Synthesis of a Titaniumsilicoaluminate Isomorphous to Zeolite Beta and its Application as a Catalyst for the Selective Oxidation of Large Organic Molecules

Miguel A. Camblor, Avelino Corma, Agustín Martínez and Joaquín Pérez-Pariente

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain

The isomorphous substitution of Si by Ti in the zeolite Beta framework by direct hydrothermal synthesis gives rise to useful catalysts for the selective oxidation of small and large organic compounds.

The selective oxidation of organic compounds by H_2O_2 has been shown to be catalysed by Ti-containing zeolites.[1,2] In these materials, Ti atoms are believed to be placed in the framework of the zeolite and its coordination number depends on the hydration state of the sample.[3] For the medium-pore pentasil family the isomorphous substitution of Si by Ti has been claimed (materials denoted as TS-1[4] and TS-2[5] with MFI, and MEL structures, respectively), and the selective oxidation of alcohols, alkenes and alkanes with H_2O_2 have been shown to be catalysed by these Ti-zeolites.[1,2]

However, the steric hindrance that large organic molecules encounter in reaching the active Ti sites in medium-pore zeolites (≈ 5.5 Å) restricts the usefulness of this type of catalyst to the oxidation of small organic compounds.[2] Then, large-pore, high-silica Ti-zeolites would be desirable in order to have suitable catalysts for the selective oxidation of large molecules. Ti has been claimed to be introduced into zeolite Beta and Y by a post synthesis treatment with $TiCl_4$,[6] but these materials show poor performance in the oxidation of phenol with H_2O_2 and it is still uncertain if the Ti is located in framework positions.

We report here the isomorphous substitution of Si by Ti in the zeolite Beta framework by direct synthesis.[7] Moreover, we show that this large-pore Ti-zeolite is more active than Ti-silicalites for the selective oxidation of cyclododecane with H_2O_2. Synthesis mixtures were prepared using amorphous silica (Aerosil 200, Degussa), tetraethylammonium hydroxide (TEAOH) (40% aqueous solution, K <1 ppm, Na <3 ppm, Alfa), aluminium nitrate nonahydrate (Merck), and tetraethyl orthotitanate (Alfa).

Gels with the following molar chemical composition were prepared:

$$Al_2O_3 : 400\,[x\text{Ti}, (1-x)\,\text{Si}]\,O_2 : 6000\,H_2O : 108\,(TEA)_2O.$$
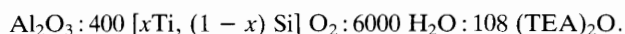
The synthesis procedure was as follows: TEAOH was diluted with the required amount of water to which tetraethyl orthotitanate and Aerosil were added at room temperature with stirring. Finally, a solution of aluminium nitrate was also added. The resulting gels were poured into 60 ml poly-(tetrafluoroethylene)-lined stainless-steel autoclaves which were rotated at 60 rpm and heated at 408 ± 1 K in an oven for selected periods of time. After cooling the autoclaves, the samples were centrifuged at 10 000 rpm and the recovered solids were washed till pH ≈ 9, dried at 353 K, and calcined at 853 K. The Ti contents of the fully crystalline calcined zeolites are given in Table 1.

The isomorphous substitution of Si by Ti in the zeolite Beta framework can be assessed by means of powder X-ray
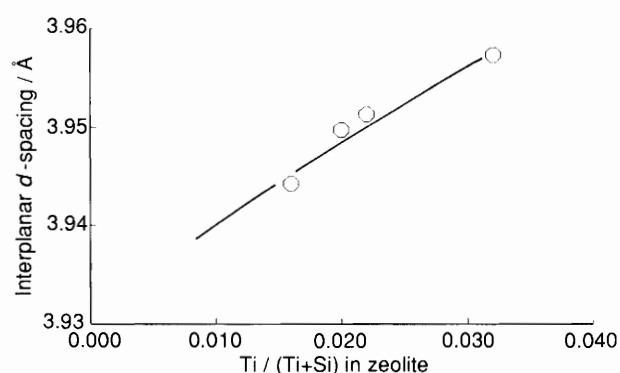
Fig. 1 Interplanar d-spacing corresponding to the most intense XRD peak in zeolite Beta ($2\theta \approx 22.4°$) as a function of the Ti content of the zeolite
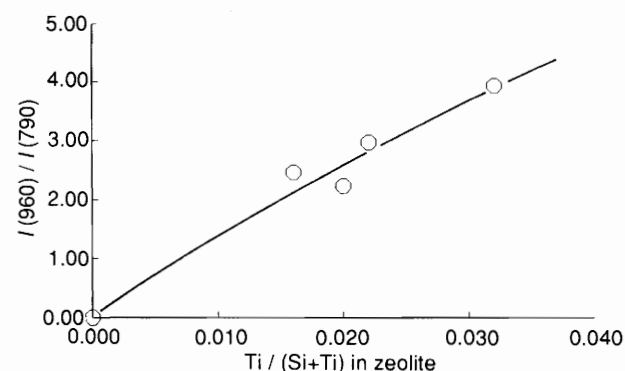
Fig. 2 Ratio of intensities of the 960 and 790 cm^{-1} IR bands as a function of the Ti content of the zeolite Beta-Ti

Table 1 Molar Ti content of the Beta-Ti samples ($T^{IV}/Al \approx 50$ for all samples; $T^{IV} = Si + Ti$)

Ti/(Si + Ti) in gel	Ti/(Si + Ti) in zeolite
0.008	0.016
0.016	0.020
0.024	0.022
0.048	0.032

Table 2 Catalytic oxidation of cyclododecane with H_2O_2 on Ti-zeolites[a]

Catalyst	Al/uc[c]	TiO$_2$ (wt.%)	Time/h	Yields[b] (mol%)				Total conversion (%)
				OL	ONE	ENE	DIOL	
Beta-Ti	1.2	4.2	2.0	0.9	1.6	0.2	0.0	2.7
			5.3	2.2	4.9	0.7	0.0	7.8
			7.5	2.5	7.4	0.8	0.4	11.1
			8.4	4.7	11.1	1.2	1.4	18.4
			9.7	6.1	15.2	1.4	2.3	25.0
TS-1	0.0	5.2	2.9	0.8	1.2	0.3	0.0	2.3
			4.7	3.7	6.7	1.4	0.7	12.5
			10.0	3.6	6.9	1.4	0.7	12.6

[a] *Reaction conditions*: 373 K reaction temperature; mole ratios H_2O_2:cyclododecane = 3.3, butan-2-one:cyclododecane = 21.8 and 3.6 g of zeolite per 100 g of alkane. [b] OL = cyclododecanol; ONE = cyclododecanone; ENE = cyclododecene; DIOL = cyclododecanediol. [c] Al/uc = no. of Al atoms per unit cell (there are 64 atoms in tetrahedral positions per unit cell in the zeolite Beta framework).

Table 3 Catalytic oxidation of cyclohexane with H_2O_2 on Ti-zeolites[a]

Catalyst	Al/uc[b]	TiO$_2$ (wt.%)	Time/h	Yields (mol%)		Total conversion (%)
				Cyclohexanol	Cyclohexanone	
Beta-Ti	1.2	4.2	2.0	0.7	4.0	4.7
			4.0	1.2	7.3	8.5
Ts-1	0.0	5.2	2.0	0.7	1.5	2.2
			4.0	1.9	4.5	6.4

[a] *Reaction conditions*: 373 K reaction temperature; mole ratios, H_2O_2:cyclohexane = 3.3, butan-2-one:cyclohexane = 21.8 and 7.3 g of zeolite per 100 g of alkane. [b] See Table 2, footnote c.

diffraction (XRD) (Philips, Cu-Kα radiation) and mid-infrared (Nicolet) characterization. The higher covalent radius of Ti compared with Si causes an increase in the interplanar d-spacing of the zeolite as the Ti content of the zeolite increases (Fig. 1). This has been measured by the change in position of the most intense XRD peak ($2\theta \approx 22.4°$), after dehydration at 383 K for 1 h and rehydration overnight over a CaCl$_2$ saturated solution (35% relative humidity). Similar results have been reported for TS-1[4] and TS-2.[5] From the XRD pattern, it was not possible to see any effect of the incorporation of Ti on the relative amounts of the two polymorph structures of zeolite Beta.

The samples showed a band at about 960 cm^{-1} in the IR spectra (KBr pellet technique), which increases linearly with the Ti content of the zeolite (Fig. 2). After impregnation with H$_2$O$_2$ this band disappears and the zeolite becomes yellow, the initial condition being restored by heating the sample at 353 K overnight. The IR band at 960 cm^{-1} has been assigned to Ti=O or Si–O–(Ti) groups in the zeolite framework[8] and is usually taken as evidence of the isomorphous substitution of Si by Ti. The presence of this band in the IR spectra of TS-1 has been related to the catalytic activity exhibited by this material in the selective oxidation of organic molecules in mild conditions.[9]

In our case, the behaviour of Beta-Ti as a catalyst for the selective oxidation of cycloalkanes has been studied by carrying out the oxidation of cyclododecane (Fluka) and cyclohexane with H$_2$O$_2$ (30%, Foret) at 373 K in a batch reactor with agitation (500 rpm) and using butan-2-one (Probus) as solvent. The products were analysed by gas chromatography (Hewlett-Packard 5890A) using a capillary column (methylphenylsilicone, 25 m). As a reference catalyst, a sample of TS-1 with 5.1 wt.% TiO$_2$ was prepared according to the patent literature (ref. 10, example 6, without addition of Ga) and used in the same reaction. This sample has an intense IR band at about 960 cm^{-1}. The final conversion and yields at different reaction times for the oxidation of cyclododecane on both Beta-Ti (4.2 wt.% TiO$_2$) and TS-1 are listed in Table 2. Despite its lower Ti content, Beta-Ti exhibits a higher activity and slightly higher selectivity to the ketone than TS-1 during the selective oxidation of cyclododecane. In the same way it

has been found that Beta-Ti is also able to oxidize cyclohexane, and its activity is also higher than the reference TS-1. In the case of cyclohexane the Beta-Ti also gives a higher selectivity to cyclohexanone than the TS-1 (Table 3). In the case of zeolite Beta-Ti, at long reaction times, small amounts (<2%) of products formed by the reaction of the solvent on the acid sites of the zeolite were detected.

In conclusion, a large-pore zeolite with Ti in the framework has been synthesized for the first time, which is able to selectively oxidize cycloalkanes at low temperatures. The synthesis of these materials increase the possibilities of actual medium-pore Ti-zeolites, to oxidize bulkier molecules.

References

1 U. Romano, A. Esposito, F. Maspero, C. Neri and M. G. Clerici, in *New Developments in Selective Oxidation*, ed. G. Centi and F. Trifiro, Elsevier, Amsterdam, 1990, 33.
2 D. R. C. Huybrechts, L. De Bruycker and P. A. Jacobs, *Nature*, 1990, **345**, 240.
3 A. López, Thesis, Université de Haute-Alsace, France, 1990.
4 M. Taramasso, G. Perego and B. Notari, US Pat. 4 410 501, 1983.
5 J. S. Reddy, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **58**, L1.
6 C. Ferrini and H. W. Kouwenhoven, in *New Developments in Selective Oxidation*, ed. G. Centi and F. Trifiro, Elsevier, Amsterdam, 1990, 53.
7 M. A. Camblor, A. Corma and J. Pérez-Pariente, SP Pat. 9 101 798, 1991.
8 G. Bellussi and V. Fattore, in *Zeolite Chemistry and Catalysis*, ed. P. A. Jacobs, N. I. Jaeger, L. Kubelková and B. Wichterlová, Elsevier, Amsterdam, 1991, 79.
9 D. R. C. Huybrechts, I. Vaesen, H. X. Li and P. A. Jacobs, *Cat. Lett.*, 1991, **8**, 237.
10 G. Bellussi, M. G. Clerici, A. Carati and A. Esposito, EP Appl. 266 825, 1988.