Influence of Different Organic Bases on the Crystallization of Titanium Silicate ETS-10

Valentin P. Valtchev

Institute of Applied Mineralogy, Bulgarian Academy of Sciences, 92 Rakovsky Str., 1000 Sofia, Bulgaria

The influence of different templates on the crystallization of titanium silicate ETS-10 has been investigated; the presence of tetramethylammonium stabilizes the structure formation and decreases the significance of initial gel composition.

Progress in the hydrothermal synthesis of molecular sieves has resulted in a large number of structure that are crystalline three-dimensional microporous solids composed of interconnected tetrahedra.[1] High-silica zeolites, the AlPO-*n*, SAPO-*n* and MeAPO-*n* families of microporous materials have been studied and claimed in the open or patent literature.[2]

Recently interest has turned towards a potentially large class of novel molecular sieve materials composed of interconnected octahedral and tetrahedral oxide polyhedra.[3] Members of this family are titanium silicates ETS-4 and ETS-10.[4] The framework topology of ETS-4 is related to the structure of zorite, a naturally occurring titanium silicate.[5,6] The structure of ETS-10 has all the traditional properties of a classical molecular sieve with a large pore channel system. It has been synthesised in the $Na_2O–K_2O–TiO_2–SiO_2–H_2O$ system in a very narrow range of pH values (10.2 ± 0.2).[4]

The purpose of this paper is to investigate the influence of different organic bases on the crystallization of titanium silicate ETS-10. The hydrothermal synthesis of titanium silicate ETS-10 was carried out using gels of the following molar composition: $40R : 52Na_2O : 42K_2O : 20TiO_2 : 100SiO_2 : 7030H_2O$, where R is pyrrolidine (Py), tetramethylammonium chloride (TMA), tetraethylammonium chloride (TEA), tetrapropylammonium bromide (TPA), tetrabutylammonium chloride (TBA), 1,2-diaminoethane (En) and 1,6-diaminohexane (Dh) (from Merck). The inorganic reactants used were $Na_2SiO_3{\cdot}nH_2O$ (SiO_2, 63%; Na_2O 18%) (Riedel de Haën), $TiCl_4$ (Merck), NaOH (Merck), KOH (Merck) and distilled water. The experiments were carried out in Teflon-lined stainless steel autoclaves at 200 °C for 2–30 days. The pH measurements were performed with a Philips PW 9409 digital pH meter. The solid products were characterised by X-ray diffraction (Philips APD 15), thermal analysis (Stanton Redcroft 780) and scanning electron microscopy (SEM Philips 515).

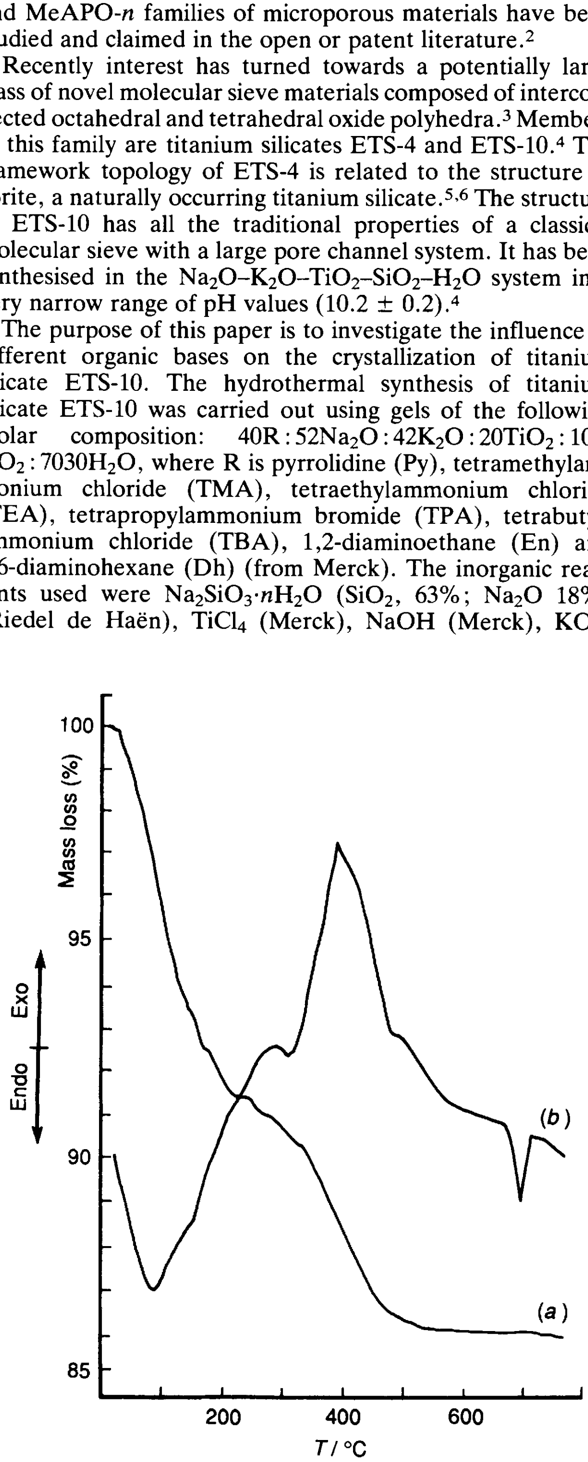

Fig. 1 (*a*) TGA and (*b*) DTA curves of [TMA]-ETS-10 (heating rate 10 °C min^{-1})

In the absence of an organic base the crystallization of the gel produced ETS-10 after 7 days at 200 °C. In most cases organic bases, *i.e.* En, Py, TEA and TPA increased the time of crystallization of ETS-10 and produced mixed crystalline products. In the syntheses with these templates the product contains impurities of quartz, ETS-4, crystobalite and a molecular sieve with the MFI-type structure. Using TBA and Dh as templates ETS-10 was not observed. The TMA cation seemed to be an exception among the templates investigated. [TMA]-ETS-10 crystallized in two days, with a high degree of crystallinity, and X-ray and SEM analyses proved that ETS-10 was the only phase present.

Differential thermal analysis (DTA) and thermogravimetric (TG) measurements of [TMA]-ETS-10 are shown in Fig. 1. The DTA curve showed that the decomposition temperature of the organic cation was in the range 290–570 °C. This was in good agreement with the TG results. The mass loss in this temperature range was 5.5%. TMA itself decomposes in the temperature range 260–400 °C with sharp endothermic effects of 260, 330 and 375 °C. The increased temperature of TMA decomposition is an indication of its presence in the channel system of the ETS-10.

Additional experiments were carried out to study the influence of the pH of the initial gel on the crystallization of [TMA]-ETS-10. The desired pH was obtained by changes in the sodium hydroxide concentration. Gels with pH 9.6, 10.5, 11.3, 11.9, 12.4 and 12.9 were held at 200 °C for 7 days. No crystalline product was obtained from the gel with pH 9.6, but under all other conditions ETS-10 was formed. At pH values higher than 11.9 ETS-4 co-crystallized with the ETS-10 and at pH 12.9 ETS-4 was the main crystalline product.

Of the templates investigated only TMA influenced the crystallization of titanium silicate ETS-10. The other templates had 'structure-breaking' rather than 'structure-directing' properties. The TMA clearly had a pore-filling function in the crystallization of ETS-10 owing to the good correlation between the size of TMA (7.4 Å) and the diameter of the channels of ETS-10 (about 8 Å). Its presence stabilized the formation of ETS-10, decreasing the influence of the initial gel composition.

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