Epoxidation of unsaturated fatty esters over large-pore Ti-containing molecular sieves as catalysts: important role of the hydrophobic–hydrophilic properties of the molecular sieve

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Ti-β and Ti-MCM-41 catalysts are able to epoxidize methyl oleate using hydrogen peroxide or *tert*-butyl hydroperoxide as oxygen donors with high conversions and epoxide selectivities.

Epoxidized fatty acids and their derivatives are useful commercial chemicals used, *e.g.* as stabilizers in halogen-containing polymers, as additives in lubricants, in the manufacture of cosmetics and pharmaceuticals, fungicidal and algicidal solutions, and in wood treatment.[1–5] In existing industrial processes the epoxide is produced by reacting the unsaturated compound with a peracid either preformed[6] or synthesized *in situ*[7] with an organic acid, usually acetic or formic acid, and hydrogen peroxide. Using this procedure, the yields to epoxide are relativelly low as a consequence of the low H_2O_2 selectivities. Thus, it would be interesting to replace the processes based on peracids by a more desirable catalytic one.[8–12]

Recently, it has been shown that the incorporation of Ti into the framework of zeolites produce oxidation catalysts with unique shape-selective properties.[13] Large-pore Ti-β zeolite[14] and the mesoporous material Ti-MCM-41,[15] when properly prepared, are active for the selective oxidation of bulky substrates that can not diffuse inside the Ti-silicalite channels.[16–17] Because of their oxidation properties and the advantages related to the use of solid catalysts in industrial processes, Ti-β and Ti-MCM-41 could open new possibilities in the field of fatty acids and esters if they could selectively epoxidize the double bound, forming stable epoxides.

Here we report a new and interesting application of large-pore zeolites containing Ti in the framework such as the selective epoxidation of unsaturated fatty acids using organic and inorganic peroxides. We will show that the hydrophobic–hydrophilic properties of the zeolite play an important role when, as in this case, the organic reactant has two moieties with different polarities and an aqueous solution of H_2O_2 is used as oxidant.

Hydrophilic Ti-β samples were prepared as follows: samples 1 and 2 were synthesized by diluting tetraethylammonium hydroxide (TEAOH) (35%, Aldrich, Na < 1 ppm, K < 47 ppm) with the required amount of water to which tetraethylorthotitanate (TEOTi, Alfa) and tetraethylorthosilicate (TEOS, Merck) were added at room temperature with stirring. Finally, a solution of aluminium nitrate (Merck) was also added. Sample 4 was prepared by the hydrolysis of TEOS in an aqueous solution of TEAOH and H_2O_2 (35%, Fluka) under stirring. TEOTi was added and the mixture was left under stirring to allow the evaporation of the ethanol produced. Finally, dealuminated zeolite-β seeds were added under stirring (4 g of solid per 100 g of total SiO_2 in the reaction mixture). Sample 3 was synthesized in the same way but using non-dealuminated zeolite-β seeds which determined the total Al content of the reaction mixture.

A hydrophobic Ti-β sample (sample 5) was prepared as follows: TEOS was hydrolysed in an aqueous solution containing TEAOH and H_2O_2 followed by the hydrolysis of TEOTi and allowing evaporation of ethanol and water to the resultant clear solution, water lost in the evaporation and the appropriate amount of HF (48%) were added.

The chemical composition of the gels are listed in Table 1. After crystallization at 413 K and rotation at 60 rpm, the solids were separated, washed until pH = 9, dried at 353 K and calcined at 853 K.

A Ti-MCM-41 sample was synthesised as follows: an aqueous solution of tetramethylammonium silicate (25% TMAOH, 10% SiO_2, Aldrich) was added to an aqueous solution containing 29.0% hexadecyltrimethylammonium bromide (CTAB, Merck). When the solution was homogenized, amorphous silica (Aerosil 200, Degussa) and titanium isopropoxide (Alfa) were added. The molar chemical composition of the synthesis mixture was: $SiO_2:0.15$ $CTAB:24.3$ $H_2O:0.26$ $TMAOH:0.016$ TiO_2. The gel was heated at 413 K under static conditions. After filtering, the solid was washed, dried and calcined at 813 K for 1 h in a flow of N_2, followed by 6 h in air. The Ti content of the final solid was 2.5 mass% expressed as TiO_2.

Reactions were carried out batchwise in a 5 ml round-bottomed flask with continuous stirring. The flask contained the catalyst (30 mg), the substrate (1 mmol of methyl oleate), the solvent, when used (2 ml), and the peroxide (0.25 mmol). Products were analysed by capillary gas chromatography (25 m, 5% methylphenylsilicone) and their identification was established by GCMS. Unreacted peroxide was determined by iodometric titration.

Table 2 shows the results obtained in the epoxidation of methyl oleate with hydrogen peroxide on Ti-β and Ti-MCM-41 catalysts. As can be seen, higher conversions and H_2O_2

Table 1 Chemical composition of Ti-β samples

	Gel synthesis						Solid	
Sample	SiO_2/TiO_2	SiO_2/Al_2O_3	$TEAOH/SiO_2$	H_2O_2/SiO_2	H_2O_2/SiO_2	HF/SiO_2	Si/Al	$\%TiO_2$
1[a]	60	769	0.54	10.0	—	—	112	3.92
2	60	400	0.55	12.0	—	—	138	4.04
3	60	1660	0.55	6.3	0.34	—	590	2.96
4	60	—	0.55	6.8	0.34	—	∞	2.36
5	25	—	0.56	7.5	0.34	0.62	∞	2.10

[a] Aerosil (Degussa) used as silica source.

Table 2 Epoxidation of methyl oleate with H_2O_2 over Ti-β and Ti-MCM-41 catalysts[a]

Catalyst	Solvent	Oleate Conv. (% of max.)	Epoxide selectivity (%)	H_2O_2 conv. (%)	H_2O_2 selectivity (%)
Ti-β[b]	MeCN	45.3	97.2	89.6	50.6
	MeOH	40.1	31.8	62.0	64.6
Ti-MCM-41	MeCN	26.7	88.3	86.7	30.8
	MeOH	21.9	42.9	81.8	26.7

[a] *Reaction conditions*: 296 mg methyl oleate, 2 ml solvent, 24 mg H_2O_2 (35 mass%), 30 mg catalyst. 50 °C, 8 h. [b] Sample 1.

Table 3 Effect of Al content on Ti-β catalysts for the epoxidation of methyl oleate with H_2O_2[a]

	Chemical composition					
Sample	Si/Al	%TiO_2	Oleate conv. (% of max.)	Epoxide selectivity (%)	H_2O_2 conv. (%)	H_2O_2 selectivity (%)
2	138	4.04	65.4	10.8	87.7	74.6
3	590	2.96	64.2	20.4	80.3	79.9
4	∞	2.36	78.6	34.9	90.2	87.2
5	∞	2.10	56.6	64.6	63.1	90.4
Na-Ti-β (4)	∞	2.36	59.1	90.1	85.2	69.4

[a] Reaction conditions as in Table 2. Methanol used as solvent.

Table 4 Epoxidation of methyl oleate with TBHP over Ti-β and Ti-MCM-41 catalysts[a]

Catalyst	Oleate conv. (% of max.)	Epoxide selectivity (%)	TBHP conv. (%)	TBHP selectivity (%)
Ti-β[b]	49.3	97.4	51.9	95.0
Ti-MCM-41	64.6	91.1	65.3	98.9

[a] *Reaction conditions*: 296 mg methyl oleate, 112 mg TBHP (80% in *tert*-butyl peroxide), 30 mg catalyst. 70 °C, 8 h. [b] Sample 5.

selectivities were obtained on Ti-β. It has been reported[18] that polar solvents, such as methanol or acetonitrile, enhance the activity of hydrophilic materials as epoxidation catalysts. However, the higher hydrophility of Ti-MCM-41, as compared to Ti-β, has a detrimental effect because it decreases the adsorption of the organic substrate and, consequently, it favours H_2O_2 decomposition.[17]

The epoxide is practically the only product obtained in acetonitrile with both catalysts while the epoxide selectivities are lower in methanol. In the case of Ti-β, the Al atoms present in the zeolite framework generate surface acid groups which catalyse the ring opening of the epoxide by addition of a protic molecule. When decreasing the zeolite acidity, *i.e.* decreasing the Al content in the catalyst, the epoxide selectivity increases (Table 3). This increase is even larger when the hydrophobic Ti-β, sample 5, is used. When there are no Al atoms in the catalyst framework (Al-free Ti-β and Ti-MCM-41), opening of the oxirane ring still occurs. This means that there are sites other than those associated with the Al framework which are able to catalyse the side reaction. These acid sites have been assigned to peroxo or hydroperoxo species formed by the interaction of hydrogen peroxide with Ti atoms in the zeolite.[19,20] The selectivity to the epoxide is significantly improved (*ca.* 90%) when the Al-free Ti-β sample is washed with an aqueous solution containing Na^+ cations (Table 3), although the activity of the catalyst slightly decreased.

As the presence of water inhibits the catalytic activity of Ti-MCM-41, the epoxidation of methyl oleate was also carried out using *tert*-butyl hydroperoxide (TBHP) as oxygen donor (Table 4). In this case, no solvent is needed to perform the epoxidation, with corresponding savings in reactor volume and separation costs. Under such reactions conditions Ti-MCM-41 was a highly effective catalyst with high conversions and selectivities to the epoxide and TBHP (*ca.* 91 and 99%, respectively). Ti-β is also able to epoxidize methyl oleate using TBHP as oxidant. Although the reaction rate is slower with respect to H_2O_2 due to steric restrictions to the formation of the transition state, the epoxide and TBHP selectivities are $>80\%$.

In conclusion, hydrophobic Ti-β/H_2O_2 and Ti-MCM-41/TBHP have been demonstrated to be effective catalytic systems to prepare epoxidized fatty esters with high conversions and selectivities to epoxide.

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