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Ultra fast and efficient synthesis of Ti-ITQ-7 and positive catalytic implications

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Incorporation of germanium into a zeolite framework allows the synthesis of Ti-Ge-ITQ-7 without seeding in <12 h, instead of 12 days when seeding or >40 days without seeding for the Ge-free ITQ-7; the synthesis reported also increases the efficiency of Ti incorporation and allows the preparation of almost nanocrystaline Ti-ITQ-7 materials with a corresponding beneficial effect on the final catalytic activity.

The synthesis of zeolite containing framework transition metals has opened new catalytic possibilities for the use of such materials in the synthesis of chemicals and fine chemicals.[1] This is especially true for Ti zeolites, Ti-silicalite and Ti-beta being good examples of stable materials which can catalyse epoxidation of olefins, oxidation of alcohols, hydroxylation of phenol and sulfoxidation of sulfurs containing species among other reactions.[2] The potential applications of Ti-zeolites have been extended to bulkier reactants by the synthesis of mesoporous Ti-MCM-41[3,4] and delaminated Ti-zeolite ITQ-6.[5] The interest in Ti-zeolites is still high, but while the incorporation of Ti has been attempted in numerous structures very limited success has been observed. Indeed, isomorphic substitution of Ti in the framework of zeolites has been shown to occur in very few cases,[6–8] and in others[9] the introduction of Ti in the synthesis gel not only fails to lead to its incorporation in the final structure, but in many cases the presence of Ti slows down, or even prevents growth of the desired structure. This has also been the case in a recent publication on the synthesis of Ti-ITQ-7,[10] a zeolite with a three-directional system of large pore channels. When the synthesis was attempted in the absence of seeds and using a Si/Ti ratio of 30 in the synthesis gel, the crystallisation did not proceed to completion and stopped when the crystallinity reached *ca*. 30%. On the other hand, in the presence of seeds it was found that Ti-ITQ-7 grows much more slowly than the analogous pure silica zeolite; furthermore the efficiency in the incorporation of Ti is low and, also lower than that found for Ti-beta zeolite. These results seem to indicate that the presence of Ti slows the nucleation of ITQ-7 and can also severely affect the zeolite growth. We have carried out a theoretical study using *ab initio* methods with periodic systems on the effect of the incorporation of Ge in the framework of zeolites *viz-à-viz* the stabilisation of the Ti atoms in the framework structure.[11] It was found that substitution of Si atoms by Ge close to the Ti sites results in a stabilisation of the system owing to the additional framework flexibility provided by the less rigid GeO_4 units, similar to that occurring during the direct synthesis of Al-Ge-ITQ-7 catalysts.[12]

On this basis, we have attempted the synthesis of Ti-ITQ-7 by introducing Ge in the synthesis gel. Thus, a sample of Ti-Ge-ITQ-7 was synthesised in the following manner: 0.63 g of GeO_2 were dissolved in 34.31 g of a 0.97 M aqueous solution of 1,3,3-trimethyl-6-azoniumtricyclo[3.2.1.4^{6,6}]dodecane hydroxide (SDAOH). Then, 0.61 g of tetraethylorthotitanate and 12.61 g of tetraethylorthosilicate (TEOS) were hydrolysed in the above solution, and the reaction mixture was stirred until complete elimination of ethanol and water, to reach the desired gel composition. Finally, 1.38 g HF (48.1 wt%) were added and the mixture was transferred to a Teflon-lined stainless steel autoclave and left to crystallise under static conditions at 150 °C. An analogous synthesis was carried out without adding Ge to the synthesis gel. Different crystallisation times were considered in order to obtain the kinetic curves for the crystallisation of the zeolite (Fig. 1). The final compositions of the gels were: 0.90 SiO_2 : 0.10 GeO_2 : x TiO_2 : 0.50 SDAOH : 0.50 HF : 3 H_2O and SiO_2 : 0.05 TiO_2 : 0.50 SDAOH : 0.50 HF : 3 H_2O, for the Ge and the Ge-free synthesis, respectively. The solids were recovered by filtration, and after exhaustive washing with distilled water, were dried at 100 °C, overnight. In all the syntheses, the yields of the solids recovered, in terms of oxides, were $>90\%$ with respect to the initial gel composition.

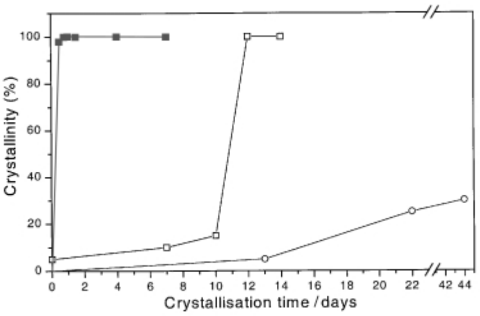

Fig. 1 Crystallization curves for the synthesis of Ti-Ge-ITQ-7 (■) and Ti-ITQ-7 with (□) and without seeds (○).

The XRD pattern (Fig. 2) of the Ti-Ge-ITQ-7 zeolite (sample D) shows a shift of the diffraction peaks to higher *d*-values when compared to the analogous Ti-ITQ-7 material (sample A) (*i.e.* without Ge and having a similar T^{IV}/Ti ratio in its composition) which indicates that the unit cell volume expands upon Ge incorporation in the zeolitic ITQ-7 framework. This result can be taken as unambiguous proof of the effective isomorphous substitution of Si by Ge in the Ti-Ge-ITQ-7 material.

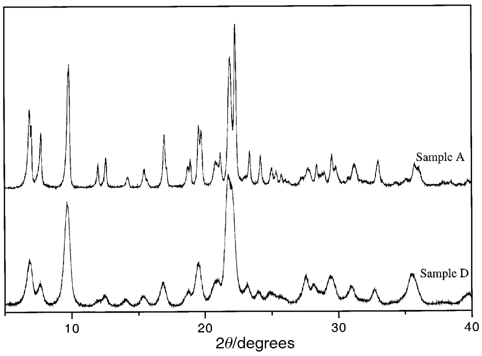

Fig. 2 XRD patterns of as-made samples: (a) Ti-ITQ-7 (sample A) and (b) Ti-Ge-ITQ-7 (sample D).

It was found (see Fig. 1) that when Ge is introduced on the synthesis gel, Ti-Ge-ITQ-7 is fully crystallised, even in the absence of seeds, in only 12 h (crystallinity measured in terms of the peak area between $2\theta = 20.15$ and 23.65° and referred to a sample arbitrarily assigned a value of 100%). Moreover, the nucleation period is strongly reduced with respect to the Ge-free

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Table 1 Efficiency for Ti incorporation as a function of gel composition

Sample	Si/Ge	F source	% TiO_2[a] (gel)	% TO_2 (solid)[b] SiO_2	GeO_2	TiO_2	% Ti incorporated
A[c]	∞	HF	6.64	98.86	—	1.14	17.2
B	10	HF	2.46	87.35	12.05	0.60	24.4
C	10	HF	5.01	85.67	12.93	1.40	28.0
D[c]	10	NH_4F	2.46	86.78	11.97	1.25	50.8
E	10	HF	0	87.65	12.35	0	—

[a] % TiO_2 calculated as: $TiO_2 \times 100/(SiO_2 + GeO_2 + TiO_2)$. [b] Measured by atomic absorption; % SiO_2 is calculated as difference. [c] Samples used for catalytic activity testing.

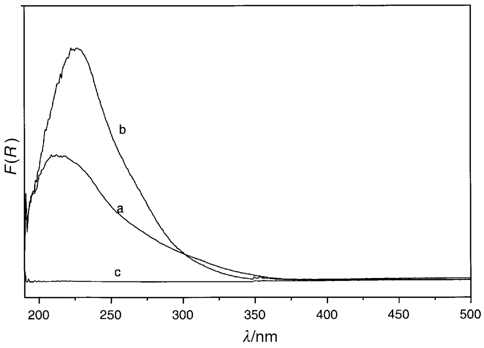

Fig. 3 Diffuse reflectance UV–VIS absorption spectra of calcined samples: (a) Ti-ITQ-7 (sample A), (b) Ti-Ge-ITQ-7 (sample D) and (c) Ge-ITQ-7 (sample E).

Table 2 Catalytic activity of Ti-ITQ-7 for olefin epoxidation[a]

Olefin	Sample	X_{olefin}[b]	Selectivity to epoxide (%)	Selectivity to H_2O_2 (%)	TON[c]
Oct-1-ene	Ti-ITQ-7 (A)	14.9	98	55	27
	Ti-Ge-ITQ-7 (D)	25.9	100	52	41
Dodec-1-ene[d]	Ti-ITQ-7 (A)	0.8	100	17	3
	Ti-Ge-ITQ-7 (D)	4.8	100	43	16

[a] *Reaction conditions*: 16.5 mmol olefin; 11.8 g acetonitrile; 4.5 mmol H_2O_2 (slowly added); 200 mg of catalyst; 333 K, 3.5 h. [b] Conversion of olefin (mol% referred to the maximum possible). [c] TON = mol olefin converted/mol Ti. [d] 100 mg of catalyst.

synthesis even if seeds were added to the synthesis gel. These facts, important in themselves, are even more impressive by considering that the efficiency of Ti incorporation is higher in the presence of Ge (Table 1), and more specifically when NH_4F is used instead of HF. In this case, the efficiency of the Ti incorporation is close to that found for Ti-beta zeolite. The high incorporation of Ti in the zeolite framework can be inferred from the UV–VIS band appearing at 220 nm (Fig. 3) which is much more intense than that of the Ge-free Ti-ITQ-7 synthesised by the previously reported procedure.[10] The higher intensity of the band is not due to the presence of Ge, since Ti-free Ge-ITQ-7 does not absorb in this region of the UV-visible spectrum (Fig. 3). Furthermore, anatase is not detected in the sample synthesised in the presence of Ge, either by UV–VIS (Fig. 3) or by Raman spectroscopy. By contrast some anatase formation was observed for Ge-free Ti-ITQ-7 samples[10] having similar Ti content as Ti-Ge-ITQ-7 catalysts described here.

The more efficient incorporation of Ti in the synthesis with Ge has an impact on the catalytic activity for the epoxidation of a linear olefin (*n*-octene) which can diffuse easily in the pores of ITQ-7 structure. The results presented in Table 2 show that a higher activity is observed for the Ti-Ge-ITQ-7 sample (D).

It is important to point out that the fast nucleation rate obtained in the presence of Ge produces much larger number of nuclei, giving Ti-Ge-ITQ-7 samples with a much smaller crystallite size (< 0.1 μm) than ITQ-7 synthesised by the previous method (1–2 μm).[9] This has important catalytic implications when reacting molecules diffuse slowly. Under these circumstances, a zeolite with smaller crystallite size is preferred in order to increase the number of Ti sites that can be reached by the reactants. We have proven this here by carrying out the epoxidation of dodec-1-ene with two Ti-ITQ-7 samples with different crystallite sizes. As seen before,[13,14] for Ti-silicalite and Ti-beta zeolites, a decrease in conversion occurs from oct-1-ene to dodec-1-ene owing to a decrease in the diffusion rate upon increasing the length of the hydrocarbon chain; this is also seen for Ti-ITQ-7. The results presented in Table 2 clearly show the increased activity of the smaller crystallites of Ti-Ge-ITQ-7 which results in a five fold increase in the turnover number with respect to the conventional Ti-ITQ-7 material.

In conclusion, we have found that it is possible to strongly increase the rate of nucleation and/or crystallisation of Ti-ITQ-7, to increase the efficiency of Ti incorporation in the framework and to produce an almost nanocrystalline zeolite, by introducing Ge to the ITQ-7 zeolite framework. All this has a clear beneficial effect on the catalytic activity of the resultant Ti-Ge-ITQ-7. It is remarkable that by a rigorous theoretical study, it was possible to predict that the incorporation of Ge should facilitate the synthesis of Ti-zeolites, as established here for Ti-ITQ-7.

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Notes and references

1 R. A. Sheldon, *J. Mol. Catal. A: Chem.*, 1996, **107**, 75.
2 B. Notari, *Adv. Catal.*, 1996, **41**, 253.
3 A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 47
4 K. A. Koyano and T. Tatsumi, *Microporous Mater.*, 1997, **10**, 259.
5 A. Corma, U. Díaz, M. E. Domine and V. Fornés, *Chem. Commun.*, 2000, 137.
6 C. B. Dartt, C. B. Khouw, H. X. Li and M. E. Davis, *Microporous Mater.*, 1994, **2**, 425.
7 B. Sulikowski, *Heterog. Chem. Rev.*, 1996, **3**, 203.
8 G. Bellusi and M. S. Rigutto, *Stud. Surf. Sci. Catal.*, 1994, **85**, 177.
9 M. J. Díaz Cabañas, Ph.D. Thesis, Universidad Politécnica de Valencia, 1999.
10 M. J. Díaz-Cabañas, M. A. Camblor and L. Villaescusa, *Chem. Commun.*, 2000, 761.
11 C. M. Zicovich-Wilson and A. Corma, *J. Phys. Chem. B*, 2000, **104**, 4134.
12 A. Corma, M. J. Días-Cabañas and V. Fornés, *Angew. Chem., Int. Ed.*, 2000, **39**, 2346.
13 M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.
14 A. Corma, P. Esteve, A. Martínez and S. Valencia, *J. Catal.*, 1995, **152**, 18.