Synthesis of microporous titanosilicates ETS-10 and ETS-4 using solid TiO_2 as the source of titanium

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Microporous titanosilicates ETS-10 and ETS-4 are synthesized under hydrothermal conditions using solid TiO_2 as a source of titanium; the transformation of anatase and rutile phases to the ETS products is found to be direct without involving intermediate amorphous phases.

Isomorphous substitution of zeolite frameworks has led to the discoveries of many new types of zeolites. Among these are the titanosilicate zeolites which are of importance.[1–8] The titanium-containing silicalite TS-1 has shown to be an efficient oxidative catalyst for many oxidation reactions.[1] ETS-10 and ETS-4, discovered by Kuznicki,[2,3] have exhibited interesting structures and unique adsorption properties. The Ti in TS-1 is identified to be four-oxygen coordinated,[1] while the Ti in ETS-10 and -4 is six-oxygen coordinated.[2,3] In the former no framework charge is possible, while in the latter two negative charges are brought in by each TiO_6 octahedron, requiring the presence of charge-balancing cations such as Na^+ or K^+ in the channels. The TiO_6 octahedra in ETS-10 organize themselves into chains by corner-sharing their oxygens and connecting laterally with SiO_4 tetrahedra, forming a structure that has no direct exposure of TiO_6 octahedra to the surface of the large channels (see ref. 4). These structural characteristics make the ETS-10 zeolite unique in its structure, ion exchange and adsorption. The structure of ETS-4 was proposed to be similar to that of zorite, a natural microporous titanosilicate.[2,3]

The titanosilicate zeolites ETS-10 and ETS-4 reported in the literature[2–6] were synthesized using titanium chlorides as titanium sources. Recently several new types of titanosilicate zeolites such as GTS-1[7] and the titinosilicate of Poojary *et al.*[8] were synthesized using organotitanium compounds as titanium sources. Because they are very sensitive to moisture, these Ti compounds are very difficult to handle and require special facilities for their transfer during the gel preparation. In this communication, we report the synthesis of ETS-10 and ETS-4 using the crystalline forms of TiO_2 (anatase, rutile, or mixtures of these two such as P25) as the source of titanium.

The synthesis of ETS-10 was carried out in Teflon-lined autoclaves under hydrothermal conditions with temperatures ranging from 180 to 230 °C. A typical procedure is as follows: 4.0 g P25 (Degussa, 76% anatase and 24% rutile) was dispersed, by stirring, into 62.5 g deionized water, to which 6.0 g NaOH pellets (Fisher) and 2.15 g anhydrous KF (Aldrich) were added. After 5 min of stirring, 37.5 g colloidal silica (Aldrich, 40% silica) was poured into the mixture while stirring vigorously, and the stirring was continued for 30 min. The slurry was then transferred into an autoclave and heated to 200 °C and maintained at this temperature for 2 days. The product was isolated by centrifugation, washed twice by redispersing it into deionized water, and dried in air.

A similar procedure was employed for the synthesis of ETS-4 where the initial mixture contains 4.0 g titanium oxide (P25), 37.5 g colloidal silica (40% SiO_2), 62.5 g water, 10 g NaOH and 1.0 g NaF. The crystallization was carried out statically at 200 °C for 44 h.

Powder X-ray diffraction (XRD) measurements of the products gave identical patterns to those of ETS-10 and ETS-4 reported in the literature[2–4] (Fig. 1). The XRD pattern of ETS-10 shows several diffuse peaks indicating the presence of structural defects as proposed and demonstrated by Anderson *et al.*[4] and Bozhilov and Valtchev.[9] Further structural characterization of the products was made using a combination of XRD, Fourier-transform IR spectroscopy, thermal gravimetric analysis, and solid state nuclear magnetic resonance techniques. The results confirm that pure ETS-10 and ETS-4 are obtained from the syntheses using solid TiO_2 as the Ti source.

Examination of factors such as SiO_2/TiO_2, H_2O/SiO_2 and M_2O/SiO_2 (M = Na or K or K + Na) gives gel compositions in terms of molar ratios of oxides in which the titanosilicate ETS-10 and ETS-4 can be synthesized: 1.0 $M_2O:TiO_2:1.2–6$ $SiO_2:5–50$ H_2O for ETS-4 and 1.0 $M_2O:TiO_2:2–8$ $SiO_2:5–50$ H_2O for ETS-10.

The transformation of the crystalline TiO_2 to ETS-10 and -4 products was found to be direct. No intermediate amorphous phases could be detected by powder XRD during the crystallization process in which a yield of *ca.* 15 g of air-dried product was normally obtained from the synthesis. The peak intensity of the ETS-10 or -4 product increased at the expense of the solid TiO_2 phase. Fig. 2 shows the crystallization curve of ETS-10 together with the changes of the content of P25 during the crystallization.

The particle size of the solid TiO_2 is an important factor for the formation of ETS products. For P25 with very fine particles (*ca.* 200 Å), a complete transformation is easily achieved, while for anatase (*ca.* 0.6 μm)† and rutile (*ca.* 1 μm)† (both obtained from Aldrich), an incomplete transformation to ETS products is often seen. The transformation rate parallels the particle size of these materials in the order: P25 > anatase > rutile.

Adding fluoride compounds to the synthesis gel was found to be essential in the formation of ETS-10, while it might not be necessary for that of ETS-4. This was shown in the syntheses where pure ETS-4 could be obtained without adding any fluoride compounds. The presence of K^+ ion favours the

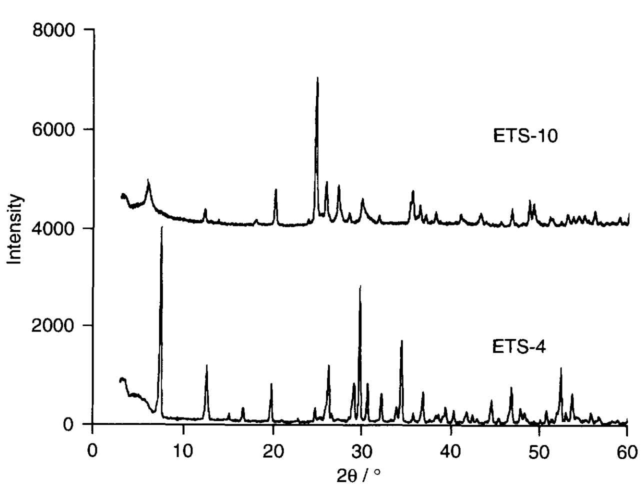

Fig. 1 Powder X-ray diffraction patterns of ETS-10 (*a*) and -4 (*b*) synthesized using solid TiO_2 (P25) as a titanium source

formation of ETS-10, while Na^+ shows preference for the formation of ETS-4.

The work shown here demonstrates that under proper conditions, the thermodynamically stable TiO_2 phases of anatase and rutile can be used as Ti sources for the synthesis of titanosilicate molecular sieves. In Kuznicki's original patents,[2,3] he tried a solid titanium oxide, Ti_2O_3, but failed to produce ETS-10 and -4, and instead a dense phase material was obtained. A very recent study[10] on the synthesis of porous titanosilicates has reported the use of solid TiO_2 as a titanium source, but the temperature used in the study[10] was 700 °C, which is too high to be suitable for hydrothermal synthesis. Our results on the preparation of microporous titanosilicates ETS-10 and ETS-4 reported here provide new and more practical avenues to the synthesis of these types of materials. Successful attempts have been made to produce all the structures of microporous titanosilicates containing TiO_6 octahedra reported in the literature[2–10] using solid TiO_2 as the source of titanium. Some new structures are also produced.[11,12]

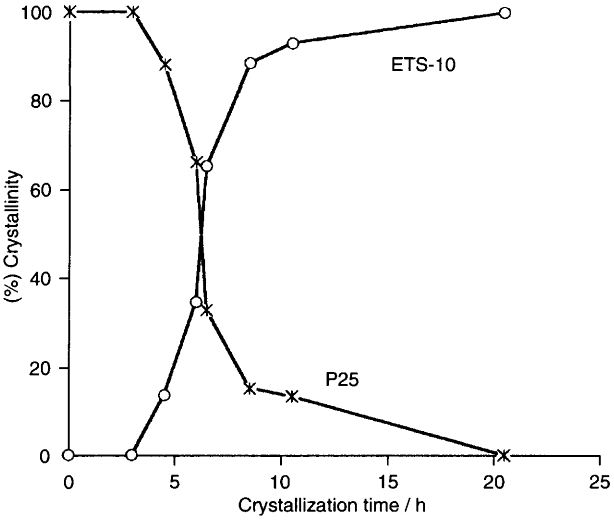

Fig. 2 Changes of the crystallinity of product ETS-10 and of the content of P25 as a function of crystallization. The crystallinity of ETS-10 during crystallization was determined by taking the final pure ETS-10 as a reference.

We would like to thank the National Science Foundation of the United States for the financial support of this work.

Footnote

† Technical information was obtained from Aldrich Customer Service.

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Received, 29th January 1996; Com. 6/00656F