CHEMCOMM
Communication
www.rsc.org/chemcomm

Synthesis of pure polymorph C of Beta zeolite in a fluoride-free system

Avelino Corma,* Mª Teresa Navarro, Fernando Rey and Susana Valencia

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain. E-mail: acorma@itq.upv.es; Fax: +34(96)3877809; Tel: +34(96)3877800

Received (in Cambridge, UK) 10th May 2001, Accepted 28th June 2001
First published as an Advance Article on the web 18th July 2001

Pure polymorph C (denoted ITQ-17) resulting from the intergrowth of zeolite Beta has been synthesized in the presence of Ge from a fluoride-free synthesis mixture; this shows that fluoride is not necessary to obtain structures containing D4MR units that were believed to be stabilised by fluoride; on the other hand, the presence of Ge directs the synthesis towards the formation of pure polymorph C.

Zeolites are porous crystalline aluminosilicates that have found important applications in catalysis, adsorption and as ion exchangers. For many of these applications, it would be interesting to carry out an *a priori* design of zeolites. Unfortunately, despite the efforts made by several groups,[1,2] the existing knowledge on nucleation and crystallization mechanisms at the molecular level is limited, and the synthesis of new structures has advanced mainly by accumulated experience using different structure directing agents (SDAs) and synthesis conditions. More specifically, in the case of high silica/alumina large pore three-dimensional zeolites, the number of existing structures is quite limited[3] and up to now only Beta zeolite has found commercial applications.[4] Zeolite Beta is a highly faulted intergrowth of two polymorphs A and B. Newsam *et al.*[5] described a hypothetical framework, denoted as polymorph C, which is related to polymorphs A and B of zeolite Beta, and could be generated from polymorph A simply by the recurrent application to the building layers of a shear operation along both *a* and *b* axes. The structure of polymorph C has a three-dimensional system of 12MR channels that intersect perpendicularly, and in contrast with polymorphs A and B, all the channels in the structure C are linear.[5] Furthermore, polymorph C contains double four-membered ring (D4MR) cages as secondary building units [two D4MR cages per unit cell (u.c.)], while polymorphs A and B do not contain such secondary building units.

It has been reported[6] that, among a large number of pure silica structures, those that contain mainly triple 4-MRs are the least stable frameworks with enthalpies of transition for quartz → molecular sieve (ΔH^{298}_{trans}) $\geq$ 10.8 kJ mol^{-1}, indicating that the presence of large fractions of multiple 4-MRs seems to lead to a destabilization of the framework, at least for less dense structures such as CHA, ISV, FAU and AST. It is apparent from this point of view that structure C which presents D4MRs should be less stable than zeolite Beta formed by polymorphs A and B. Then, while it is true that purely thermodynamic data cannot answer questions about the kinetics of zeolite synthesis, they can nevertheless help to rationalize driving forces for synthesis.[6] On this basis it is not surprising that the polymorph C has been elusive, whereas zeolite Beta has been synthesized with several SDAs.[7–9] However, it has been shown[10] that fluoride ions can stabilize D4MR small cages and, consequently, a synthesis procedure in fluoride media, in principle, could favour the synthesis of polymorph C. Very recently, Liu *et al.*[11] have found polymorph C as an impurity of the pure silica Beta zeolite, when this was synthesized in fluoride media using tetramethylenebisquinuclidinium diquaternary cation (M_4BQ^{2+}) as structure directing agent. It was suggested that the presence of fluoride ions was required for the formation of the observed impurity. However, pure polymorph C (ITQ-17) was not obtained until Corma *et al.*[12] showed that in the presence of fluoride ions this structure is formed when Ge is also introduced in the synthesis media. Then, it appears that both F^- and Ge stabilise the presence of double four-membered rings in the structure and then it is possible to prepare the pure polymorph C of Beta with a large number of organic structure directing agents.

Unfortunately, the presence of F^- in the synthesis media is not desirable from an industrial point of view and, therefore, it is of interest to find a fluoride-free synthesis of the pure polymorph C, not only for practical reasons but also from a conceptual point of view in order to establish whether the presence of F^- anions is mandatory for the stabilization of D4MR units, which are present in that structure.

Here, we will show that the synthesis of pure polymorph C (ITQ-17) of the intergrowth of Beta zeolite has now been achieved in the absence of fluoride ions.

The synthesis was carried out in OH^- media, using 1-methyl-4-aza-1-azoniabicyclo[2,2,2]octane hydroxide (DABMe(OH)) as the structure directing agent. The 1-methyl-4-aza-1-azoniabicyclo[2,2,2]octane cation (DABMe$^+$) was synthesised in its iodide form in the following way: a solution of iodomethane (Aldrich) (3.7 g) in tetrahydrofuran (THF, 15 ml) was added dropwise to a solution of 1,4-diazabicyclo[2,2,2]octane (DABCO) (Aldrich) (5.6 g) in THF (200 ml) at room temperature, and the mixture was stirred for 20 h. The resulting solid was filtered off and washed with diethyl ether. Finally the salt, DABMeI, was exchanged into its hydroxide form using an anion-exchange resin (Amberlite IRN-78, Supelco). More specifically, a synthesis gel with the following composition was prepared:

$$0.666\ SiO_2 : 0.333\ GeO_2 : 0.5\ DABMe(OH) : 3.5\ H_2O.$$

This was obtained by adding GeO_2 (powder) and TEOS (tetraethylorthosilicate) to an aqueous solution of DABMe(OH). The homogenized mixture was stirred vigorously at room temperature in order to eliminate the ethanol produced during the hydrolysis of TEOS and to adjust the water content to that of the gel composition. The resulting gel was introduced

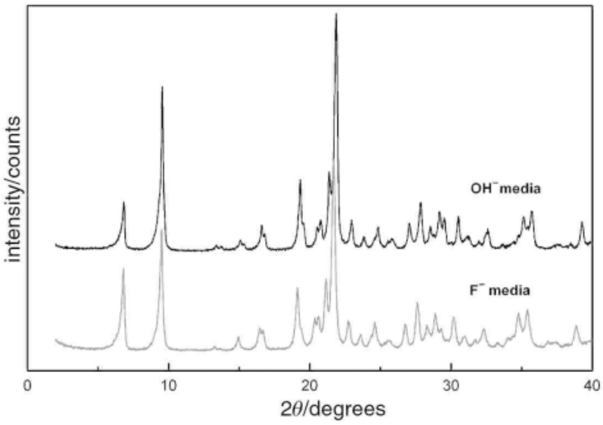

Fig. 1 X-Ray diffraction patterns of as-synthesized ITQ-17 zeolites prepared in fluoride-free media (top) and in the presence of fluoride[12] (bottom).

into new, Teflon-lined autoclaves that had never been in contact with a solution containing F$^-$, and were heated at 150 °C under static conditions. The fluoride-free gel after 12 days gives a sample, the X-ray diffractogram of which is given in Fig. 1. This is compared with a sample of ITQ-17 obtained in a fluoride system and whose structure was found to correspond to that of the pure polymorph C of zeolite Beta.[12] From the comparison, it becomes evident that well crystallized pure polymorph C has been obtained in OH$^-$ media and in the absence of F$^-$. Elemental analysis of this sample gives a C/N atomic ratio of 3.5, as would be expected, which indicates that the SDA must be intact inside of the pores of the zeolite. A Si/Ge ratio of 2.5 was found for this sample when analysed whereas F$^-$ anions were not detected by chemical analysis or by ^{19}F MAS NMR spectroscopy. Pure ITQ-17 samples with higher Si/Ge ratios have been obtained by this procedure. It should be remarked that even if pure polymorph C can be synthesized in the absence of F$^-$ when Ge is introduced, the combination of both F$^-$ and Ge accelerates the synthesis of this zeolite (Fig. 2).

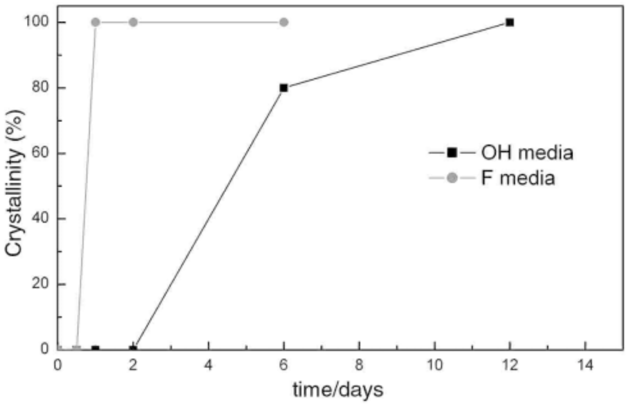

Fig. 2 Crystallization curves of ITQ-17 zeolite synthesized in fluoride-free media (■) and in the presence of fluoride (◍).

The results presented here clearly prove that pure polymorph C of Beta intergrowth can be obtained in the absence of F$^-$ anions. Ge seems to direct the synthesis towards the formation of this structure due to the stabilization effect of D4MR units present in ITQ-17 materials. These results are in line with the fact that the presence of Ge in the synthesis media strongly accelerates the nucleation of Ti-ITQ-7[13] and Al-ITQ-7[14] zeolites that also contain D4MRs in the structure.

We thank the Spanish CICYT for financial support (Project MAT2000-1392). M. T. N. thanks the Fundación José y Ana Royo for a postdoctoral fellowship.

Notes and references

1 D. W. Lewis, D. J. Willock, C. R. A. Catlow and J. M. Thomas, *Nature*, 1996, **382**, 604.
2 D. W. Lewis, C. R. A. Catlow and J. M. Thomas, *Faraday Discuss.*, 1997, **106**, 451.
3 Atlas of Zeolite Structure Types, *Zeolites*, 1996, **17**.
4 C. Flego, G. Pazzuconi, E. Bencini and C. Perego, *Stud. Surf. Sci. Catal.*, 1999, **126**, 461.
5 J. M. Newsam, M. M. J. Treacy, W. T. Koetsier and C. B. de Gruyter, *Proc. R. Soc. London A*, 1988, **420**, 375.
6 P. M. Piccione, Ch. Laberty, S. Yang, M. A. Camblor, A. Navrotsky and M. E. Davis, *J. Phys. Chem. B*, 2000, **104**, 10001.
7 R. L. Wadlinger, G. T. Kerr and E. J. Rosinski, *US Pat.,* 3 308 069, 1967.
8 J. C. van der Waal, M. S. Rigutto and H. van Bekkum, *J. Chem. Soc., Chem. Commun.*, 1994, 1241.
9 K. Tsuji, L. W. Beck and M. E. Davis, *Microporous Mesoporous Mater.*, 1999, **28**, 519.
10 H. Kessler, J. Patarin and C. Schott-Darie, *Stud. Surf. Sci. Catal.*, 1994, **85**, 75.
11 Z. Liu, T. Ohsuna, O. Terasaki, M. A. Camblor, M. J. Díaz-Cabañas and K. Hiraga, *J. Am. Chem. Soc.*, 2001, **123**, 5370.
12 A. Corma, M. T. Navarro, F. Rey, J. Rius and S. Valencia, *Angew. Chem., Int. Ed.*, 2001, **40**, 2277.
13 A. Corma, M. J. Díaz-Cabañas, M. E. Domine and F. Rey, *Chem. Commun.*, 2000, 1725.
14 A. Corma, M. J. Díaz-Cabañas and V. Fornés, *Angew. Chem., Int. Ed.*, 2000, **39**, 2346.