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Synthesis of ITQ-21 in OH^- media

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ITQ-21 has been synthesized from F^- free gels; aluminum can be incorporated and this does not affect the rate of nucleation. The introduction of stoichiometric amounts of NH_4F with respect to the number of double four rings (D4R) present in the structure leads to an increase in the nucleation and crystallization rate with a quantitative incorporation of fluoride ions into the solid.

ITQ-21 is a recently discovered zeolite with a large range of possibilities for catalytic applications.[1] This is so, due its unique pore topology formed by large cavities of 1.18 nm accessible through six circular 12 ring pore windows with an aperture of 0.74 nm. In our earlier report on ITQ-21 it was synthesized in fluoride media, and it was thought that this was an important parameter for its crystallization, as occurs for other zeolites, such as octadecasil,[2] which possess double four ring secondary building blocks (D4R) in their structures. Indeed, it was found that the fluoride anions were exclusively located at the centre of these small cages. However, in the case of ITQ-21, and differently to octadecasil, the structural driving effect of the fluoride ions towards the formation of the zeolite structure is not enough for ITQ-21, and the presence of Ge atoms was found to be crucial for the formation of ITQ-21. Effectively, when germanium is absent of the synthesis gel, CIT-5 was the product observed under the synthesis conditions studied, indicating that, as has been found for other zeolites (ITQ-7[3] and ITQ-17,[4] pure polymorph C of Beta zeolite[5]) the presence of Ge in the synthesis media strongly increases the crystallization rates of D4R-containing zeolites. Additionally, in these cases it was found that there is a preferential occupation by Ge atoms at the D4R sites,[6] but avoiding the formation of Ge–O–Ge linkages, as was predicted previously in a theoretical work.[7] The determinant role of Ge in the preparation of ITQ-17 was clearly established by carrying out the synthesis of this material in the absence of F anions, but incorporating Ge in the synthesis mixture.[8]

The fundamental and applied interest of ITQ-21 zeolite has motivated us to attempt its synthesis in fluoride-free media, using OH anions as mobilizing agents (denoted OH syntheses). This will show the determinant role of germanium in the nucleation of D4R containing zeolitic structures, opening a new fluoride-free synthesis route, which is industrially preferred.

Thus, the synthesis conditions employed to obtain ITQ-21 in OH media correspond to gels with the following composition:

$(1 - x)\ SiO_2 : x\ GeO_2 : 0.50$ MSPTOH $: 4\ H_2O$

A typical F^- free synthesis of ITQ-21 was prepared by dissolving 2.08 g of GeO_2 in 25.44 g of a *N*-methylsparteinuium (MSPT) hydroxide with a concentration of 0.59 mol kg^{-1}. Then, 4.16 g of tetraethylorthosilicate were hydrolysed in this solution and the mixture was stirred to evaporate the ethanol formed and to adjust the water content to the final composition.

The mixture was crystallised at 175 °C in brand new Teflon-lined stainless steel autoclaves for 12 days, giving an ITQ-21 sample of which the X-ray difraction pattern is shown in Fig. 1. The Si/Ge ratio found for this ITQ-21sample was 1.9 and no fluorine was detected by chemical analysis or ^{19}F MAS NMR. The C/N ratio is 8.1, indicating that the MSPT is occluded intact in the zeolite pores.

In Fig. 1, the XRD pattern of the sample obtained in OH media is compared to the diffractogram corresponding to a highly crystalline ITQ-21 sample synthesized in fluoride media.[1] Both samples have similar crystallinities, proving that ITQ-21 can be synthesized in fluoride-free media, but germanium is needed for its crystallization.

However, the major interest of ITQ-21 materials is based on their catalytic applications, and therefore, acidity is needed. This can be achieved by Al incorporation into framework positions. Aluminium containing samples were also obtained in fluoride-free media without affecting the crystallization process. In the resultant Al-ITQ-21 ((Si + Ge)/Al = 50), the presence of a unique resonance at 53 ppm in the ^{27}Al MAS NMR indicates that Al is tetrahedrally coordinated, which is taken as a proof of isomorphical substitution of Al in the zeolite framework. We have seen that the acidity of Al-ITQ-21 samples, especially those with lower germanium content, is similar to Faujasite zeolite.

As stated above, the fluoride anions have an important role in the crystallization of D4R containing zeolites. In order to achieve the exact influence of these anions in the formation of Ge-ITQ-21, we studied the crystallization curves at very low fluoride concentrations in the synthesis gels. The results presented in Fig. 2 show that the crystallization rate decreases on lowering the F concentration. Furthermore, the comparison of the crystallization curves obtained at different Si/Ge ratios indicates that the crystallization rate decreases as the Ge content is reduced, this effect being less marked when a large excess of fluoride ions is present in the synthesis media. It is worth mentioning that the addition of a stoichiometric amount of ammonium fluoride to the above synthesis mixture ($NH_4F/(SiO_2 + GeO_2) = 0.083$ (*i.e.*, just the necessary to fulfil the D4R units present in the final ITQ-21 materials) leads to obtain highly crystalline samples in short crystallization times and with high Si/Ge ratios. Interestingly, a very selective occupation of F

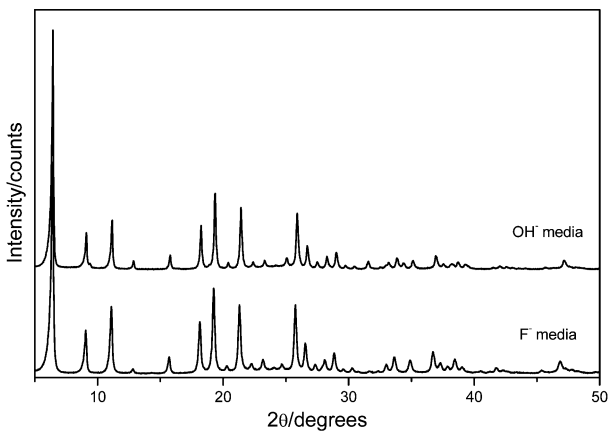

Fig. 1 XRD pattern of ITQ-21 samples synthesized in fluoride media (bottom) and OH media (fluoride-free) (top).

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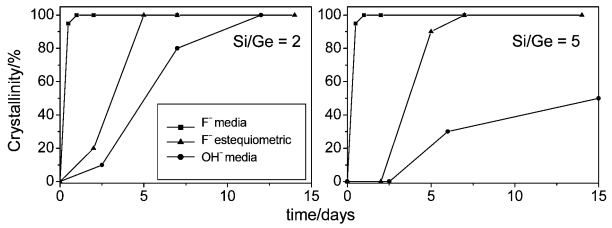

Fig. 2 Crystallization curves of ITQ-21 materials with different Si/Ge ratio in fluoride media, in OH media (fluoride-free) and with the stoichiometric amount of fluoride necessary to fulfil the D4R units present in the ITQ-21 materials.

into the D4R, as shown by ^{19}F MAS NMR, with practically quantitative incorporation into the material (1.5 wt% F for Si/Ge = 2 and 1.75 wt% F for Si/Ge = 5) and negligible fluoride concentration in the remaining mother-liquor was achieved. The above results indicate that the presence of Ge in the synthesis gel is mandatory to produce pure ITQ-21 zeolite, in either F or OH media. However, the presence of fluoride anions has a positive effect in the crystallization of this zeolite.

In conclusion, it has been shown that ITQ-21 can be synthesized from fluoride-free gels and aluminium can be incorporated in framework positions. Furthermore, introducing the stoichiometric amount of NH_4F with respect to the D4R cages present in the final material can increase the crystallization rate of ITQ-21 in OH media. By performing the syntheses in this way, practically quantitative incorporation of fluoride in the zeolite is achieved.

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