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Oxidation of Olefins with Hydrogen Peroxide and *tert*-Butyl Hydroperoxide on Ti-Beta Catalyst

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The oxidation of a number of linear, branched, and cyclic olefins catalyzed by the large-pore Ti-Beta catalyst in the presence of H_2O_2 and TBHP as oxidants has been carried out under mild conditions. The influence of the olefin structure on its reactivity towards oxidation has been studied. Depending on the particular olefin structure, the reaction rate was seen to be mostly influenced by the intrinsic reactivity of the double bond, diffusional limitations, or steric factors. The latter were seen to be more pronounced in the oxidations with TBHP, owing to the bulkier Ti–OO–$C(CH_3)_3$ species which would be formed inside the zeolite pores. Oxidations with TBHP also proceeded at a lower rate than with H_2O_2. Close to 100% selectivities to epoxides were found when TBHP was used as oxygen donor. In the case of H_2O_2 solvolysis of the oxirane ring in methanol solutions was the major secondary reaction observed. The rate of this reaction was seen to depend on the structure of the epoxide formed in the first step. In both cases, very little peroxide decomposition was observed under the reaction conditions used.

INTRODUCTION

The incorporation of titanium into the framework of high-silica zeolites has expanded the application of these materials, especially in the field of organic synthesis. Titanium silicalite-1 (TS-1) having the MFI structure was the first Ti-containing zeolite prepared by direct synthesis (1, 2). TS-1 was found to be an effective catalyst for the selective oxidation of a number of organic substrates using diluted hydrogen peroxide as an oxidizing agent under mild conditions, i.e., hydroxylation of aromatics and phenol (3), epoxidation of olefins (4), oxidation of paraffins to the corresponding alcohol and ketones (5, 6), and oxidation of alcohols and amines (7). After this success, intensive research on this topic led to the synthesis of other medium-pore Ti-zeolites, e.g., titanium silicalite-2 (TS-2) having the MEL structure (8) and more recently the Ti–ZSM-48 (TS-48) (9). However, while TS-2 showed similar catalytic properties to those of TS-1 (10, 11), TS-48 was seen to be inactive for the hydroxylation of phenol (12) and the oxidation of *n*-octane and 1-hexene (13). Although differences in the titanium environment can not be excluded, the unidimensionality of the channels and the narrower pore openings of TS-48 with respect to the pentasyl zeolites may also be responsible for the lack of activity found in the former. Furthermore, the use of TS-1 and TS-2 is restricted to oxidation of relatively small organic molecules due to diffusion limitations and/or transition state shape selectivity effects (5, 6, 14). Moreover, oxidations with medium pore Ti-zeolites are also restricted to the use of H_2O_2 as oxidant, as they show little activity when using other peroxides, such as *tert*-butyl or cumene hydroperoxide (15).

Recently, we reported the synthesis of the first large-pore Ti–zeolite isostructural to zeolite Beta (Ti-Beta) (16) and that in this way the possibilities of application of these materials could be expanded to the oxidation of bulkier substrates. Thus, Ti-Beta was seen to be more active than TS-1 for the oxidation of cyclic and long linear alkenes (17), such as cyclohexene and 1-dodecene, as well as for oxidating cyclic and branched alkanes (17). By means of IR spectroscopy, XRD, thermal analysis, XPS, EXAFS–XANES, and DRS–UV techniques (18), it has been shown that when Ti-Beta is properly synthesized from alkali-free solutions, the titanium atoms are located in the framework positions, with a four- to six-fold coordination depending on the state of the sample. Thus, in the calcined dehydrated state a four coordination with Ti linked to four Si–O groups was observed. After rehydration, the coordination increases from four to five, as has also been observed for the medium-pore TS-2, in contrast to the six coordination observed for Ti in the calcined hydrated state of TS-1.

In this paper we have performed a more detailed study of the influence of alkene structure, as well as of the type of oxidant used (H_2O_2 or *t*-butyl hydroperoxide), during the oxidation of olefins on a Ti-Beta catalyst. Diffusional effects were studied by carrying out the oxidation of linear

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α-olefins with increasing chain length (1-hexene, 1-octene, 1-decene) and degree of branching (2-methyl-2-pentene, 4-methyl-1-pentene), and using a substituted cycloalkene (1-methylcyclohexene) as a substrate. The influence of the chemical reactivity of the alkene on reaction rate and selectivity was derived from the influence of the position of the double bond in the hydrocarbon chain (1-hexene, 2-hexene, 3-hexene) and from the oxidation of the corresponding cyclic olefin (cyclohexene), which was seen not to be impeded in the open structure of Ti-Beta (17). Finally, the results obtained when using both hydrogen peroxide and *t*-butyl hydroperoxide as oxidants on the large-pore Ti-Beta are compared with those obtained on the standard EURO-TS-1 sample under the same experimental conditions.

EXPERIMENTAL

Preparation and Characterization of Ti-Beta Catalyst

The Ti-Beta sample used in this study was synthesized hydrothermally using tetraethylorthotitanate (TEOTi) and Aerosil as titanium and silica sources, respectively. The detailed synthesis procedure can be found elsewhere (19). The gel thus prepared had the following molar composition: $TO_2/Al_2O_3 = 800$ and $Ti/(Si + Ti) = 0.016$. After crystallization at 135°C and rotation at 60 rpm, the solid was separated, washed until pH $\approx$ 9, dried at 80°C, and finally calcined at 580°C. The crystallinity of the final Ti-Beta sample measured by X-ray powder diffraction (Phillips PW-1830, Cu*Kα* radiation) was 80% with respect to the as-synthesized sample. The chemical composition of the calcined solid was $TO_2/Al_2O_3 = 303$ and $Ti/(Si + Ti) = 0.025$. The IR spectrum of the sample (Nicolet FTIR 710, KBr pellet technique) revealed the presence of the band at ~960 cm^{-1} in a relative intensity of 2.5 with respect to the band at 795 cm^{-1}. The diffuse reflectance (DR) spectrum in the UV region of this sample shows bands at ~205 and 215 nm with a very small shoulder at ~230 nm, which, according to the assignments earlier made for titanium silicalite (20, 21), would correspond to framework Ti atoms in a four- to six-fold coordination. Moreover, no bands at ~270 and 330 nm assigned to hexacoordinated Ti in an amorphous titanosilicate phase and anatase (18), respectively, are observed in the DR–UV spectrum of the calcined Ti-Beta catalyst. The crystal size of the Ti-Beta sample, as measured by TEM, was seen to be less than 0.2 μm in diameter.

The Ti-silicalite used in this work as reference is the EURO-TS-1 (Si/Ti ratio of 36) which has been used as a standard sample in several European laboratories (22).

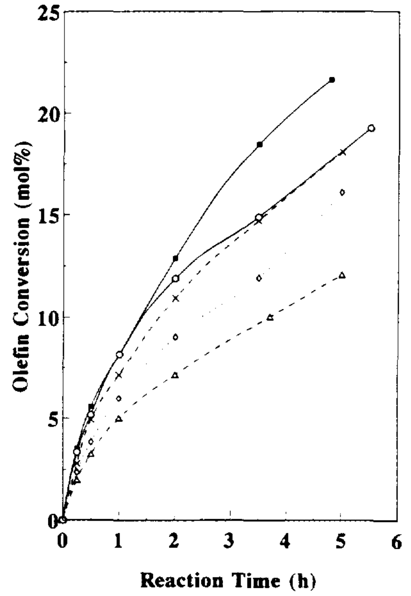


FIG. 1. Kinetics of oxidation of linear olefins with H_2O_2 on Ti-Beta catalyst: (○) 1-hexene, (◇) 1-octene, (△) 1-decene, (■) 2-hexene, (X) 3-hexene.

Catalytic Experiments

The oxidation reactions were carried out at 50°C reaction temperature in a glass round bottom flask with reflux and a magnetic stirrer. In a typical experiment when using H_2O_2 as oxidant, 33 mmol of olefin, 23.6 g of methanol as solvent, and 0.8 g of diluted (35 wt%) hydrogen peroxide are mixed in the flask and heated to the desired temperature under vigorous agitation. Then, 0.2 g of catalyst is added to the reaction mixture (time zero). The experiments using *t*-butyl hydroperoxide (TBHP) (80 wt% TBHP in di-*tert*-butyl peroxide) as oxidant were performed using 25 mmol of olefin, 6.25 mmol of TBHP, 0.3 g of catalyst, and 10 g of acetonitrile as solvent.

In both cases, the kinetics of the reaction was followed by taking aliquots at different reaction times. The reactants and products were separated and analyzed by gas chromatography in a capillary column (5% methylpenylsilicone, 25 m length) using an FID detector. The amount of unreacted hydrogen peroxide and TBHP (23) was determined by iodometric titration.

RESULTS AND DISCUSSION

Oxidations with Hydrogen Peroxide

The kinetic experiments on the conversion of the different alkenes are represented in Figs. 1 and 2. It can be seen there that very high substrate conversions are obtained with the most reactive olefins on Ti-Beta catalyst

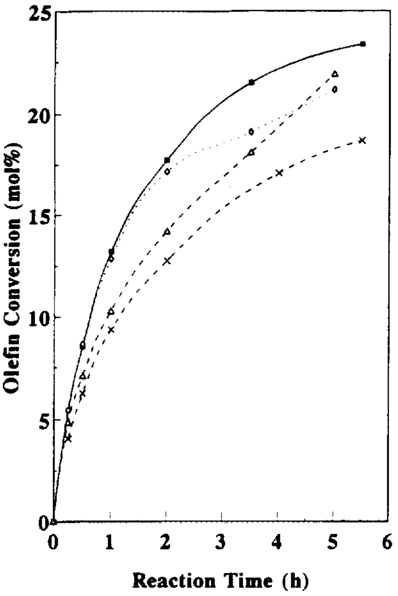
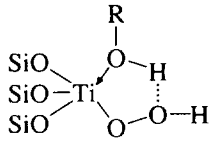


FIG. 2. Kinetics of oxidation of branched and cyclic olefins with H_2O_2 on Ti-Beta catalyst: (◇) 2-methyl-2-pentene, (△) 4-methyl-1-pentene, (■) cyclohexene, (X) 1-methyl-1-hexene.

after few hours of reaction (note that the H_2O_2/substrate ratio is ca. 1/4 mol/mol for all the olefins). These curves also show that the reactivity of the olefin towards oxidation with H_2O_2 clearly depends on the particular structure of the substrate. Indeed, for linear α-olefins, a decrease of the reactivity is observed when increasing chain length (Fig. 1). As the intrinsic reactivity of the double bond is expected to be very similar for 1-hexene, 1-octene, and 1-decene and, in any case, it should increase slightly when increasing chain length, the observed order of reactivity can be explained in terms of increasing diffusion limitations through the zeolite channels when going from 1-hexene to 1-decene.

The influence of the position of the double bond in linear alkenes can be discussed from the results presented in Fig. 1. The order of reactivity observed for the Ti-Beta catalyst is 2-hexene > 1-hexene ≥ 3-hexene. Epoxidation of olefins on Ti–zeolite catalysts is thought to occur through an electrophilic attack by the Ti species (24), and consequently, the reactivity would increase when increasing electron density on the double bond. Then, internal olefins should react faster than terminal olefins, and this would explain the higher reactivity found for 2-hexene than for 1-hexene. On this basis, 3-hexene should react even faster than those two olefins, but this is not observed experimentally. In this case, steric constraints should play a major role for the relatively lower reactivity observed for 3-hexene. Indeed, it has been proposed for TS-1 (24) that the active species during the epoxidation of olefins with H_2O_2 in protic solvents, such as for instance alcohols, is a complex formed by the Ti peroxo species and the solvent, as shown below:



[I]

Then, one would expect the double bond in 3-hexene to be more impeded to coordinate with the complex shown in the above scheme.

Furthermore, Fig. 2 shows that cyclohexene reacts faster than 1-hexene (Fig. 1) on the Ti-Beta catalyst, in agreement with the higher reactivity of the double bond in the former olefin. This also indicates that no steric restrictions exist for cyclohexene to diffuse through the channels of zeolite Beta, as was predicted by means of molecular docking simulation (17). By comparing the results obtained for 4-methyl-1-pentene and 2-methyl-2-pentene with 1-hexene and 2-hexene, respectively, it can be stated that the branched hexenes react about 1.5 times faster than the corresponding linear olefins, as could be expected from the increasing electron density on the double bond produced by the presence of the electron donating methyl group. These results contrast with those observed on TS-1 and which show that the activity for olefin epoxidation is strongly reduced for branched olefins owing to diffusivity effects and restricted transition state shape selectivity (24). This was confirmed in our case, and the results presented in Table 1 clearly show that, while the order of reactivity on the Ti-Beta zeolite is cyclohexene = 2-methyl-2-pentene > 4-methyl-1-pentene > 1-methyl-1-cyclohexene > 2-hexene > 1-hexene > 3-hexene > 1-octene > 1-decene, in the case of the TS-1 it is 2-hexene ≫ 1-hexene > 1-octene > 1-decene > 2-methyl-2-pentene ⋙ 1-methyl-1-cyclohexene. The above results clearly show that not only is Ti-Beta zeolite an active catalyst for oxidation of olefins with H_2O_2, but also that its larger pores makes it a superior catalyst to TS-1 for oxidation of branched and cyclic olefins.

It has to be pointed out that the introduction of a methyl group near the double bond of the cyclic olefin (see 1-methyl-1-cyclohexene in Fig. 2) produces a decrease in the reactivity of the molecule with respect to cyclohexene. These results suggest that diffusion limitations and/or steric constraints to form the complex between the olefin and the active species of [I] could explain why the reactivity found for 1-methyl-1-cyclohexene was lower on Ti-Beta than expected from the chemical point of view. However, TS-1 was practically inactive for 1-methyl-1-cyclohexene oxidation.

The selectivity of Ti-Beta to the different reaction prod-

TABLE 1

Oxidation of Alkenes with H_2O_2 on Ti-Beta and TS-1 Catalysts[a]

Alkene	Catalyst	$r_0 \times 10^6$ (mol/g s)[b]	Olefin conv. (mol%)	Epoxide selectivity (mol%)	H_2O_2 selectivity (%)
1-Hexene	Ti-Beta	6.14	11.9	3.9	93
	TS-1	13.50	14.3	94.7	100
2-Hexene	Ti-Beta	6.45	12.8	4.4	100
	TS-1[c]	30.45	25.0	99.9	100
3-Hexene	Ti-Beta	5.13	11.0	10.0	100
	TS-1[d]	—	—	—	—
1-Octene	Ti-Beta	4.32	9.0	6.1	79
	TS-1	10.43	11.1	80.3	97
1-Decene	Ti-Beta	3.66	7.1	5.9	67
	TS-1	8.58	7.9	79.5	79
4-Methyl-1-pentene	Ti-Beta	8.96	14.2	14.0	91
	TS-1[d]	—	—	—	—
2-Methyl-2-pentene	Ti-Beta	10.01	17.2	0.6	92
	TS-1	3.94	3.9	76.7	90
Cyclohexene	Ti-Beta	10.01	17.7	0.0	95
	TS-1[d]	—	—	—	—
1-Methyl-1-cyclohexene	Ti-Beta	7.46	12.8	0.9	91
	TS-1	0.00	0.00	—	—

[a] 50°C, 2 h, 33 mmol olefin, 0.8 g H_2O_2 (35 wt%), 23.6 g methanol, 0.2 g catalyst.

[b] r_0 = (moles of olefin converted)/(g of catalyst × s).

[c] Values obtained after 1 h reaction time.

[d] Not determined.

ucts during the oxidation of 1-hexene is plotted in Fig. 3 as a function of olefin conversion. These results indicate that the epoxide formed in a first step suffers a very rapid nucleophilic attack by the methanol molecules present as solvent with the corresponding formation of monomethylglycolethers (MGE). This reaction is catalyzed by the acid sites present in our Al-containing Ti-Beta zeolite. A similar mechanism, but occurring at a much lower rate owing to the lower concentration of water, works for the formation of the glycols.

Table 2 shows the selectivities obtained at 15 min reaction time on Ti-Beta for all the olefins studied. These results indicate that the rate of solvolysis depends on the particular structure of the epoxide formed in the first reaction step. Thus, while the rate of solvolysis is very similar for the three α-olefins studied (1-hexene, 1-octene, and 1-decene), it is lower for the β-olefin (2-hexene), and even lower for the γ-olefin (3-hexene). The effect of branching on the stability of the epoxide is also worth noting. When the methyl group is located far from the double bond (4-methyl-1-pentene) the rate of solvolysis decreases with respect to 1-hexene, but when it is situated near the double bond (2-methyl-2-pentene), opening of the epoxide ring occurs much faster than for 2-hexene. This can be explained taking into account the higher reactivity of the epoxide ring towards the nucleophilic attack according to a SN1 mechanism, which is probably operating here.

The rate of solvolysis is also very high in the case of reaction with cyclic olefins (cyclohexene and 1-methyl-1-cyclohexene). In this case, the epoxide must be formed with the cyclohexane ring in the "bote" conformation,

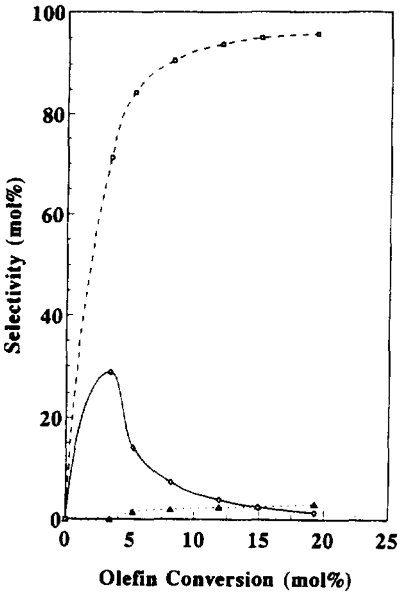


FIG. 3. Selectivity to epoxide (◇) monomethylglycolethers (□), and glycols (▲) as a function of olefin conversion obtained in the oxidation of 1-hexene with H_2O_2 on Ti-Beta catalyst.

TABLE 2

Alkene Conversion and Product Selectivities Obtained after 15 min Reaction Time on the Ti-Beta Catalyst[a]

Alkene	Conversion (mol%)	Selectivity (mol%)		
		Epoxide	MGE[b]	Glycols
1-Hexene	3.35	28.9	71.1	0.0
2-Hexene	3.52	40.5	58.1	1.4
3-Hexene	2.80	65.2	34.8	0.0
1-Octene	2.36	30.6	69.4	0.0
1-Decene	2.00	24.5	75.5	0.0
4-Methyl-1-Pentene	4.88	57.0	43.0	0.0
2-Methyl-2-Pentene	5.46	3.3	90.1	6.6
Cyclohexene	5.46	2.0	95.0	3.0
1-Methyl-1-Cyclohexene	4.07	2.5	91.5	6.0

[a] Reaction conditions are as in Table 1.

[b] MGE, monomethylglycolethers.

which is known to be more reactive owing to its higher strain, thus increasing the rate of solvolysis.

Results in Table 1 show clear differences between Ti-Beta and TS-1 towards selectivity to the epoxide. This is very high on TS-1 and very low on Ti-Beta at high olefin conversions, as has been discussed before. The results are explained on the basis of the presence of aluminum in Ti-Beta, which introduces Brønsted acid sites and catalyzes the solvolysis of the epoxide ring. With respect to the hydrogen peroxide selectivity, this is very high for the two catalysts (above 90%) and slightly decreases from 1-hexene to 1-decene.

Oxidations with tert-Butyl Hydroperoxide

Epoxidation of olefinic compounds on Group IV–VI metal-based catalysts is usually carried out using TBHP as oxidant (25). However, this oxygen donor was seen to be ineffective for carrying out oxidations on TS-1 (15), owing to the difficulty of TBHP to diffuse and to coordinate the Ti sites inside the narrow channels of this zeolite. Furthermore, if one assumes a similar mechanism operating in the oxidation of olefins with H_2O_2 and TBHP, it is obvious that the transition state involving the Ti–OOR and the olefin must be bulkier when TBHP is used as oxygen donor. These restrictions are overcome when a Ti-zeolite with larger pore dimensions, such as Ti-Beta, is used as catalyst.

In this part of the study we have performed the oxidation of the olefins on Ti-Beta using TBHP as oxidant. The initial reaction rates, r_0, as well as the olefin conversions and selectivities to epoxide and TBHP after 5 h reaction time, are summarized in Table 3. From these results it can be seen that the oxidation reaction proceeds on Ti-Beta about 30 times faster than on TS-1. In general, the influence of the structure of the olefin on its reactivity follows the same trend already observed when H_2O_2 is used as oxidant, even though the absolute rates are lower with TBHP. Thus, the reactivity of the α-olefins decreases when increasing chain length, i.e., 1-hexene > 1-octene > 1-decene, and increases when increasing electron density on the double bond, i.e., cyclohexene > 2-hexene > 1-hexene. However, and contrary to what was observed with H_2O_2, 4-methyl-1-pentene reacts slower than 1-hexene when using TBHP, despite the higher intrinsic reactivity of the former. This would suggest that steric restrictions inside the pores of Ti-Beta are enhanced when using a bulkier oxidant such as TBHP, in agreement with the bulkier transition state that would be formed in the oxidations with TBHP with respect to H_2O_2. Indeed, Table 4 shows that the reaction rate of hindered olefins relative to that of 1-hexene decreases when the oxidation is performed with TBHP instead of H_2O_2. In addition to the above-discussed transition state selectivity, the lower electrophilic character of the Ti–OO–C–$(CH_3)_3$ species with respect to Ti–OOH (in the case of H_2O_2) can also explain the general lower reactivity found with TBHP when compared to the oxidations with H_2O_2.

Finally, the very high selectivities to the corresponding epoxides obtained on Ti-Beta and TBHP in acetonitrile as solvent, as well as the very low decomposition of the peroxide under these reaction conditions, can be seen in Table 3. The selectivity to epoxide is practically 100% for all the olefins studied, except for 1-methyl-1-cyclohexene, for which selectivity is 90%. Furthermore the TBHP selectivities are above 90% for most of these olefins.

CONCLUSIONS

The reactivity of alkenes towards epoxidation on the large pore Ti-Beta catalyst in the presence of H_2O_2 is greatly influenced by the particular structure of the olefin. Thus, increasing the chain length of α-olefins from 1-hexene to 1-decene results in a decrease of the reactivity. The order of reactivity found for unhindered olefins is in agreement with the expected reactivity of the double bond towards an electrophilic attack by the Ti-active species; that is, it increases when increasing the electron density on the double bond. In this way, β-olefins (2-hexene) and methyl substituted α- and β-pentenes react faster than the corresponding α- or β-linear olefins. Cyclic olefins also react faster than linear olefins, showing the lack of steric impediments in the pores of Ti-Beta.

Solvolysis of the oxirane ring is the main secondary reaction on Ti-Beta when using H_2O_2 as oxygen donor,

TABLE 3

Oxidation of Alkenes with TBHP on Ti-Beta Catalysts[a]

Alkene	$r_0 \times 10^6$ (mol/g s)[b]	Olefin conversion (mol%)	Epoxide selectivity (mol%)	TBHP selectivity (%)
1-Hexene[c]	1.64 (0.06)	8.4 (0.1)	100 (100)	100 (100)
2-Hexene	2.29	12.4	100	100
1-Octene	0.85	4.7	100	98
1-Decene	0.60	3.7	100	95
4-Methyl-1-pentene	0.80	5.5	100	94
Cyclohexene	3.46	8.5	99	92
1-Methyl-1-cyclohexene	1.79	6.3	90	86

[a] 50°C, 5 h, 25 mmol olefin, 6.25 mmol TBHP, 10 g acetonitrile, 0.3 g catalyst.

[b] Values in brackets correspond to the Euro-TS-1 sample under the same experimental conditions.

[c] r_0 = (moles of olefin converted)/(g of catalyst × s).

leading to low epoxide yields at high levels of conversion. This probably results from the nucleophilic attack of water and methanol molecules to the previously activated oxirane ring on the Brønsted acid sites of the Ti-Beta catalyst. The rate of solvolysis is seen to strongly depend on the particular structure and reactivity of the epoxide formed in the first step. While the intrinsic activity of Ti-Beta for oxidation of *n*-olefins is lower than for TS-1, it is much higher for the oxidation of branched and cyclic olefins.

Ti-Beta catalyst has also been shown to be much more active than TS-1 for epoxidation of olefins using *tert*-butylhydroperoxide as oxidant, though the reaction proceeds at a lower rate than when using hydrogen peroxide. This is attributed to a higher steric constraint for the transition state to be formed inside the zeolite pores and also to the lower electrophilic character of the Ti–OO*R* species (R=C–$(CH_3)_3$) as compared to Ti–OOH. Oxidations with TBHP on Ti-Beta showed a transition state selectivity more pronounced than for oxidations with H_2O_2. This is manifested by a higher relative decrease of the reactivity of hindered olefins in the former case. Under our reaction conditions, practically 100% selectivity to the corresponding epoxides has been obtained, together with a very low TBHP decomposition, when using Ti-Beta as catalyst.

TABLE 4

Relative Reaction Rates between Different Olefins and 1-Hexene Obtained on Ti-Beta with H_2O_2 and TBHP[a]

	1-octene	1-decene	4-m-1-pentene	1-m-1-cyclohexene
Oxidant	1-hexene	1-hexene	1-hexene	1-hexene
H_2O_2	0.70	0.60	1.45	1.22
TBHP	0.52	0.37	0.49	1.09

[a] The individual reaction rates on H_2O_2 and TBHP are taken from Tables 1 and 3, respectively.

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REFERENCES

1. Taramasso, M., Perego, G., and Notari, B., U.K. Patent 2,071,071 (1981).
2. Taramasso, M., Perego, G., and Notari, B., U.S. Patent 4,410,501 (1983).
3. Esposito, A., Taramasso, M., Neri, C., and Buonomo, F., U.S. Patent 2,116,974 (1985).
4. Neri, C., Esposito, A., Anfossi, B., and Buonomo, F., Eur. Patent Appl. 100,119 (1984).
5. Tatsumi, T., Nakamura, M., Negishi, S., and Tominaga, H., *J. Chem. Soc. Chem. Commun.*, 476 (1990).
6. Huybrechts, D. R. C., De Bruycker, L., and Jacobs, P. A., *Nature* **345,** 240 (1990).
7. Esposito, A., Neri, C., and Buonomo, F., U.S. Patent 4,480,135 (1984).
8. Reddy, J. S., Kumar, R., and Ratnasamy, P., *Appl. Catal.* **58,** L1 (1990).
9. Serrano, D. P., Li, H.-X., and Davis, M. E., *J. Chem. Soc. Chem. Commun.*, 745 (1992).
10. Reddy, J. S., and Sivasanker, S., *Catal. Lett.* **11,** 241 (1991).
11. Reddy, J. S., and Kumar, R., *J. Catal.* **130,** 440 (1991).
12. Reddy, K. M., Kaliaguine, S., Sayari, A., Ramaswamy, A. V., Reddy, V. S., and Bonneviot, L., *Catal. Lett.* **23,** 175 (1994).
13. Khouw, C. B., Dartt, C. B., Li, H. X., and Davis, M. E., *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **38,** 769 (1993).
14. Tatsumi, T., Nakamura, M., Yuasa, K., and Tominaga, H., *Catal. Lett.* **10,** 259 (1991).
15. Romano, V., Esposito, A., Maspero, F., Neri, C., and Clerici, M. G., *in* "New Developments in Selective Oxidation" (G. Centi and F. Trifirò, Eds.), p. 33. Elsevier, Amsterdam, 1990.
16. Camblor, M. A., Corma, A., Martínez, A., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.*, 589 (1992).

17. Corma, A., Camblor, M. A., Esteve, P., Martínez, A., and Pérez-Pariente, J., *J. Catal.* **145,** 151 (1994).
18. Blasco, T., Camblor, M. A., Corma, A., and Pérez-Pariente, J., *J. Am. Chem. Soc.* **115**(25), 11806 (1993).
19. Camblor, M. A., Corma, A., and Pérez-Pariente, J., *Zeolites* **13,** 82 (1993).
20. Zecchina, A., Spoto, G., Bordiga, S., Ferrero, A., Petrini, G., Leofanti, G., and Padovan, M., *Stud. Surf. Sci. Catal.* **69,** 251 (1991).
21. Geobaldo, F., Bordiga, S., Zecchina, A., Giamello, E., Leofanti, G., and Petrini, G., *Catal. Lett.* **16,** 109 (1992).
22. Martens, J. A., Buskens, Ph., Jacobs, P. A., van der Pol, A., van Hooff, J. H. C., Ferrini, C., Konwenhoven, H. W., Kooyman, P. J., and van Bekkum, H., *Appl. Catal.* **99,** 71 (1993).
23. Hanson, R. M., and Sharpless, K. B., *J. Org. Chem.* **51,** 1922 (1986).
24. Clerici, M. G., and Ingallina, P., *J. Catal.* **140,** 71 (1993).
25. Sheldon, R. A., *J. Mol. Catal.* **7,** 107 (1980).