

Solvent Effects during the Oxidation of Olefins and Alcohols with Hydrogen Peroxide on Ti-Beta Catalyst: The Influence of the Hydrophilicity–Hydrophobicity of the Zeolite

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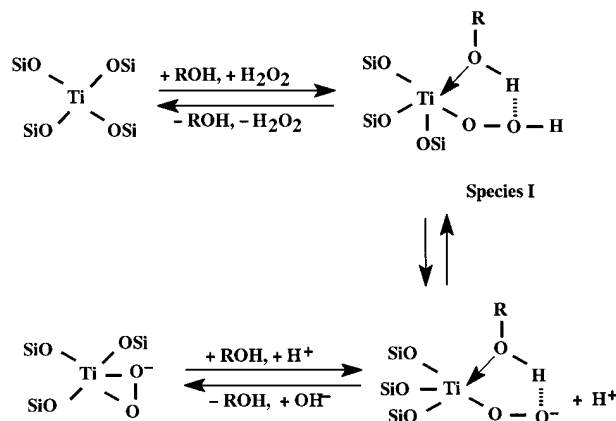
It is presented in this paper that the hydrophilic–hydrophobic characteristics of Ti-zeolites play a very important role in their reactivity for liquid phase oxidations using H₂O₂ and organic hydroperoxides. To show this, the influence of the nature of solvent on the reactivity and selectivity features of the large pore Ti-beta catalyst has been studied during the oxidation of 1-hexene and cyclohexanol, as representative substrates, using aqueous hydrogen peroxide as oxidant and under single liquid phase conditions. It has been shown that the reactivity of Ti-beta was highest in acetonitrile, a polar and nonprotic solvent, for both 1-hexene and cyclohexanol oxidations. In contrast, the reactivity of the medium pore TS-1 for 1-hexene oxidation was seen to be much higher in methanol (protic) than in acetonitrile (aprotic) solvent. These differences have been related to the hydrophilic character of Ti-beta, in contrast to the hydrophobic character of TS-1. The selectivities to the epoxide and to the ketone during 1-hexene and cyclohexanol oxidations, respectively, on Ti-beta were also highest in acetonitrile. This was associated to the poisoning of the Brønsted acid sites associated with framework aluminum by the basic acetonitrile molecules, thus avoiding acid-catalyzed secondary reactions. The different effects that solvents have on the catalytic properties of Ti-beta and TS-1 are of prime importance from the point of view of the application of these catalysts, since, as can be seen from this work, the optimum operating conditions would be quite different for both the Ti-beta and the TS-1 materials. © 1996 Academic Press, Inc.

INTRODUCTION

Titanium silicalites (TS-1 and TS-2) are highly efficient catalysts for the selective oxidation of a large number of organic substrates, such as alkenes, alcohols, aromatics and phenol, and alkanes (1–5), using H₂O₂ as oxidant under mild reaction conditions. Unlike the Group IV–VI metal oxide based catalysts, Ti-silicalites are active in the presence of diluted aqueous solutions of hydrogen peroxide, whereas anhydrous organic hydroperoxides, such as TBHP, are the oxidants of choice for the former catalysts (6). These differences can be partially ascribed to the hydrophobic character

of TS-1, which favors the adsorption of the organic substrates over the more polar water molecules present in the aqueous H₂O₂ solution, thus maintaining the Ti sites inside the zeolite pores in an organic-rich environment. Indeed, it has been recently shown (7) that the activity for the oxidation of 1-hexene and *n*-octane on TS-1 is not modified by the use of either aqueous or anhydrous solutions of H₂O₂, whereas it is strongly inhibited in the case of an amorphous TiO₂–SiO₂ coprecipitate catalyst when the aqueous H₂O₂ solution was used as oxidant.

Furthermore, the nature of the solvent is known to have a major influence on reaction kinetics and product selectivity during the oxidations on TS-1. Thus, methanol and other protic solvents were shown to enhance the catalytic activity of TS-1 for the epoxidation of propylene (8) and other lower alkenes (9), provided that the size of the solvent is small enough to enter the pores of the medium pore Ti-silicalite. The relevant role played by protic solvents on the oxidation activity of TS-1 was explained assuming the formation of a stable five-membered cyclic structure (species I), in which the protic molecule, ROH, coordinates the Ti centers and stabilizes the Ti–peroxo complex through hydrogen bonding (10). This species is modified by acids and bases according to the following equilibria (9).



SCHEME I

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Thus, formation of species I could account for the positive effect of protic solvents on reaction kinetics of TS-1, as well as for the effects observed on the catalytic properties of TS-1 when adding acids or bases (9, 10).

More recently (11), the same type of species has been proposed in order to explain the effect of protic solvents on the kinetics of oxidation of alcohols over TS-1. Then, differences in the kinetic orders when using MeOH, *t*-BuOH, and water were interpreted on the basis of differences in adsorption between the protic solvent and the alcohol substrate. However, reaction rates were much less affected by the type of solvent used, which was explained assuming that the solvent does not take part in the slow step of the reaction mechanism (11).

Although it appears to be a general agreement on protic molecules being the preferred solvents for the oxidation of unfunctionalized alkenes and alcohols over TS-1, the unanimity is broken when other substrates are to be oxidized. Thus, acetone and acetonitrile (nonprotic solvents) were the best solvents in terms of both activity and selectivity for the epoxidation of allyl alcohol on TS-1 (12), whereas water and acetone gave a slightly higher activity than methanol during phenol hydroxylation (13). This probably occurs because in these cases the role played by the solvent is not so simple, and other factors, such as polarity, solubility of reactants and products, diffusion and counterdiffusion effects, and possible interaction with the active centers, should contribute to the differences observed.

Recently (14) a large pore Ti-containing zeolite, Ti-beta, has been synthesized and proved to be an active catalyst for the oxidation of alkanes and alkenes, either by using H₂O₂ or TBHP as oxidants (15, 16). Taking advantage of its larger pore size, Ti-beta was shown to be more active than TS-1 for the oxidation of bulkier substrates, such as cyclic and branched molecules (15, 16). Moreover, there is an additional factor that can contribute to the different catalytic behavior observed between Ti-beta and TS-1, and this is the presence of aluminum in the framework of the former catalyst (17). This framework Al introduces additional acidity in Ti-beta, which is reflected in a lower selectivity to the epoxide during olefin epoxidation as compared to TS-1, since residual protons associated to Al catalyze the opening of the oxirane ring with the corresponding formation of glycols and glycol derivatives (16, 17). Besides these selectivity effects, the presence of Al and a large concentration of internal and external silanol groups confers to Ti-beta a hydrophilic character, in contrast to the organophilic characteristics of TS-1. This may lead to significant differences in the adsorption properties of both materials, which at the end should be reflected in a different catalytic behavior when considering the effect of solvents on reaction kinetics and selectivity.

In this context, it is the aim of this work to investigate the influence of the nature of the solvent on the catalytic acti-

vity and selectivity of Ti-beta for the oxidation of alkenes and alcohols using diluted H₂O₂ as oxidant. For this purpose we have selected two representative substrates, i.e., 1-hexene and cyclohexanol, and six solvents having different polarities (dielectric constants). Moreover, the influence of the protic/aprotic nature of the solvent has also been studied by using three protic molecules: methanol, ethanol, and *t*-butyl alcohol, and three aprotic solvents: acetone, methyl ethyl ketone (MEK), and acetonitrile. These solvents were also chosen because they form a single phase with the organic substrate and the hydrogen peroxide solution, so mass transfer problems associated to the presence of different liquid phases were avoided.

EXPERIMENTAL

Synthesis and Characterization of Ti-Beta Catalyst

A sample of Ti-beta zeolite was synthesized following the procedure described in Ref. (17), and using tetraethyl orthotitanate (TEOTi) and Aerosil (Degussa) as titanium and silica sources, respectively. The synthesis gel having the molar composition TO₂/Al₂O₃ = 800; Ti/(Si + Ti) = 0.016; TEAOH/TO₂ = 0.54; H₂O/TO₂ = 10 was crystallized in Teflon-lined autoclaves at 135°C and 60 rpm rotation. After crystallization the solid was filtered, washed with deionized water until it reached pH 9, dried at 80°C, and finally calcined at 580°C for 5 h.

The chemical composition of the calcined Ti-beta sample measured by atomic absorption spectrometry was 4.0 wt% TiO₂, and SiO₂/Al₂O₃ = 312. The crystallinity of the sample measured by X-ray powder diffraction (Phillips PW-1830, CuK α radiation) was 75%, referred to the as-synthesized material. The IR spectrum (Nicolet 710, KBr technique) presented the band at ca. 960 cm⁻¹ and a large concentration of external (ca. 3736 cm⁻¹) and internal (ca. 3530 cm⁻¹) silanol groups can be appreciated in the OH region of the IR spectrum (Fig. 1). The DRS UV-vis spectrum showed bands in only the 205- to 230-nm range assigned to framework Ti atoms in a four- to sixfold coordination (18). The average crystallite size ranged between 0.1 and 0.2 μ m as revealed by transmission electron microscopy (TEM).

Catalytic Experiments

The oxidation reactions have been carried out in a 50-ml round-bottom flask immersed in a thermostatted bath and equipped with a condenser, a thermometer, and a magnetic stirrer. In a typical experiment 33 mmol of substrate, 23.6 g of solvent, and 0.8 g of diluted hydrogen peroxide (35 wt% in water) are mixed in the flask and heated at the desired reaction temperature under stirring. Then, 0.20 g of catalyst are instantaneously added to the mixture (time zero), and small samples are taken with a syringe for analysis at different reaction times through a septum fitted with the flask.

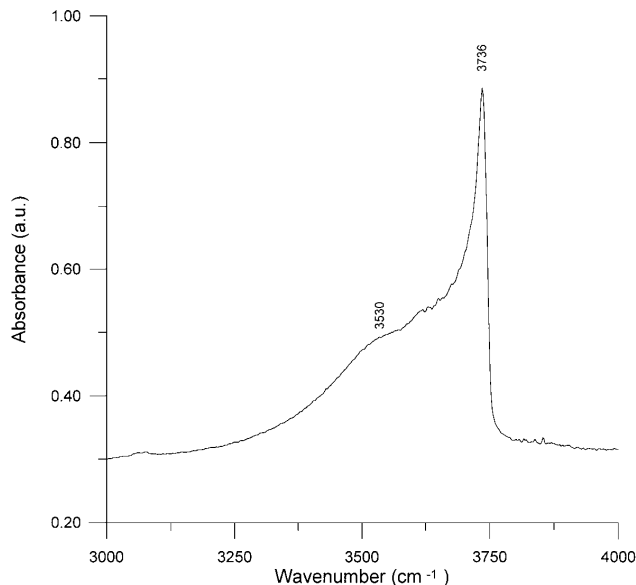
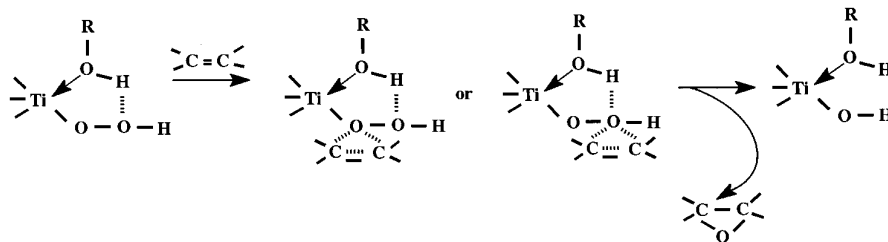


FIG. 1. IR spectrum in the OH region of Ti-beta catalyst after degassing at 400°C and vacuum.

The reaction temperature was set to 50°C for the oxidation of 1-hexene and to 65°C in the case of cyclohexanol.

The products were analyzed by gas chromatography (Varian 3400) equipped with a capillary column (5%



SCHEME II

methylphenylsilicone, 25 m length) and a flame ionization detector (FID). Identification of the reaction products was performed by mass spectrometry and using standard compounds. The consumption of hydrogen peroxide was measured by iodometric titration.

Blank experiments were also carried out under the same reaction conditions as described above. Under these conditions no substrate oxidation nor hydrogen peroxide consumption was observed in the absence of catalyst.

RESULTS AND DISCUSSION

Influence of Solvent on the Reactivity of Ti-Beta Catalyst

1-Hexene oxidation. In the first part of the work we studied the influence of the polarity of the solvent on the activity of Ti-beta during the oxidation of 1-hexene and

TABLE 1
Characteristics of the Solvents Used in the Oxidation of 1-Hexene and Cyclohexanol on the Ti-Beta Catalyst

Solvent	Protic (P) or aprotic (A)	Dielectric constant	Boiling point (°C)
Methanol	P	32.7	64.7
Ethanol	P	24.5	78.3
<i>t</i> -Butyl alcohol	P	10.9	82.2
Acetonitrile	A	37.5	81.6
Acetone	A	20.7	56.3
Methyl ethyl ketone	A	18.5	79.6

cyclohexanol. Table 1 shows the characteristics of the different solvents used and their protic/aprotic nature.

The influence of the nature of solvent on the initial reaction rate, r_0 , for the oxidation of 1-hexene is shown in Fig. 2. It can be seen that the activity increases with solvent polarity for both the protic and aprotic series, the increase being much more pronounced with the aprotic solvents. It has been reported that the activity of TS-1 for epoxidation of olefins is enhanced by the use of protic solvents (9). The positive effect of protic solvents was explained assuming the formation of a cyclic species I prior to the approximation of the olefin to the Ti-peroxo complex, according to the following proposed mechanism (9).

The epoxidation activity of TS-1 was seen to decrease in the order MeOH > EtOH > *t*-BuOH as a result of decreasing electrophilicity and increasing steric constraints of species I (9). The reactivity trends obtained for the Ti-beta catalyst in the epoxidation of 1-hexene (Fig. 2) when using protic solvents are in agreement with that reported for TS-1, i.e., MeOH > EtOH > *t*-BuOH, but the differences in reactivity between these alcohols are lower for Ti-beta. This can be ascribed to the lower steric impediments imposed by the larger pores of Ti-beta with respect to the medium pore TS-1.

In the case of nonprotic solvents, which would not form the cyclic species I, the order of reactivity observed in Fig. 2, i.e., acetonitrile > acetone > MEK, may be explained by the increase of substrate concentration in the hydrophilic pores of Ti-beta as the polarity of the solvent increases. Indeed, the higher the solvent polarity, the higher the concentration

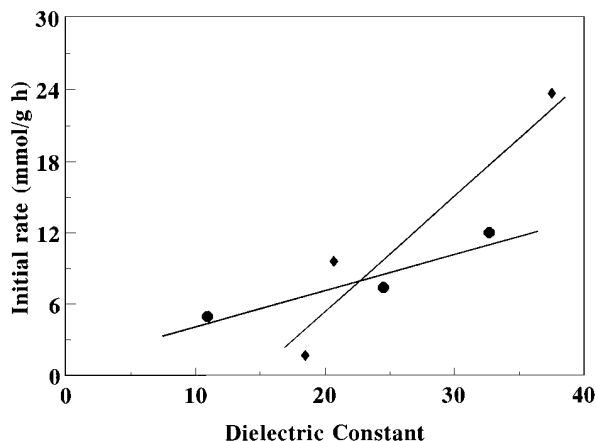


FIG. 2. Initial reaction rate for 1-hexene oxidation on Ti-beta with H_2O_2 as a function of the polarity (dielectric constant) of protic (●) and aprotic (◆) solvents.

of substrate in the vicinity of the active sites and the higher the reaction rate will be, as indicated by the experimental results.

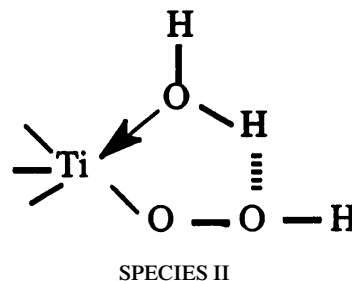
The higher reactivity obtained in MeCN with respect to MeOH cannot be explained in terms of polarity, since both solvents have similar dielectric constants (Table 1), and is in contrast with the reported positive effect of protic solvents on the reactivity of TS-1. In order to explain these discrepancies, it could be considered that the electrophilicity of the Ti sites, and therefore their catalytic activity, in Ti-beta may be changed upon interaction of the basic acetonitrile molecules with the strong Brønsted acid sites of framework Al. Indeed, it was already shown (19) that the intrinsic activity of the Ti atoms in Ti-beta was modified with the Al content of the catalyst. However, the effect of MeCN on the increased reactivity of Ti-beta cannot be ascribed to the poisoning of the acid sites, since a Na-exchanged Ti-beta sample (sodium acetate 0.16 M, 80°C, 6 h) with no Brønsted acidity, showed almost the same differences in reactivity for 1-hexene oxidation in methanol and acetonitrile, as presented in Table 2.

Another possible explanation of the higher intrinsic reactivity of the Ti sites in acetonitrile, if one assumes that the MeCN (and in general the nonprotic solvents) molecules do not form stable complexes with the Ti atoms, can be the following: considering that species I is the proposed active

TABLE 2
Relative Reactivities for 1-Hexene Oxidation in Methanol and Acetonitrile as Solvents on Untreated and Na-Exchanged Ti-Beta Samples

Sample	$(r_0(\text{MeCN})/r_0(\text{MeOH}))$
Ti-beta	1.97
Na-Ti-beta	2.14

species in the presence of protic solvents, and taking into account the hydrophilic character of Ti-beta, it may be suggested that in nonprotic solvents a cyclic species is formed in which water, instead of alcohol, is the ligand of Ti as is represented below (species II).



Due to the lower donor properties of water with respect to alcohols, species II would have a higher electrophilic character than species I and consequently would have a higher intrinsic reactivity for oxidation. Thus, while this species would be the predominant species formed in Ti-beta in nonprotic solvents, its concentration will be negligible in protic solvents owing to the much higher alcohol/water ratio in the reaction medium, and then the catalytic activity will be mainly determined by the reactivity of species I, as it is the case of TS-1.

If this is so, the concentration of water, and therefore of species II, in the zeolite pores will be much lower in TS-1 than in Ti-beta owing to the higher hydrophilicity of the latter material. This would explain the lower reactivity of TS-1 observed at high water/alcohol ratios (8) and the beneficial effect of protic solvents (lower alcohols) on its reactivity (9). When we studied the reactivity of the reference EURO-TS-1 sample (20) for 1-hexene oxidation in methanol and acetonitrile under the same reaction conditions used for Ti-beta, the results obtained (Fig. 3) show

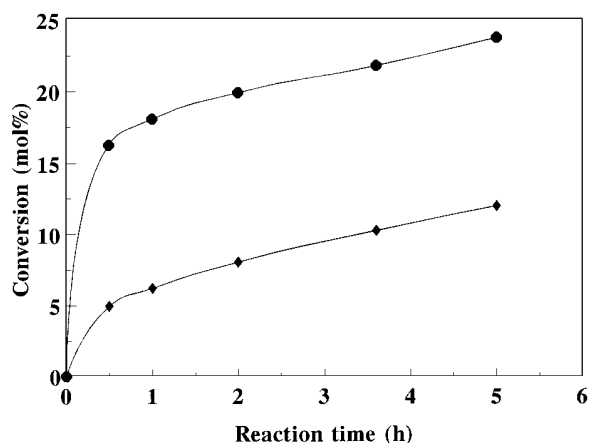


FIG. 3. Influence of solvent on the catalytic activity of the reference EURO-TS-1 sample for 1-hexene oxidation with H_2O_2 : (●) methanol, (◆) acetonitrile.

TABLE 3

Influence of the MeOH/MeCN Ratio in the Solvent Mixture on the Selectivity Features of Ti-Beta during 1-Hexene Oxidation with H₂O₂ at Similar 1-Hexene Conversion Levels

MeOH/MeCN ratio	Initial rate (mmol g ⁻¹ h ⁻¹)	1-Hexene conv. (mol%)	Epoxide select. (mol%)	H ₂ O ₂	
				Conv. (%)	Select. (%)
100/0	12.0	10.5	6.2	43	97
66/34	10.5	9.7	83.5	41	94
50/50	12.7	10.7	90.9	47	91
34/66	15.3	10.9	94.3	56	78
0/100	23.6	9.7	100	55	71

that TS-1 is more than three times more active in methanol than in acetonitrile, in agreement with the above hypothesis. Indeed, it has been shown (21) that silicalite absorbs about five times more methanol than water at 20 Torr. It is worth nothing here that Ti-beta is more active than TS-1 for 1-hexene oxidation when the reaction is carried out in acetonitrile as solvent.

The effect of the concentration of acetonitrile on the reactivity of Ti-beta has been studied by performing oxidation experiments within different methanol/acetonitrile mixtures. The initial reaction rate for 1-hexene oxidation increases only above 50% of MeCN in the solvent mixture (Table 3), which may indicate that below this value species I is the main species responsible for the catalytic activity, and only at lower concentrations of MeOH the competition of water with methanol to form the more active species II becomes significant.

Cyclohexanol oxidation. The initial reaction rates obtained during cyclohexanol oxidation in different solvents are shown in Fig. 4. As it was shown for 1-hexene oxidation,

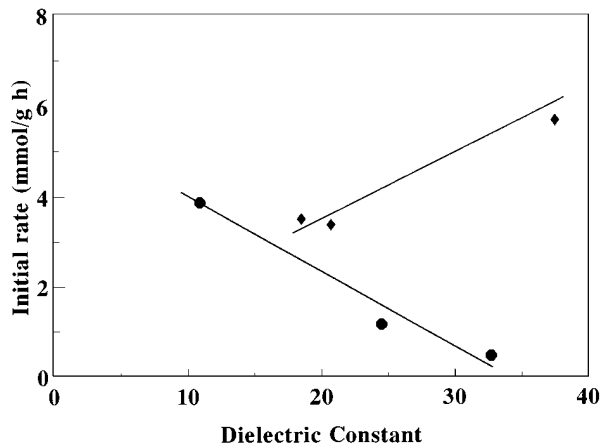
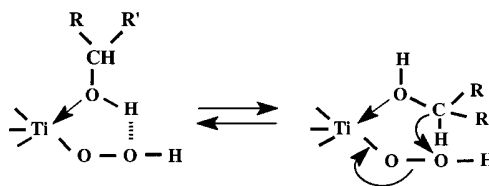


FIG. 4. Initial reaction rate for cyclohexanol oxidation on Ti-beta with H₂O₂ as a function of the polarity (dielectric constant) of protic (●) and aprotic (◆) solvents.

the activity increases with solvent polarity for the aprotic series, but in this case the opposite behavior is observed for the protic series.

In the case of alcohol oxidation, Maspero and Romano (11) have recently proposed the formation of the cyclic adducts (species I) to account for the selectivity and kinetic features of TS-1. However, and since the alcohol oxidation may involve the activation of a C-H bond, the authors suggested that the following rearrangement may occur before the oxygen transfer step (11).



SCHEME III

If one assumes that the species of Scheme III are indeed formed before the oxidation step, it becomes then clear that a competition between the alcohol substrate and protic solvents for adsorption on the Ti sites is established. This competition must be extended to the water molecules in the case of the hydrophilic Ti-beta catalyst. Competition between the alcohol substrate with protic solvents and water molecules would decrease the reactivity of the catalyst. Since the concentration of water is practically constant in our experiments when working with initial reaction rates, the amount of substrate molecules coordinated to Ti (and hence susceptible to be oxidized) will increase when decreasing the polarity of the protic solvent. This is in accordance with the reactivity trends presented in Fig. 4. The competition substrate/solvent for adsorption on the Ti sites would not occur in the case of aprotic solvents. Indeed, we did not observe appreciable changes in the initial reaction rate for cyclohexanol oxidation when the amount of acetonitrile in the reaction mixture is reduced to $\frac{1}{2}$ and $\frac{1}{4}$ of the initial amount. This would lead to higher reaction rates than when using protic solvents, and to increased reactivity as the solvent polarity increases due to the concentration effect, as is observed in Fig. 4.

Effect of water on the oxidation activity. From the above discussion, and since in the case of aprotic solvents the alcohol substrate will only compete with water for adsorption on the Ti sites, one would expect a lower reactivity as the concentration of water in the reaction medium increases. This has been checked by preparing a nearly water-free hydrogen peroxide solution in acetonitrile (8 wt% H₂O₂) and performing the oxidation experiments under the same conditions as those using the aqueous hydrogen peroxide solution. It was seen that the initial reaction rate for cyclohexanol oxidation in acetonitrile increases from 5.7 to 10.2 mmol g⁻¹ h⁻¹ and that for 1-hexene oxidation decreases

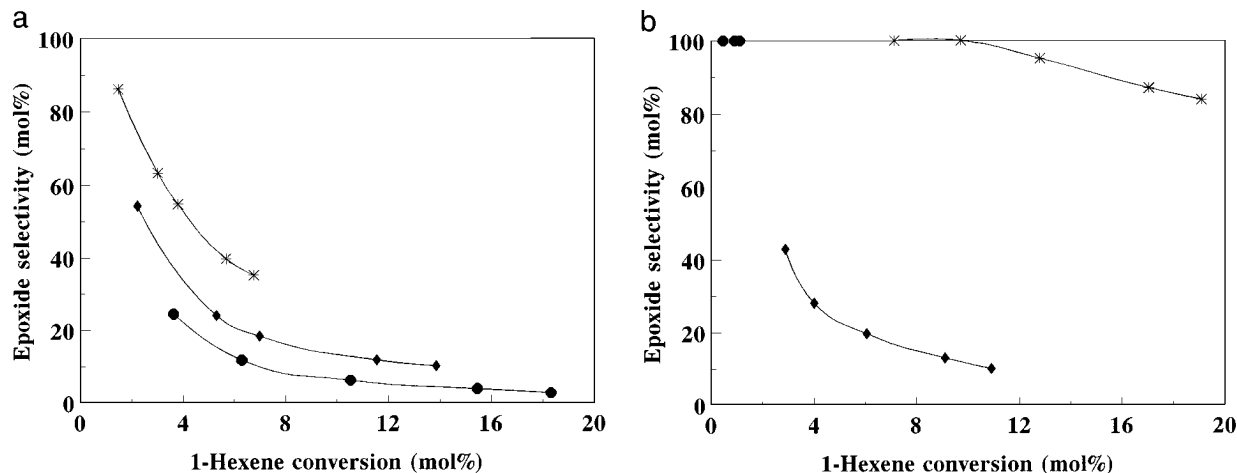


FIG. 5. Selectivity to the epoxide versus 1-hexene conversion for Ti-beta catalyst. (a) Protic solvents: (●) MeOH, (◆) EtOH, (*) *t*-BuOH. (b) Aprotic solvents: (●) MEK, (◆) acetone, (*) MeCN.

from 23.6 to 16.3 mmol g⁻¹ h⁻¹ when the H₂O₂/acetonitrile solution is used instead of the H₂O₂/water solution. In the case of 1-hexene oxidation water does not compete with the substrate for coordination on the Ti sites (see Scheme II), and then the higher the water content, the higher the concentration of species II would be, and consequently the oxidation activity of Ti-beta in MeCN would increase, in agreement with the experimental results.

On the other hand, we did not see appreciable changes in the reaction rate for 1-hexene oxidation in methanol when increasing the MeOH: water ratio from 93:7 to 98:2 (results not shown). This is probably due to the much higher concentration of MeOH in these experiments, which would determine that species I are the predominant species under these conditions. In these experiments we avoided the use of higher concentrations of water because of the formation of two liquid phases, thus making a direct comparison of the reaction rates more difficult because of the contribution of mass transfer effects.

Then, it can be concluded that from the point of view of the intrinsic chemical reactivity of the Ti-beta catalyst, the most polar aprotic solvent used (acetonitrile) is the best solvent for both olefin and alcohol oxidations with H₂O₂ under single liquid phase conditions. This clearly evidences substantial differences with respect to the catalytic features of TS-1 for which methanol, and in general lower alcohols, are the solvents of choice for these reactions. The different catalytic behavior of Ti-beta and TS-1 can be related to the different hydrophobic/hydrophilic character of both catalysts, and this must be taken into account for the optimization of each catalytic system during the oxidation of different substrates.

Influence of Solvent on the Selectivity Features of Ti-Beta

Besides the differences in reactivity discussed above, the nature of the solvent also has a large influence on prod-

uct selectivity. Thus, the selectivity to the epoxide during 1-hexene oxidation with H₂O₂ at different 1-hexene conversion levels is given in Figs. 5a and 5b for the protic and aprotic solvents, respectively. In the first case, the epoxide ring is selectively opened by the water and alcohol molecules forming the glycols and alkyl glycol ethers, respectively. This reaction is thought to be catalyzed in the case of the Ti-beta zeolite, by Brønsted acid sites associated to framework aluminum atoms present in the material. The rate of alcoholysis decreases in the order: MeOH > EtOH > *t*-BuOH (Table 4), which is the same trend observed for TS-1 (8). Since there would not be large differences in the nucleophilic character of these alcohols, the alcoholysis trend observed in Fig. 5a may be explained by a higher steric hindrance as the size of the alcohol increases.

The selectivity to the epoxide when using aprotic solvents has been represented in Fig. 5b. The selectivity was 100%

TABLE 4
Influence of Solvent on Conversion and Selectivity Obtained after 2 h during the Oxidation of 1-Hexene on Ti-Beta^a

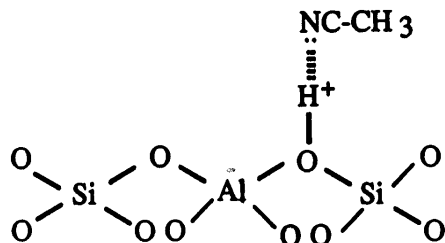
Solvent	1-Hexene Conv. (mol%)	Selectivity (mol%)			H ₂ O ₂	
		Epoxide	Glycols	Others	Conv. (%)	Select. (%)
MeOH	10.5	6.2	0.3	93.5 ^b	43	97
EtOH	6.7	18.4	3.1	78.5 ^b	32	87
<i>t</i> -BuOH	3.8	54.8	6.2	39.0 ^b	26	58
MeCN	12.8	95.1	4.9	—	70	73
MeCOMe	6.1	19.7	2.5	77.8 ^c	31	78
MEK	1.2	100	—	—	18	26

^a Reaction conditions: 50°C, 33 mmol 1-hexene, 0.8 g H₂O₂ (35 wt% in water), 23.6 g solvent, 0.2 g catalyst.

^b Alkyl glycol ethers.

^c Cyclic ketal formed by reaction of acetone with the diols.

in acetonitrile up to ca. 10% 1-hexene conversion (ca. 40% of the maximum attainable), and then slightly decreased at higher conversions with formation of glycols. The very low rate of hydrolysis obtained in acetonitrile can be ascribed to the poisoning of the strong framework Brønsted acid sites by the weak basic acetonitrile molecules, as represented below.



Unlike the activity results, the changes in selectivity to the epoxide in the experiments using different MeOH/MeCN mixtures can be readily observed from low concentrations of MeCN (Table 3). The epoxide selectivity drastically increases from 6% in pure methanol to 83% (Compared at the same 1-hexene conversion level) in the 34 wt% acetonitrile solvent mixture. A further increase of the MeCN concentration leads to a continuous increase of the epoxide selectivity. On the contrary, the selectivity based on H₂O₂ continuously decreases from 97 to 71% as the concentration of acetonitrile increases, indicating that a higher H₂O₂ decomposition occurs in this latter solvent. The effect of solvent on the extent of hydrogen peroxide decomposition will be discussed later.

Coming back to the selectivity results obtained for the aprotic solvents (Fig. 5b), a relatively high rate of hydrolysis is observed in the presence of acetone. In the latter case the major product is a cyclic ketal formed by the acid-catalyzed reaction of the solvent with the diols formed upon hydrolysis of the epoxide ring:

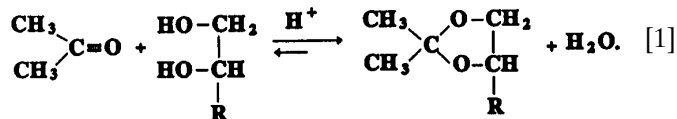


Table 4 shows the influence of solvent on the selectivity to the different reaction products obtained after 2 h on Ti-beta during 1-hexene oxidation. Hydrogen peroxide conversions and selectivities based on H₂O₂ are also given in Table 4. It is seen that decomposition of H₂O₂ in protic solvents increases in the order MeOH < EtOH < *t*-BuOH, while it is similar for acetonitrile and acetone, and much lower for MEK in the case of aprotic solvents. In general, the rate of H₂O₂ decomposition increases when the oxidation rate decreases, indicating that both reactions probably take place on the same Ti sites of the Ti-beta catalyst.

On the other hand, the selectivity features of Ti-beta in the different solvents during the oxidation of cyclohexanol

TABLE 5

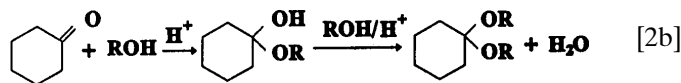
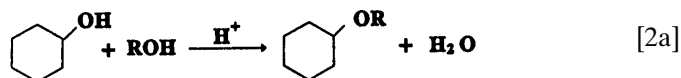
Influence of Solvent on Conversion and Selectivities Obtained after 5 h during the Oxidation of Cyclohexanol on Ti-Beta^a

Solvent	Alcohol conv. (mol%)	Selectivity ^b (mol%)				H ₂ O ₂ conv. (%)	H ₂ O ₂ select. (%)
		1	2	3	4		
MeOH	2.8	34.8	—	42.2	23.0	36	31
EtOH	3.3	83.5	—	6.1	10.4	28	47
<i>t</i> -BuOH	6.9	85.8	11.1	3.1	—	58	42
MeCN	9.8	100	—	—	—	82	48
MeCOMe	3.6	100	—	—	—	22	65
MEK	5.5	100	—	—	—	35	63

^a Reaction conditions: 65°C, 33 mmol alcohol, 0.8 g H₂O₂ (35 wt% in water), 23.6 g solvent, 0.2 g catalyst.

^b Reaction products (see text): 1, cyclohexanone; 2, cyclohexyl alkyl ether; 3, hemiketal; 4, ketal.

are presented in Table 5. In this case, the cyclohexanone selectivity was 100% in the aprotic solvents, whereas it was lower in the alcoholic solutions due to the occurrence of two acid-catalyzed secondary reactions between cyclohexanol (reaction [2a]) or cyclohexanone (reaction [2b]) with the solvent ROH. In the first case a cyclohexyl alkyl ether is formed, while reaction [2b] leads first to the formation of a hemiketal and then to a ketal upon further reaction with a solvent molecule:



Reactions [2a] and [2b] occur to a higher extent in the presence of MeOH as solvent, probably because of the higher steric constraints in the case of EtOH and *t*-BuOH. The extent of these undesired secondary reactions is strongly reduced when the Na-exchanged Ti-beta sample is used as catalyst. Indeed, the selectivity to the ketone was 100% with Na-Ti-beta in *t*-BuOH and slightly lower in EtOH and MeOH.

Decomposition of Hydrogen Peroxide in Different Solvents

As was seen in Table 4, the selectivity based on H₂O₂ during 1-hexene oxidation on the different solvents increases, in general, with increasing oxidation rate, except for acetonitrile, which gives a relatively low H₂O₂ selectivity in spite of its high oxidation reactivity (Figs. 2 and 4). Furthermore, the rates of H₂O₂ decomposition are generally higher for cyclohexanol than for 1-hexene oxidation, which could be due to the higher reaction temperature used in the former case. Indeed, it has been shown that the rate

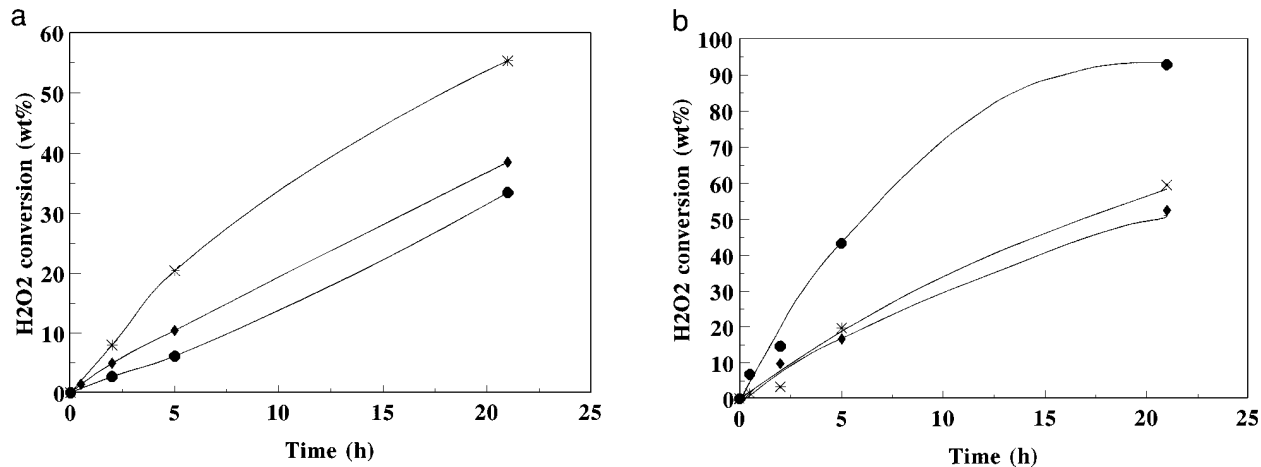


FIG. 6. Decomposition of H₂O₂ at 50°C on Ti-beta in the absence of substrate in protic (a) and aprotic (b) solvents. Same symbols as in Fig. 5.

of hydrogen peroxide decomposition on the TS-1 catalyst rapidly increases above 50°C (7).

In order to study the influence of reaction temperature and nature of the solvent on the rate of H₂O₂ decomposition, we have performed blank experiments (without substrate) under the same experimental conditions used for 1-hexene (50°C) and cyclohexanol (65°C) oxidation. Under these conditions no solvent oxidation was observed, except in the case of ethanol, which was oxidized in a 0.19 mol% after 5 h at 50°C. This represented ca. 10% of the initial H₂O₂ consumed for solvent oxidation. Moreover, the oxidation of ethanol was lower during the 1-hexene and cyclohexanol oxidation experiments than it was in the absence of any substrate.

The H₂O₂ conversion in different solvents and in the absence of substrate as a function of reaction time at 50 and 65°C is presented in Figs. 6 and 7, respectively. At

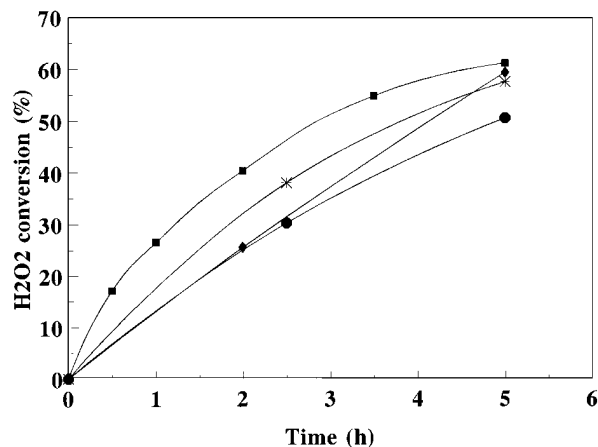


FIG. 7. Influence of solvent on the decomposition of H₂O₂ at 65°C on Ti-beta in the absence of substrate: (●) MeOH, (◆) *t*-BuOH, (×) MEK, (■) MeCN.

50°C the hydrogen peroxide decomposition increases in the order MeOH < EtOH < *t*-BuOH for the protic solvents (Fig. 6a) and MeCOMe < MEK < MeCN for the aprotic solvents (Fig. 6b). In general, lower decomposition rates are observed for the protic solvents, which is in agreement with the higher H₂O₂ selectivities obtained with MeOH and EtOH during 1-hexene oxidation (Table 4). Since the selectivity based on H₂O₂ is the net result of two competing reactions, i.e., substrate oxidation and H₂O₂ decomposition, it increases with increasing oxidation rate. This would explain the relatively high (ca. 70%) H₂O₂ selectivity obtained in acetonitrile, in spite of its high activity for hydrogen peroxide decomposition (Fig. 6b) in the absence of 1-hexene. Similarly, the very low oxidation activity observed in MEK accounts for the low H₂O₂ selectivity obtained in this solvent, although its tendency to decompose H₂O₂ without substrate is lower than that in acetonitrile and similar to that of EtOH and *t*-BuOH.

At 65°C, which is the temperature used for cyclohexanol oxidation, the rates for H₂O₂ decomposition (Fig. 7) are much higher for all the solvents than those observed at 50°C (Fig. 6). Moreover, although the decomposition activity follows the same trends obtained at the lower temperature, i.e., MeCN > MEK > *t*-BuOH > MeOH, the differences between the solvents are much lower at 65°C, which is due to the higher contribution of thermal decomposition of H₂O₂ at the higher temperature. This is also in accordance with the higher decomposition rates observed for TS-1 above 50°C (7) and with H₂O₂ selectivities generally obtained during the oxidation of cyclohexanol being lower than those obtained during 1-hexene oxidation. In the former case, the very low selectivity obtained in MeOH can be ascribed to the very low oxidation rate observed in this solvent, and the lower selectivity obtained in acetonitrile, as compared to the other aprotic solvents, may be due to its higher decomposition rate.

The higher decomposition rates obtained for the aprotic solvents may be related with a higher decomposition activity of species II, which has been tentatively proposed here as the main species formed in Ti-beta and nonprotic solvents. Then, in the absence of substrate, the H₂O₂ decomposition rate could be related with the concentration of species II and therefore will increase with the polarity of the aprotic solvents and will decrease when increasing the polarity of the protic solvents due, in this latter case, to the competition of alcohol and water. This would explain the decomposition trends observed in Figs. 6 and 7.

CONCLUSIONS

It has been shown in this work that the reactivity of the large pore Ti-beta catalyst for the selective oxidation of olefins and alcohols with hydrogen peroxide under single liquid phase conditions depends on both the polarity and the protic/aprotic nature of the solvent used. Thus, the reactivity of Ti-beta for both 1-hexene and cyclohexanol oxidation was higher in the most polar aprotic acetonitrile solvent. These results are in contrast with those reported for the medium pore TS-1 catalyst, for which protic solvents, and especially methanol, are the solvents of choice. Indeed, we have shown that the reactivity of TS-1 for 1-hexene oxidation is more than three times higher in MeOH than in MeCN. This opposite behavior can be related with the different hydrophobic/hydrophilic characteristics of both materials. It is tentatively suggested that in the presence of nonprotic solvents the active species is a cyclic species similar to that proposed for explaining the higher reactivity of TS-1 in protic solvents, but in which a water molecule is coordinating the Ti atoms (denoted as species II in this work), instead of species I in which an alcohol molecule is the ligand of Ti. Due to the lower donor properties of water, species II would have a higher electrophilic character, and therefore a higher intrinsic oxidation activity than species I, and could be stabilized in the hydrophilic pores of Ti-beta, while it could be hardly formed in the hydrophobic pores of TS-1.

Besides the influence on catalyst reactivity, the nature of the solvent has been shown to have a large influence on product selectivity. Thus, higher selectivities to the epoxide and ketone during 1-hexene and cyclohexanol oxidation, respectively, were obtained when using acetonitrile as solvent. This can be explained by the poisoning of the strong Brønsted acid sites present in the Ti-beta catalyst by the basic acetonitrile molecules, thus decreasing the extent of acid-catalyzed secondary reactions.

Finally, the tendency to decompose H₂O₂ was seen to be higher for the aprotic solvents, which was reflected in lower selectivities based on the H₂O₂ consumed. The decomposition trends observed could be tentatively explained by a

higher intrinsic decomposition activity of species II than species I.

Nevertheless, the results presented in this work clearly evidence that, owing to the different hydrophilic/hydrophobic character of Ti-beta and TS-1, both catalysts may present different reactivity trends depending on the nature of the solvent used, but also on the hydrophilic/hydrophobic characteristics of the substrates to be oxidized. This may lead to completely different optimum conditions operating for both catalysts, which can be of great importance for possible industrial applications.

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