JOURNAL OF CATALYSIS **145**, 151–158 (1994)

Activity of Ti-Beta Catalyst for the Selective Oxidation of Alkenes and Alkanes

A. Corma,[1] M. A. Camblor, P. Esteve, A. Martínez, and J. Pérez-Pariente

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

Received March 9, 1993; revised July 17, 1993

Ti-Beta zeolites with different titanium and aluminum contents have been prepared by changing the concentration of Ti and Al in the synthesis gel and the crystallization time. The gels were prepared from Aerosil as silica source. Ti-Beta samples were characterized by XRD, I.R., SEM, and diffuse reflectance (DR) spectroscopy in the UV–visible region. According to the characterization data, in the calcined dehydrated samples, titanium is incorporated into the framework of the zeolite Beta in a tetracoordinated state. No anatase phase was observed in the DR spectra. The catalytic activity for the selective oxidation by H_2O_2 of alkanes and alkenes with different molecular sizes was measured and compared with that of TS-1 under the same experimental conditions. For molecules whose diffusion is not restricted in either MFI or BEA structures, the intrinsic activity of the Ti centers is lower in Ti-Beta than in TS-1. However, the large-pore Ti-Beta catalyst shows superior activity compared to the medium-pore TS-1 for the oxidation of bulkier molecules.

INTRODUCTION

A major breakthrough in the zeolite field occurred when a group at ENI synthesized a Ti-containing silicalite, called TS-1, and demonstrated its activity, for H_2O_2-oxidation of olefins (1), amines and alcohols (2), hydroxylation of aromatics (3), and ammoximation of cyclohexanone (4). The capability of this material, as well as that of its MEL analogue (TS-2), was extended to other important reactions such as functionalization of alkanes to produce alcohols and ketones (5–7). The success of these catalysts prompted others (8) to prepare Ti-containing zeolites by isomorphous substitution using $TiCl_4$ in the gas phase (8), but their catalytic activity was much lower than that of the Ti-containing samples prepared by hydrothermal synthesis. Since the discovery of TS-1, another medium-pore-size Ti-containing zeolite with a ZSM-48 structure has been synthesized (9). However, the latter, as well as TS-1 and TS-2, are limited in their catalytic properties to relatively small reactants, which are the only ones able to penetrate in the narrow channels of their structures (6). It was therefore desirable to expand the potential catalytic applications of these materials by synthesizing large-pore Ti-containing zeolites with Ti in the appropriate coordination state to become active as oxidation catalysts. Recently (10), we have presented a hydrothermal synthesis of a zeolite, Ti-Beta, which is active for the oxidation of cycloalkanes. Moreover, this catalyst showed a higher conversion than TS-1 in the oxidation of bulky olefins which have serious problems diffusing through the pores of Ti-silicalite (6). The presence of aluminum in the crystals of the Ti-Beta samples was shown to affect the activity of the titanium atoms during the oxidation of 1-hexene (18).

In this work we have studied the catalytic activity of Ti-Beta zeolite in the selective oxidation of alkanes and alkenes of different molecular sizes, and the results have been compared with those obtained on a TS-1 catalyst. The influence of the framework composition of Ti-Beta on the intrinsic activity of the Ti centers in the oxidation of cyclohexene has also been investigated.

EXPERIMENTAL

Synthesis Procedure

Ti-Beta samples of different compositions were synthesized hydrothermally using tetraethylorthotitanate (TEOTi) and Aerosil as titanium and silica sources, respectively. A description of the synthesis procedure has been given elsewhere (20).

The Ti-silicalite used as a reference in this work is the Euro-TS-1 sample, containing a 1.7 wt% of Ti given as TiO_2.

Characterization

X-ray powder diffraction (XRD) was done with a Phillips PW 1830 diffractometer using Cu$K\alpha$ radiation, after dehydration of the samples at 383 K for 1 h and further rehydration over a $CaCl_2$ saturated solution (35% relative humidity) for 16 h XRD was used to measure the crys-

---

[1] To whom correspondence should be addressed.

0021-9517/94 $5.00

TABLE 1

Composition of the Different Ti-Beta Samples

Sample	In gel		In zeolite			
	Ti/(Si + Ti)	$T^{IV}O_2/Al_2O_3$	Ti/(Si + Ti)	%Beta (XRD)	$T^{IV}O_2/Al_2O_3$	TiO_2 (wt%)
1	0.016	800	0.018	89	111	2.4
2	0.016	800	0.021	86	119	2.7
3	0.016	800	0.027	82	246	3.5
4	0.048	400	0.039	85	118	5.0
5	0.048	400	0.040	85	210	5.2
6	0.048	400	0.044	85	244	5.7
7[a]	0.016	400	0.044	63	116	5.7

[a] Synthesized in the presence of alkali cations: $(Na + K)/T^{IV}O_2 = 0.12$.

tallinity of the samples and to assess the incorporation of Ti into the zeolite framework by measuring the expansion of the interplanar *d*-spacing corresponding to the most intense XRD peak in zeolite Beta ($2\Theta \approx 22.4°$). Mid-infrared spectra were recorded with a Nicolet 710° FTIR spectrometer using KBr pellets to follow the appearance of a band at ca. 960 cm^{-1}. The Ti content of the samples was determined by X-ray fluorescence (XRF) with an Outokumpu X-MET 840.

Scanning electron microscopy (SEM) has been used to determine the crystal size of the zeolites.

Diffuse reflectance (DR) spectra were recorded on a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference.

Molecular docking was simulated with Biosym's graphic molecular package, Insight II.

Catalytic Experiments

The reactions were carried out under stirring in a glass flask with reflux. The flask was heated in a temperature controlled oil bath. In a typical experiment, 33 mmol of reactant, 23.57 g of solvent, and a given amount of diluted hydrogen peroxide (35 wt%) were mixed in the flask and heated, if required, under agitation until the reaction temperature was reached. At that moment, 200 mg of catalyst were added to the reaction mixture. Aliquots were taken at selected reaction times and catalyst particles separated

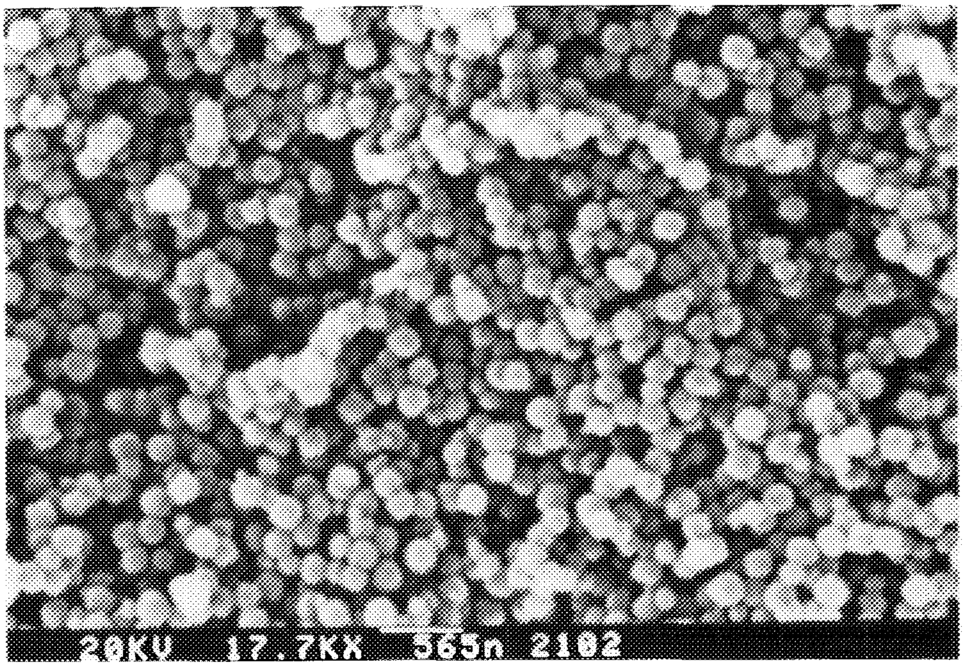


FIG. 1. Scanning electron microscopy (SEM) microphotographs of Ti-Beta sample 1.

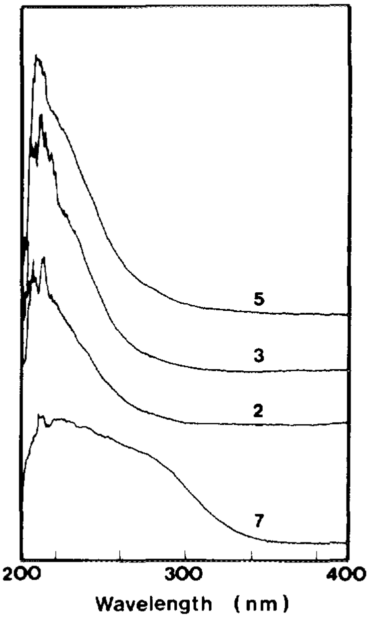


FIG. 2. Diffuse reflectance spectra in the UV–visible region of calcined Ti-Beta samples with different Ti content.

by filtration. The products were separated and analyzed by gas-chromatography in a capillary column (5% methylphenylsilicone, 25 m length) using an FID detector. Identification of the different compounds was done by GC–MS using available reference standards. Finally, unreacted hydrogen peroxide was measured by standard iodometric titration.

RESULTS AND DISCUSSION

Chemical Composition and Characterization of Ti-Beta Zeolites

Table 1 shows the composition of the Ti-Beta samples. When the synthesis is carried out in the absence of alkali cations (samples 1 to 6) highly crystalline Ti-Beta samples are obtained.

A continuous increase in the interplanar *d*-spacing (XRD) and in the intensity of the 960 cm^{-1} IR band with increasing Ti content was observed for the Ti-Beta samples synthesized without alkali cations (20). Although the assignment of the 960-cm^{-1} IR band is still under discussion (11), the above results are usually taken as evidence of Ti incorporation into the zeolite framework of Ti-silicalites (12, 13). However, a clear deviation from linearity was observed for samples containing alkali cations (20).

The SEM micrographs of Ti-Beta revealed very homogeneous, round shaped crystals of a mean crystal size below 0.2 μm for all the samples studied (Fig. 1).

Figure 2 shows the diffuse reflectance (DR) spectra in the UV–visible region of calcined Ti-Beta samples with titanium contents from 2.4 to 5.7 wt% (given as TiO_2). Note first that there is no peak at ca. 330 nm corresponding to anatase. Second, the DR spectrum of sample 7, which was synthesized in the presence of alkali cations, is different since it shows an intense broad band at ca. 270 nm that has been assigned to sixfold coordinated Ti species in an amorphous titanosilicate phase probably having Ti–O–Ti bonds (17). By contrast, this band is much less evident in the spectra of the Ti-Beta samples synthesized in the absence of alkali cations. Furthermore, the latter samples show other bands at ~205, 215, and 225 nm. The band appearing at the lowest wavelength has also been observed in the UV–visible spectra of dehydrated TS-1 and assigned to isolated Ti atoms in tetrahedral coordination (14). After hydration, the band shifts to ~230 nm, and the coordination of Ti increases from four- to sixfold. Considering the above assignments, and the characterization results discussed until now, one may conclude that most of the Ti atoms in Ti-Beta synthesized from alkali-free reaction mixtures probably occupy framework positions, and have coordination numbers between 4 and 6. This seems to be valid for a wide range of zeolite compositions (Table 1).

Influence of Ti-Beta Composition on Its Catalytic Activity in the Oxidation of Cyclohexene

The catalytic activity of the Ti-Beta samples with different Ti and Al contents has been studied for the oxidation of cyclohexene at 298 K, using H_2O_2 as oxidant. In gen-

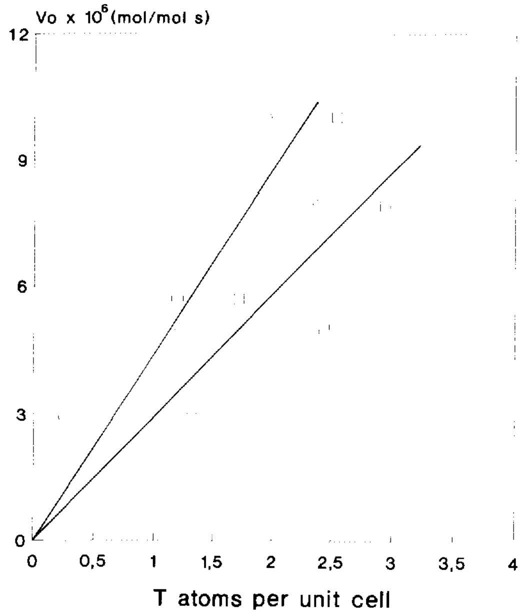


FIG. 3. Initial reaction rate for the cyclohexene oxidation reaction as a function of the number of Ti (□) and Ti minus (○) atoms per unit cell in Ti-Beta zeolite.

TABLE 2

Conversion per Ti Atom in Ti-Beta Samples of Different Composition for the Oxidation of Cyclohexene[a]

Sample	T atoms per unit cell		Turnover number[b] (mol oxid/mol Ti)
	Ti	Al	
2	1.32	1.06	5.2
3	1.71	0.52	7.7
4	2.43	1.21	4.7
5	2.53	0.60	9.2
6	2.93	0.55	6.6
7	—	—	0.1

[a] Reaction conditions: T = 298 K; 33 mmol cyclohexene; H_2O_2/olefin = 0.082; 23.57 g methanol; 0.200 g catalyst.

[b] Calculated at 1 h reaction time.

eral, the activity increased upon increasing the Ti content of samples synthesized in the absence of alkali cations. However, samples with a high Al concentration (low Si/Al ratio) were less active than expected on the basis of their Ti content. This is illustrated in Fig. 3, where the initial reaction rate, V_0, has been plotted versus the number of Ti atoms per unit cell. Indeed, a slightly better correlation is found when the number of Ti minus Al atoms per unit cell is considered instead of Ti/u.c. (Fig. 3). Similar behavior has also been observed for the oxidation of 1-hexene catalyzed by Ti-Beta (18).

Similar conclusions can be reached when the conversion per Ti site (numbers of turnovers) for the cyclohexene oxidation reaction is considered (Table 2). Samples 2 and 4, with the higher Al content, show the smallest number of turnovers with the exception of sample 7, synthesized with alkali cations, which shows a very low activity. Moreover, no direct correlation between the number of turnovers and the Ti content is observed for samples 3, 5, and 6, all of them having similar Al concentration. Note that samples 3 and 6 were obtained from the same synthesis gel as samples 2 and 4 but their crystallization time was longer. Given that Ti and Al compete for incorporation into the framework of zeolite Beta (20), and considering the composition of the corresponding gels (Table 1), we infer that those samples obtained at longer crystallization times have much higher concentration of Al in the center of the crystals, correspondingly, most of the Ti atoms would be located in an outer shell and would be in an aluminum-free environment. When pairs of samples obtained from the same gel mixture are compared (samples 2 and 3, and samples 4 and 6), a systematic increase in the number of turnovers is observed for samples obtained at higher crystallization times.

These results suggest a higher intrinsic activity of the Ti atoms in Ti-Beta if they occupy Al-free regions of the crystals. This aspect has been more extensively discussed for the oxidation of 1-hexene on Ti-Beta catalysts prepared by different procedures (19). A change in the redox ability of the Ti sites, whether or not Al is present in the vicinity of a given Ti center, can be related to changes in the electronegativity of the zeolite lattice, which may alter the electronic density around the Ti sites. It follows that not only the zeolite composition but also the Ti and Al concentration gradients along the crystals can affect the activity of Ti-Beta catalysts.

TABLE 3

Oxidation of Cyclohexene on Ti-Beta Catalysts under Different Reaction Conditions[a]

Sample	Reaction temperature (K)	g Catalyst/ g olefin (%)[b]	mol H_2O_2/ mol olefin	Solvent[c]	Olefin conversion (mol%)	H_2O_2 conversion (%)	H_2O_2 Selectivity (%)
3	298	7.4	0.082	MeOH	2.0	30	83
	323	7.4	0.082	MeOH	5.7	91	76
	333	7.4	0.082	MeOH	7.4	94	96
5	298	7.4	0.082	MeOH	3.6	48	92
	298	14.8	0.082	MeOH	5.3	65	100
	298	7.4	0.164	MeOH	3.1	26	73
	298	7.4	0.082	EtOH[d]	3.5	44	97
	298	7.4	0.082	*t*-ButOH	1.6	25	78

[a] Olefin and H_2O_2 conversion and selectivity are given at 1 h reaction time.

[b] 33 mmol of cyclohexene used.

[c] 23.57 g of solvent.

[d] Oxidation of EtOH was found to be negligible under these reaction conditions.

TABLE 4

Selective Oxidation of Different Olefins over Ti-Beta and Euro-TS-1 Catalysts

Olefin	Catalyst[c]	Reaction time (h)	Turnover (mol/mol Ti)	H_2O_2 Conversion (%)	H_2O_2 Selectivity (%)[d]	Product selectivity (mol%) Epoxide	Glycol	Glycolethers
1-Hexene[a]	TS-1	3	50	98	80	96	—	4
	Ti-Beta(6)	3	12	80	80	12	8	80
Cyclohexene[a]	TS-1	3	1	—	—	100	—	—
	Ti-Beta(5)	3.5	14	80	83	—	—	100
1-Dodecene[b]	TS-1	3.5	110	83	68	77	23	—
	Ti-Beta(1)	3.5	87	80	87	—	100	—
Cyclododecene[b]	TS-1	4	5	26	26	66	34	—
	Ti-Beta(1)	3.5	20	47	71	80	20	—

[a] Reaction conditions as in Table 2.

[b] 353 K; H_2O_2/olefin = 0.258 mol/mol; 23.57 g ethanol as solvent; other conditions as in footnote a. Some oxidation of ethanol was observed at these reaction conditions, which has been taken into account to calculate H_2O_2 conversion and selectivity.

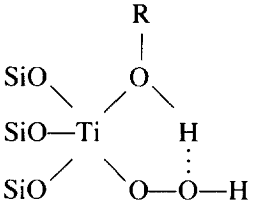
[c] Number in parentheses indicates sample number in Table 1.

[d] H_2O_2 selectivity (%) = (mol olefin oxidized/mol H_2O_2 converted) × 100.

Influence of Reaction Conditions on Activity and Selectivity for the Oxidation of Cyclohexene

The effect of reaction temperature, amount of catalyst, and type of solvent was studied for the oxidation of cyclohexene on Ti-Beta (Table 3). There it can be seen that an increase of both the reaction temperature and the amount of catalyst produces not only an increase in the olefin conversion, as would be expected, but also a better utilization of H_2O_2. If the olefin oxidation and the H_2O_2 decomposition reaction compete on the Ti sites, the increase in the H_2O_2 selectivity observed with increasing reaction temperature can indicate a higher activation energy of the epoxidation reaction.

Finally, the type of solvent used has a clear effect on the kinetics of the reaction. Various alcohols used as solvents develop the following order of activity: methanol $\geq$ ethanol $\gg$ *t*-butylalcohol. Ethanol oxidation was found to be negligible during cyclohexene oxidation under the reactions conditions used (298 K reaction temperature), as can be also deduced from the high H_2O_2 selectivity obtained. Recently (23), species I,



I

has been proposed as an intermediate during the epoxidation of olefins on TS-1 in order to account for the effects of solvent, bases, and acids on the reaction kinetics. The activity order (23)—methanol > ethanol > t-butanol—for the epoxidation of 1-pentene at 298 K, was explained on the basis of increasing electrophilicity and steric constraints of species I inside the channels of TS-1. A similar activity for the oxidation of cyclohexene found on Ti-Beta, when using methanol or ethanol as solvent, would indicate that the steric effects in this large-pore titanium zeolite are less important than in TS-1. H_2O_2 selectivity was above 90% for both solvents, and decreased slightly (78%) when *t*-butanol was used.

Activity and Selectivity of Ti-Beta Catalyst

Oxidation of alkenes and cycloalkenes. The activity and product selectivity of the Ti-Beta catalysts for the oxidation of 1-hexene, cyclohexene, 1-dodecene, and cyclododecene is compared in Table 4 with that of Ts-1. There it can be seen that the conversion is higher for the TS-1 catalyst in the case of linear alkenes, although the conversion ratio of TS-1 to Ti-Beta decreases from 4.1 to 1.3 when going from 1-hexene to 1-dodecene. Furthermore, the conversion per Ti site is higher on Ti-Beta for the oxidation of cyclic olefins. Indeed, TS-1 shows a very low conversion for cyclohexene at 298 K, while Ti-Beta gives the same, or even a larger number of turnovers for cyclohexene than for 1-hexene. The Ti-Beta/TS-1 turnover ratio is lower for cyclododecene than for cyclohexene, which would indicate some steric restrictions for the

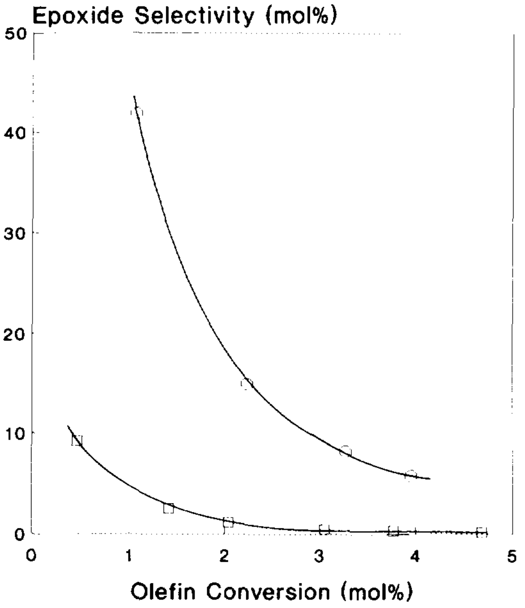


FIG. 4. Epoxide selectivity as a function of olefin conversion in the oxidation of 1-hexene (○) and cyclohexene (□) on Ti-Beta (sample 3). Reaction conditions as in Table 2.

cyclododecene molecule even in the large pores of Ti-Beta. The above results suggest that during oxidation of bulky molecules greater geometrical restrictions are imposed by the MFI than by the BEA structure, thus affecting the catalytic behavior.

The hindrance effect has been studied by docking the different alkenes of interest in the two zeolites structures. By means of an energy minimization program, the zeolite-reactant conformation corresponding to the minimum of Van der Waals and electrostatic interactions for the penetration of the reactants through the channels of the zeolite has been calculated. 1-Hexene can penetrate without problems through the channels of the MFI and BEA structures, but while cyclohexene is not impeded in the BEA structure, it has serious problems diffusing inside the channels of MFI. Furthermore, 1-dodecene can be accommodated in the BEA structure and in the linear channels of the MFI, but repulsive interactions appear when this molecule walks through the tortuous channels of the MFI structure. This means that not all the Ti sites of TS-1 are accessible to this reactant, which can explain why the activity per Ti site is about eight times higher for TS-1 for the oxidation of 1-hexene, while it is only twice for 1-dodecene. Finally, we found that cyclododecene can not penetrate the channels of zeolite Beta, although it can be accommodated in the "pockets" of the external surface, corresponding to the broken channels. This molecule neither penetrates the MFI structure nor can be accommodated in the pockets at the external surface.

Our results (Table 4) show the same efficiency in the utilization of H_2O_2 for the 1-hexene oxidation, on TS-1 and Ti-Beta but Ti-Beta is more selective for the oxidation of bulkier olefins. Nevertheless, the H_2O_2 selectivity on Ti-Beta is lower for bulkier than for smaller reactant olefins.

Looking at the product selectivity shown in Table 4, a very high selectivity to epoxide is found for the oxidation of 1-hexene, cyclohexene, and 1-dodecene on TS-1, while on Ti-Beta the opening of the epoxide occurs to a large extent, and the corresponding glycol derivatives are ob-

TABLE 5

Selective Oxidation of Different Alkanes over Ti-Beta and Euro-TS-1 Catalysts[a]

			H_2O_2		Product selectivity (mol%)	
Alkane	Catalyst[b]	Turnover (mol/mol Ti)	Conversion (%)	Selectivity[c] (%)	−OL	−ONE
n-Hexane	TS-1	48.5	77	100	91.5	8.5
	Ti-Beta	0.5	11	32	55.0	45.0
3-Methylpentane	TS-1	0.7	6	19	88.9	11.1
	Ti-Beta	0.8	17	29	84.8	15.2
Cyclohexane	TS-1	[d]	—	—	—	—
	Ti-Beta	2.3	22	51	98.9	1.1
Methylcyclohexane	TS-1	[d]	—	—	—	—
	Ti-Beta	5.2	29	88	92.8	0.9

[a] Reaction conditions: 333 K; t_r = 4 h; 33 mmol alkane; H_2O_2/alkane = 0.082 mol/mol; 23.57 g of methanol as solvent; 0.200 g of catalyst.

[b] Ti-Beta catalyst corresponds to sample 5 in Table 1.

[c] As defined in Table 4.

[d] Activity below the detection limits.

tained preferentially. This result is not surprising since in the case of Ti-Beta the acid sites associated with framework Al can catalyze the epoxide ring opening reaction. The same effect was observed when trivalent elements, such as Al, Ga, or Fe were introduced into the Ti-silicalite structure (21). Besides the strong acid sites associated with framework Al, silanol and titanol groups present on the zeolite surface can also carry out the opening of the epoxide ring to form the glycol, even if their activity is much lower than that of bridging hydroxyl groups (22). These sites can be responsible for the formation of glycols in the reaction of cyclododecene on TS-1. Indeed, as was shown above, in this case the reaction occurs on the surface of zeolite crystals, where the ratio of silanols to Ti atoms is very high.

As the formation of glycols and glycol derivatives occurs through consecutive steps, their yield increases as the olefin conversion increases. However, the relative rate of the epoxide formation and solvolysis was found to depend on the olefin used (Fig. 4).

Moreover, the high epoxide selectivity obtained on Ti-Beta for the cyclododecene oxidation may be a consequence of both the low olefin conversion achieved and the greater steric restrictions for the epoxide formed in the outer shell of the crystals to diffuse into the pores of the zeolite. It has been shown (19) that the concentration of Al in the external surface of Ti-Beta crystallites is much lower than in the crystal core. Therefore the epoxides are not subjected to transformation to glycol ethers.

Oxidation of alkanes and cycloalkanes. The oxyfunctionalization of alkanes and cycloalkanes of different molecular sizes has been carried out on Ti-Beta and TS-1 catalysts at 333 K, and the results obtained are presented in Table 5. Similarly to what has been discussed before concerning the oxidation of olefins, TS-1 catalyst shows a much higher intrinsic activity than Ti-Beta for the activation of unhindered paraffins. For instance, in the case of *n*-hexane, TS-1 gives 100% hydrogen peroxide selectivity at 77% conversion. However, the conversion per Ti site in TS-1 decreased by a factor of 7 for oxidation of a branched hexane isomer, such as 3-methylpentane, for which diffusion is restricted through the small pores of the MFI structure. Moreover, no appreciable activity was found for cyclohexane and methylcyclohexane on this medium-pore Ti-zeolite under the same experimental conditions.

On the other hand, all those molecules probably diffuse relatively easily through the channels of the large pore Ti-Beta, and thus, the catalytic activity of this catalyst is not limited by diffusion through the pores, but by the intrinsic reactivity of the alkane towards zeolite active sites. The activation of paraffin occurs probably by a homolytic mechanism, the first step of which is the H-abstraction of the molecule by the active centers of the catalyst having homolytic character (24). The turnover number of Ti-Beta (Table 5) increases in the order: *n*-hexane < 3-methylpentane < cyclohexane < methylcyclohexane, consistent with tertiary centers being more reactive than secondary or primary centers. Hydrogen peroxide conversion also increases in the same order but H_2O_2 selectivities are low, except for methylcyclohexane, when compared to the values obtained with olefins (Table 4). Furthermore, from the results presented in Table 5 we conclude that the lower the reactivity of the molecule to be oxidized, the higher the H_2O_2 decomposition rate, as a consequence of the competition of the two reactions.

CONCLUSIONS

Ti-Beta zeolite samples have been prepared by hydrothermal crystallization in a wide range of titanium and aluminum compositions. Samples synthesized in the absence of alkali cations showed good crystallinity. No band corresponding to anatase was observed in the DR UV-visible spectra of the calcined materials, even for Ti contents above 5 mol%.

Ti-Beta has been shown to be an active catalyst for the oxidation of different alkenes and alkanes. For molecules which do not present serious steric restrictions to diffuse inside the pores of Ti-Beta and TS-1 (1-hexane, 1-dodecene, and *n*-hexane) a higher turnover (activity per Ti atom) is observed for TS-1 than for Ti-Beta. However, as the size of the molecule increases, diffusion problems become predominant in Ti-silicalite, and thus Ti-Beta gives a higher activity. Moreover, a slightly higher turnover is obtained for cyclohexene than for 1-hexene on Ti-Beta, which is in agreement with the higher electrophilicity of the former, and consequently, with a greater reactivity. Branched and cyclic alkanes are more easily oxidized on Ti-Beta than on TS-1, although with a much lower conversion per Ti than occur with the equivalent olefins. The conversion per Ti site in Ti-Beta increases upon increasing the relative proportion of secondary to primary carbon atoms and with the presence of tertiary carbon atoms in the alkane molecule, according to the homolytic mechanism accepted for the oxyfunctionalization of saturated hydrocarbons.

The hydrogen peroxide decomposition reaction toward oxygen and water becomes relatively more important as the diffusional problems of the reactant molecule become more serious or as the reactivity of the substrate decreases.

The presence of aluminum in Ti-Beta seems to decrease the intrinsic activity of the Ti atoms. Furthermore, the concentration profiles of Ti and Al along the Ti-Beta zeolite crystallites plays an important role in the catalytic behavior of these materials.

ACKNOWLEDGMENTS

Financial support by the Comisión Asesora de Investigación Científica y Técnica of Spain (Project MAT 91-1152) is gratefully acknowledged. We also thank Professor P. A. Jacobs for providing the Euro-TS-1 sample.

REFERENCES

1. Neri, C., Esposito, A., Anfossi, B., and Buonomo, F., Eur. Patent Appl. 100,119 (1984).
2. Esposito, A., Neri, C., and Buonomo, F., U.S. Patent 4,480,135 (1984).
3. Esposito, A., Tamarasso, M., Neri, C., and Buonomo, F., U.S. Patent 2,116,974 (1985).
4. Roffia, P., Padovan, M., Moretti, E., and Alberti, G., EP 208,311 (1987).
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. Reddy, J. S., and Sivasanker, S., *Catal. Lett.* **11,** 241 (1991).
8. Kranshaar-Czarnetzki, B., Van Hoof, J. C., *Catal. Lett.* **1,** 81 (1988).
9. Serrano, D. P., Li, H., and Davis, M. E., *J. Chem. Soc. Chem. Commun.*, 745 (1992).
10. Camblor, M. A., Corma, A., Martínez, A., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.*, 589 (1992).
11. Camblor, M. A., Corma, A., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.*, 557 (1993).
12. Perego, G., Bellussi, G., Corno, C., Tamarasso, M., Buonomo, F., and Esposito, A., *Stud. Surf. Sci. Catal.* **28,** 129 (1986).
13. Readdy, J. S., Kumar, R., and Ratnasamy, P., *Appl. Catal.* **58,** L1 (1990).
14. Geobaldo, F., Bordiga, S., Zecchina, A., Gianello, E., Leofanti, G., and Petrini, G., *Catal. Lett.* **16,** 109 (1992).
15. Deleted in proof.
16. Deleted in proof.
17. Blasco, T., Camblor, M. A., Corma, A., and Pérez-Pariente, J., *J. Am. Chem. Soc.*, in press.
18. Camblor, M. A., Corma, A., Martínez, A., Pérez-Pariente, J., and Primo, J., *in* "Prepr. Inter. Congress on Heterogeneous Catal. and Fine Chem., Poitiers, April 5–8, 1993."
19. Camblor, M. A., Corma, A., Martínez, A., Pérez-Pariente, J., and Valencia, S., *in* "Prepr. II World Congress and IV European Workshop Meeting on "New Developments in Selective Oxidation," Benalmádena, Sept. 20–24, 1993.
20. Camblor, M. A., Corma, A., Pérez-Pariente, J., *Zeolites* **13,** 82 (1993).
21. Bellussi, G., Carati, A., Clerici, M. G., and Esposito, A., *in* "Preparation of Catalysts V," p. 421. Elsevier, Amsterdam, 1991.
22. Clerici, M. G., and Romano, V., Eur. Patent 230,949 (1987).
23. Clerici, M. G., and Ingallina, P., *J. Catal.* **140,** 71 (1993).
24. Clerici, M. G., *Appl. Catal.* **68,** 249 (1991).