Crystallization of TS-1 and TS-2 zeolites with contribution of solid–solid transformations

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The synthesis of TS-1 and TS-2 zeolites from SiO_2–TiO_2 xerogels wetness impregnated with solutions of the structure-directing agent proceeds mainly through solid–solid transformations which allow the raw amorphous network to be reordered into crystalline frameworks.

Although the possibility of solid–solid transformations during zeolite crystallization was postulated several years ago,[1,2] at present it is commonly accepted that zeolite synthesis is a solution-mediated process[3,4] with two main steps: nucleation and crystal growth. There is still no clear agreement about the mechanism of nucleation, several alternatives having been proposed to describe the formation of the nuclei: homogeneous, heterogeneous, autocatalytic and secondary nucleations. However, in all cases it is assumed that, once the nuclei are in contact with the solution, the crystal growth step takes place by a progressive incorporation of dissolved silicate species around them, whereas the role of the amorphous solid phase, if present, is just to provide the solution with additional material as it is consumed in building the zeolite framework.

TS-1 and TS-2 are zeolites with MFI and MEL topologies, which owing to the presence of tetrahedral Ti atoms in framework positions exhibit notable properties for the liquid-phase oxidation of organic substrates.[5–7] The method here used for the preparation of TS-1 is based on the previous stabilization of the Ti atoms by incorporation into amorphous SiO_2 networks to prevent the formation of TiO_2 phases.[8–11] The amorphous SiO_2–TiO_2 mixed oxide so obtained is converted into TS-1 in a subsequent step by wetness impregnation with a solution of an MFI structure-directing agent (tetrapropylammonium hydroxide, TPAOH) followed by thermal treatment at autogenous pressure. We have further extended this method to the TS-2 synthesis using tetrabutylammonium hydroxide (TBAOH) as template of the MEL structure.[12] In contrast with the conventional mechanism, we report in this work that TS-1 and TS-2 are crystallized in this system mainly through solid–solid transformations, the amorphous network being reordered into crystalline structures with participation of the liquid phase but without undergoing a complete dissolution.

The amorphous SiO_2–TiO_2 solids used as starting materials have been prepared with a Si : Ti ratio of 30 by a two-step sol-gel method:[10–12] (*a*) acid hydrolysis of tetraethylorthosilicate and titanium tetrabutoxide and (*b*) basic gelation by addition of a 1 mol dm^{-3} aqueous solution of the corresponding quaternary ammonium hydroxide. The gel so obtained was dried at 110 °C and finely ground into a powdered xerogel. The crystallization kinetics of TS-1 and TS-2 have been studied by wetness impregnation of the SiO_2–TiO_2 xerogels with 1 mol dm^{-3} solutions of TPAOH and TBAOH, respectively, and subsequent autoclaving at 170 °C for different synthesis times (2–72 h). The crystallization products were recovered by centrifugation, repeatedly washed with distilled water, dried at 110 °C and calcined at 550 °C. The samples have been characterized by a number of techniques: X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR), diffuse reflectance (DR) UV–VIS spectroscopy, *n*-hexane adsorption at 25 °C and scanning and transmission electron microscopy (SEM and TEM).

From the results obtained the following mechanism with three main stages is proposed to describe the TS-1 and TS-2 crystallization in the system here studied (see Fig. 1).

(*i*) Conversion of the raw SiO_2–TiO_2 xerogel into an amorphous particulate solid with variations in both Ti content and environment.

n-Hexane adsorption measurements and SEM images indicate that the starting xerogel is a polymeric and micro-macroporous solid, but after a few hours of synthesis it loses most of its macropores, being transformed into a micro- and mesoporous material formed by a tight packing of amorphous particles with sizes of *ca.* 50 nm (primary particles). Simultaneously, a small amount (<5 mass%) of the SiO_2–TiO_2 xerogel is dissolved leading to an increase of the Si : Ti ratio in the solid phase. Thereafter, both the yield (*ca.* 95%) and the Si : Ti ratio (46 and 55 during the TS-1 and TS-2 syntheses, respectively) of the solid products remain almost constant with time as crystallinity increases from 0 to 100%. Moreover, the Si : Ti ratio of the titanosilicate species dissolved at the beginning of the synthesis is *ca.* 5, corresponding to a Ti proportion higher than the maximum that can be incorporated into tetrahedral positions of TS-1 (Si : Ti = 40).

FTIR and DR UV–VIS data show that the Ti environment in the amorphous SiO_2–TiO_2 solids evolves at short synthesis times yielding predominantly tetrahedral Ti species prior to the formation of any crystalline material. Thus, the DR UV–VIS spectra of the amorphous and partially crystalline samples are shifted towards lower wavelengths compared to that of the starting xerogel, presenting bands centred at 210 nm and very close to those of pure TS-1 and TS-2, typical of Ti species with tetrahedral coordination. In addition, no absorption is observed at 330 nm in the DR UV–VIS spectra of the starting xerogel and of the different samples obtained along the crystallization, which shows that TiO_2 is not formed.

(*ii*) Aggregation of the primary particles into secondary units and detection of the first crystalline entities.

SEM micrographs (Fig. 2) show that the primary particles undergo an aggregation process to yield secondary units. The shapes and sizes of the latter closely resemble those of the zeolite crystals observed in pure TS-1 and TS-2 samples. Electron diffraction performed on TEM images indicates that the primary and the initially formed secondary particles are amorphous. However, as the crystallization progresses, electron diffraction properties begin to be observed in the secondary particles. The intensity and sharpness of these diffractions and

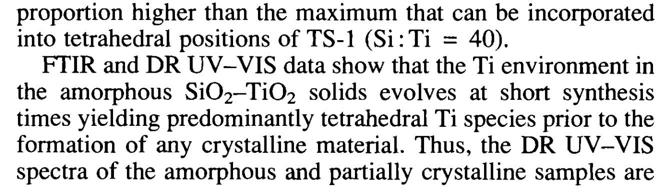

Fig. 1 Proposed mechanism for the TS-1 and TS-2 crystallization

their strength to the electron beam are considerably lower than those observed in the crystals of 100% crystalline samples, showing that these secondary particles are still only half-way crystallized.

(*iii*) Zeolitization of the secondary particles, leading to the formation of zeolite crystals with approximately the same shape and size.

TEM images combined with electron diffraction show that during the TS-1 synthesis the zeolitization of the secondary particles starts once they become individualized and isolated from the amorphous co-gel, which probably favours the supply from the solution of the additional TPAOH necessary to complete their crystallization. However, in the TS-2 synthesis, the secondary particles remain in contact with the amorphous particulate co-gel as they are crystallized, which leads to the formation of crystals with a certain degree of intergrowth and agglomeration. This difference of behaviour between the two zeolites is likely to arise from the presence of mesoporosity in the TS-2 samples and this will be discussed in detail elsewhere.[12]

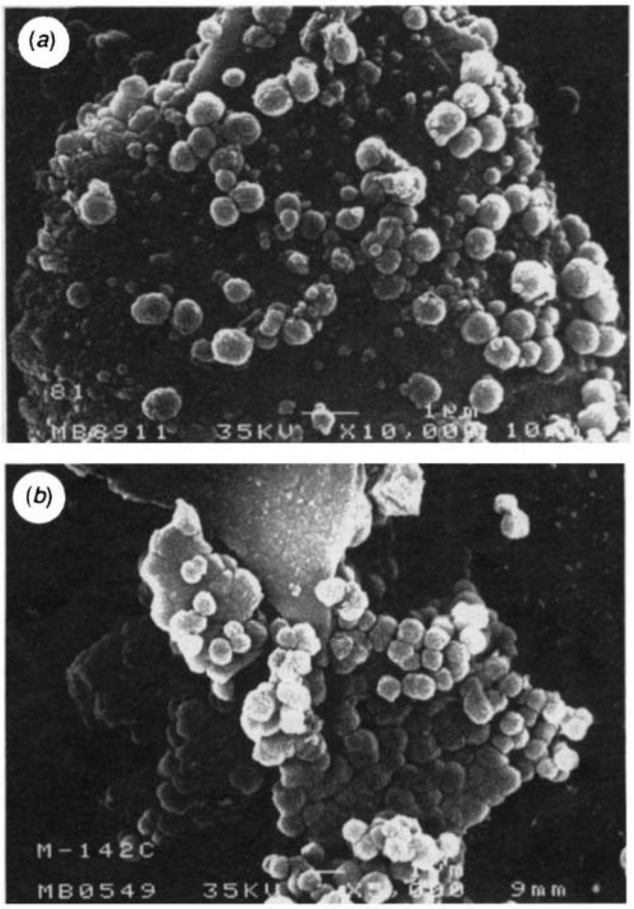

Fig. 2 SEM images of partially crystalline samples: (*a*) TS-1 synthesis, (*b*) TS-2 synthesis

According to the proposed scheme, TS-1 and TS-2 are crystallized in the system studied here by reordering the amorphous SiO_2–TiO_2 network through solid–solid transformations. Moreover, a conventional crystal growth step does not take place, rather the crystals are formed by zeolitization of amorphous particles as a whole. This finding could be of interest for tailoring the size and morphology of zeolite crystals by adjusting the properties of the starting SiO_2–TiO_2 solid. However, the process cannot be viewed as a pure solid–solid mechanism since the liquid phase plays also several roles: a small amount of the xerogel is dissolved at the earlier stages, the solution provides the additional TPAOH necessary for the crystallization and the liquid phase favours the migration and isolation of the secondary particles.

The origin of this anomalous mechanism is probably related to the high concentration of solids present compared to most conventional zeolite syntheses. Further research will be necessary to find out whether this method and mechanism can be applied to the synthesis of other zeolite structures and/or to the incorporation of elements different from Ti.

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