution of 9.3 g NaOH in 40 g distilled water was added to a vigorously stirred solution of 52.5 g sodium silicate (28.6% SiO_2, 8.82% Na_2O, 62.58% H_2O) and 40 g distilled water. This was followed by the dropwise addition of 32.75 g of a $TiCl_4$ solution (25.42 mass% $TiCl_4$, 25.92 mass% HCl, 48.60 mass% H_2O) to this mixture (colourless gel) with rapid stirring. 7.8 g $KF{\cdot}2H_2O$ was then added to the above gel (pH = 11.2 ± 0.1) and the mixture stirred well. The mixture was then transferred to a stirred stainless-steel autoclave (Parr Instruments, USA) and crystallization carried out at 473 K with a stirrer speed of 300 rpm for 14–16 h. After crystallization, the products were filtered and washed with deionized water until the pH of the filtrate was 10.7–10.8. It was dried at 373 K for 8–10 h.

Table 1 Physico-chemical characterization of ETS-10 samples

Sample	Adsorption[a] (mass %) Water	*n*-hexane	TMB[b]	Total surface area (S_{BET})/ $m^2\ g^{-1}$	Micropore volume/ ml g^{-1}
ETS-10(A)	17.0	12.1	11.2	410	0.16
ETS-10(S)[c]	16.1	10.6	10.6	361	0.11
ETS-10(D)[d]	16.2	11.8	10.4	365	0.14

[a] Gravimetric (Cahn Electrobalance); p/p_0 = 0.5 and 298 K. [b] 1,3,5-Trimethylbenzene. [c] Sample synthesized using seeds of ETS-4. [d] Sample synthesized by using *N,N,N,N′,N′,N′*-hexaethylpentanediammonium bromide as the template.

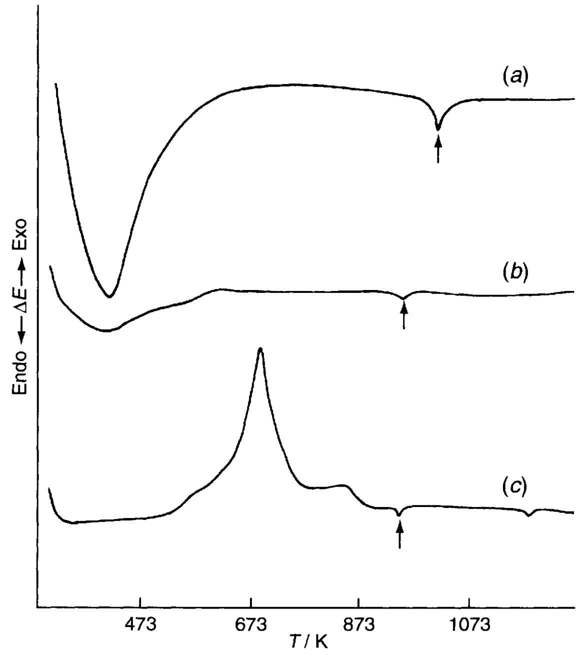

Fig. 2 DTA thermograms of ETS-10 samples: (*a*) ETS-10(A), (*b*) ETS-10(S) and (*c*) ETS-10(D). Arrow shows endotherms due to structure collapse.

For comparison purposes, two more ETS-10 samples were prepared, one using $TiCl_3$ and ETS-4 seeds [ETS-10(S)] and the other using $TiCl_3$ along with *N*,*N*,*N*,*N*′,*N*′,*N*′-hexaethylpentanediammonium bromide as the template [ETS-10(D)] following procedures already described.[4,6]

The XRD pattern of the sample prepared using $TiCl_4$ and without seeds or organic templates was similar to those reported by earlier workers[2,4–6] (Fig. 1). Earlier studies have revealed that the size and morphology of the ETS-10 crystals were dependent on the presence/absence of seeds,[4] the nature of the templates used[6,8] and synthesis parameters. In general, earlier studies had reported ETS-10 crystallites in the size range of 3–5 μm, the crystallites being often irregular in shape. In the present synthesis, highly crystalline nearly uniform cuboids of < 1 μm were obtained without any detectable impurity of ETS-4.

IR (FTIR, Nicolet 60XB) studies did not reveal noticeable differences between the samples synthesized by the different methods. Three sharp bands were observed at δ −94.69, −97.72 and −104.01 in the ^{29}Si MAS NMR spectrum (Bruker, MSL-300) of ETS-10(A). The spectrum is similar to that reported[4] earlier except for the absence of the weak band (reported earlier) at δ −90.74, attributed to the presence of ETS-4 impurities. The purity of the ETS-10(A) is further confirmed from the sorption of water, *n*-hexane and 1,3,5-trimethylbenzene at 298 K and the surface areas for the different samples (Table 1). N_2 adsorption isotherms of all the samples showed microporous type 1 curves. The larger sorption capacity and larger surface area of ETS-10(A) compared to the other two samples reveal that ETS-10(A) contains less amorphous material and less pore blockage.

Thermograms of ETS-10 prepared by $TiCl_4/TiCl_3$ are similar (Fig. 2). It is noticed that the structural integrity of the ETS-10(A) sample is maintained up to *ca.* 983 K [*cf. ca.* 933 K for ETS-10(S) and ETS-10(D)].

References

1 S. M. Kuznicki, *US Pat.*, 4,938,939, 1990.
2 M. W. Anderson, O. Terasaki, T. Ohsuna, A. Phillippou, S. P. Mackay, A. Ferreira, J. Rocha and S. Lidin, *Nature*, 1994, **367**, 347.
3 S. M. Kuznicki, *US Pat.*, 4,853,202, 1989.
4 Tapan. Kr. Das, A. J. Chandwadkar, A. P. Bhudhkar, A. A. Belhekar and S. Sivasanker, *Microporous Mater.*, 1995, **4**, 195.
5 J.Rocha, Zhi Lin, A. Ferreira and M. W. Anderson, *J. Chem. Soc., Chem. Commun.*, 1995, 867.
6 Tapan, Kr. Das, A. J. Chandwadkar, A. P. Bhudhkar and S. Sivasanker, *Microporous Mater.*, 1996, **5**, 401.
7 M. W. Anderson, A. Philippou, Z. Lin, A. Ferreira and J. Rocha, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1003.
8 V. Valtchev and S. Mintova, *Zeolites*, 1994, **14**, 697.
9 V. P. Valtchev, *J. Chem. Soc., Chem. Commun.*, 1994, 261.

Received, 20th February 1996; Com. 6/01223J