Journal of Catalysis **204,** 146–156 (2001)
doi:10.1006/jcat.2001.3355, available online at http://www.idealibrary.com on IDEAL®

Effect of the Reaction Conditions on the Epoxidation of Alkenes with Hydrogen Peroxide Catalyzed by Silica-Supported Titanium Derivatives

José M. Fraile, José I. García, José A. Mayoral,[1] and Eugenio Vispe

Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C., E-50009 Zaragoza, Spain

Received April 9, 2001; revised July 9, 2001; accepted July 13, 2001

Silica-supported titanium catalysts are active in the epoxidation of cyclohexene with diluted hydrogen peroxide at 80°C. At low H_2O_2/Ti ratio the contribution of the direct mechanism of epoxidation is important, around 40% of the productive H_2O_2 conversion and 60% of the epoxidation reaction. However, the increase in H_2O_2/Ti ratio modifies these results. The contribution of the direct epoxidation to H_2O_2 conversion is reduced to 20–30%, whereas contribution to epoxidation is kept in the range 40–60%. Neither the silanization of the silica surface nor the substitution of the isopropoxy groups by tartaric acid improves the behavior of the solid in these conditions. However, the simultaneous variation in hydrophilic character of the surface and titanium environment increases the contribution of the direct epoxidation. In contrast, the increase in H_2O_2/Ti ratio reduces the epoxide hydrolysis. The catalysts lose some titanium after reaction, but in general they show higher stability than closely related solids. The activity for direct and radical contributions changes after recovering, showing the important change in nature of the catalytic sites, which are not easily regenerated by extensive washing with different solvents. In any case, with cyclooctene, an alkene that does not form radicals, the activity for direct epoxidation shows a decline in every recycling but final turnover numbers are similar in the first three runs, showing high stability of the titanium on the solid. © 2001 Academic Press

Key Words: **heterogeneous titanium catalysts; epoxidation; allylic oxidation; hydrogen peroxide.**

INTRODUCTION

Oxidations are among the most important reactions in the chemical industry and considerable efforts are directed to the development of heterogeneous catalysts for this kind of reaction. In particular, the epoxidation of alkenes with diluted hydrogen peroxide is one of the main goals in this field.

After the success of titanium silicalites to catalyze the epoxidation of small linear olefins with diluted hydrogen peroxide (1), many attempts have been made to extend the scope of the reaction to bulkier alkenes. Thus, the incorporation of titanium atoms in the structure of a solid has been applied to zeolites with larger pores (2), crystalline mesoporous silicas (3), and amorphous xerogels (4). However, in spite of good activity with alkyl hydroperoxides, the catalytic performance of all these solids with hydrogen peroxide is far from that of TS-1. Recently, titanium was also incorporated in the K10-like delaminated structure of the ITQ-6 silicate (5), showing activity in the epoxidation with hydrogen peroxide.

The good results obtained with TS-1 have been attributed to the hydrophobic character of this zeolite (6), which has been recently confirmed by quantitative sorption experiments (7). Following this idea, the substitution of the hydrophilic surface silanol groups by more hydrophobic fluoride (8), trimethylsiloxy (9), alkyl (10), or aryl groups (11) has shown a positive effect on the activity with hydrogen peroxide.

Another approach is the preparation of silica-supported titanium materials, first described by Shell (12). More recently, the preparation of this kind of material by treatment of silica with $Ti(O^iPr)_4$ (13), TiF_4 (14) or tetraneopentyltitanium (15) has been described. The same strategy was also applied to mesoporous crystalline silicas (16), dendrimer-based xerogels (17), and elastomeric polysiloxanes (18). A highly dispersed titanium-on-silica catalyst was prepared by ion beam implantation (19). Although this kind of catalyst had been described as ineffective with hydrogen peroxide, recent work has demonstrated that the main problem is not the activity but the stability of the supported titanium species (14, 15). We recently published our first results in the epoxidation of cyclohexene with aqueous hydrogen peroxide using $Ti(O^iPr)_4$ supported on silica (20) and other authors have described the epoxidation with water-free hydrogen peroxide (21). This kind of catalyst seems to be more stable than other related catalysts given the low leaching level and the truly heterogeneous character of the epoxidation reaction (20). Moreover, the performance of this

---

[1] To whom correspondence should be addressed. Fax: +34 976 76 20 77. E-mail: mayoral@posta.unizar.es.

0021-9517/01 $35.00

catalyst can be modulated by the exchange of the isopropoxy groups by other ligands.

However, this system has some limitations, mainly the need for a high alkene/oxidant ratio to obtain high yield and moderate epoxidation/allylic oxidation selectivity. In our previous work (20), the use of the same H_2O_2/catalyst mass ratio with differently loaded solids (0.17 to 1.14 mmol of Ti g^{-1}) meant that different H_2O_2/Ti ratios were used. Under those conditions, highly loaded catalysts led to very fast reactions but low TON, whereas catalysts with low loading gave rise to slower reactions and higher TON. However, these results must be ascribed to the difference in H_2O_2/Ti ratio and it was very difficult to compare the intrinsic activity of the sites in the different catalysts. Now we have taken into account this problem and we present in this paper deeper insight into the effect of the nature of the supported species and the reaction conditions on the stability and the catalytic performance of this kind of catalyst.

METHODS

Preparation of the Catalysts

All the silica-based solids were dried at 140°C under vacuum for 12 h prior to any treatment or use as catalysts.

Si–Ti($\mathrm{O^iPr}$) was prepared by treatment of silica (Merck 60) with $\mathrm{Ti(O^iPr)_4}$ in toluene under reflux as described in Ref. (13). Water was carefully excluded to prevent the formation of titania particles. Si–Ti($\mathrm{O^iPr}$)(0.2) was prepared in the same way but only 0.3 mmol of $\mathrm{Ti(O^iPr)_4}$ per g of silica was used.

Si–Ti(TA) and Si–Ti(TA)(0.2) were prepared by treatment of Si–Ti($\mathrm{O^iPr}$) and Si–Ti($\mathrm{O^iPr}$)(0.2), respectively (1 g), with L-tartaric acid (1.5 and 0.45 mmol, respectively) in anhydrous butyl acetate (25 mL) under reflux in an Ar atmosphere for 6 h. Then, 15 mL of solution was distilled off and the content of isopropanol was analyzed by gas chromatography. The reaction mixture was cooled at room temperature and the solids were separated by filtration, washed with anhydrous butyl acetate and dichloromethane, and dried under vacuum.

Si(ec) and Si–Ti($\mathrm{O^iPr}$)(ec) were prepared by treatment of silica or Si–Ti($\mathrm{O^iPr}$) (5 g) with hexamethyldisilazane (2.5 mL, 11.8 mmol) in anhydrous toluene (15 mL) under reflux in an Ar atmosphere for 1 h. The solid was filtered, washed with ethanol, water, ethanol, and ether, and dried under vacuum. Si(ec)–Ti($\mathrm{O^iPr}$) was prepared by treatment of Si(ec) (5 g) with $\mathrm{Ti(O^iPr)_4}$ (1.5 mmol) in anhydrous toluene (25 mL) under reflux in an Ar atmosphere for 48 h (13). Si(ec)–Ti(TA) was prepared by treatment of Si(ec)–Ti($\mathrm{O^iPr}$) (1 g) with L-tartaric acid (0.5 mmol) as described above.

TABLE 1

Analyses of the Catalysts

Catalyst	Run	C (mmol/g)	Ti (mmol/g)	C/Ti
Si–Ti($\mathrm{O^iPr}$)	0	3.46	1.07	3.24
	3	6.29	0.96	6.55
	3[a]	6.04	0.74	8.16
Si–Ti($\mathrm{O^iPr}$)(0.2)	0	2.76	0.24	11.25
	3	5.66	0.13	43.53
Si(ec)–Ti($\mathrm{O^iPr}$)[b]	0	4.16	0.17	24.47[c]
	3	7.02	0.15	46.80
Si–Ti($\mathrm{O^iPr}$)(ec)[d]	0	5.38	1.01	5.33
	2	7.55	0.98	7.70
Si–Ti(TA)	0	5.09	0.99	5.14
	3	5.24	0.98	5.35
	3[a]	7.22	0.56	12.90
Si–Ti(TA)(0.2)	0	3.60	0.22	16.36
	3	4.77	0.16	29.81
	3[e]	5.16	0.20	25.79
Si(ec)–Ti(TA)	0	4.63	0.20	23.15[f]
	3	5.13	0.15	34.22

[a] After three reactions with H_2O_2/Ti ∼ 60.

[b] Prepared from Si(ec) + $\mathrm{Ti(O^iPr)_4}$.

[c] Taking into account the carbon content of Si(ec) (3.25 mmol/g), C($\mathrm{^iPrO}$)/Ti = 5.35.

[d] Prepared from Si–Ti($\mathrm{O^iPr}$) + hexamethyldisilazane.

[e] After three reactions with H_2O_2/Ti ∼ 12.

[f] Taking into account the carbon content of Si(ec), C(TA)/Ti = 6.90.

Characterization of the Catalysts

Titanium analyses (Table 1) were carried out by plasma emission spectroscopy on a Perkin–Elmer Plasma 40 emission spectrometer. Carbon analyses (Table 1) were carried out in Perkin–Elmer 2400 elemental analyzer. Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer. Self-supported or KBr wafers were treated under vacuum ($<10^{-5}$ Torr) at 140°C in a cell equipped with NaCl windows.

Catalytic Tests

All the catalysts were dried at 140°C under vacuum for 12 h prior to use. The catalyst (200 mg) was added to a solution of cyclohexene or cyclooctene (5 mL, 50 mmol), H_2O_2 (0.28 mL, 30%, 2.5 mmol), and ethylene glycol dimethyl ether (1 mL, internal standard) in *tert*-butanol (5 mL). The reaction mixture was heated at 80°C for 24 h and monitored by GC (20). After 24 h the catalyst was filtered, washed with dichloromethane (5 × 5 mL), dried under vacuum, and reused in the same conditions. The total conversion of H_2O_2 was confirmed by iodometric titration in the final solution. In some cases (see Table 2) the amount of catalyst was 5 times higher or lower to achieve similar H_2O_2/Ti ratios. In some cases the reaction was carried out under an Ar atmosphere.

TABLE 2

Productive Conversion of H_2O_2 to Oxidation Products of Cyclohexene

Entry	Catalyst	Run	H_2O_2/Ti[a]	% conv. (30 min)	TOF (h^{-1})[b]	TON[c]	% nonradical mechanism[d]
1	SiO_2^e	1	—	3.2	—	—	—
2	Si–Ti(O^{i}Pr)	1	11.7	61.4	14.4	8.7	42
3		3	13.0	29.5	7.7	4.4	2
4	Si–Ti(O^{i}Pr)(ec)	1	12.4	59.8	14.8	15.0	12
5		2	12.8	60.6	15.5	14.6	9
6	Si–Ti(TA)	1	12.6	55.7	14.0	12.3	39
7		3	12.8	51.6	13.2	10.9	26
8	Si–Ti(TA)(0.2)[f]	1	11.4	62.4	14.2	12.0	41
9		3	12.5	28.7	7.2	17.5	6
10	Si–Ti(O^{i}Pr)[f]	1	60.0	46.6	55.9	44.5	23
11		3	86.7	29.5	51.2	65.6	0
12	Si–Ti(O^{i}Pr)(0.2)	1	52.1	63.7	66.4	59.9	21
13		3	96.1	57.4	110.4	119.5	5
14	Si(ec)–Ti(O^{i}Pr)	1	73.5	63.9	94.0	85.7	10
15		3	83.3	50.1	83.5	113.7	0
16	Si–Ti(TA)[f]	1	63.0	28.3	35.6	57.5	28
17		3	111.6	43.2	96.4	120.2	11
18	Si–Ti(TA)(0.2)	1	56.8	40.8	46.4	61.7	22
19		3	78.1	40.7	63.6	92.3	9
20	Si(ec)–Ti(TA)	1	62.5	41.9	52.4	53.3	45
21		3	83.3	41.9	58.0	116.1	5

[a] In the 3rd run the ratio was calculated with the titanium analysis after the reaction.

[b] Calculated with the data of conversion after 30 min.

[c] mmol of H_2O_2 converted/mmol of Ti at the end of the reaction.

[d] Contribution of the direct epoxidation of cyclohexene with H_2O_2 to the total productive conversion of H_2O_2.

[e] The same amount of silica (200 mg) as used in the reactions with titanium catalysts.

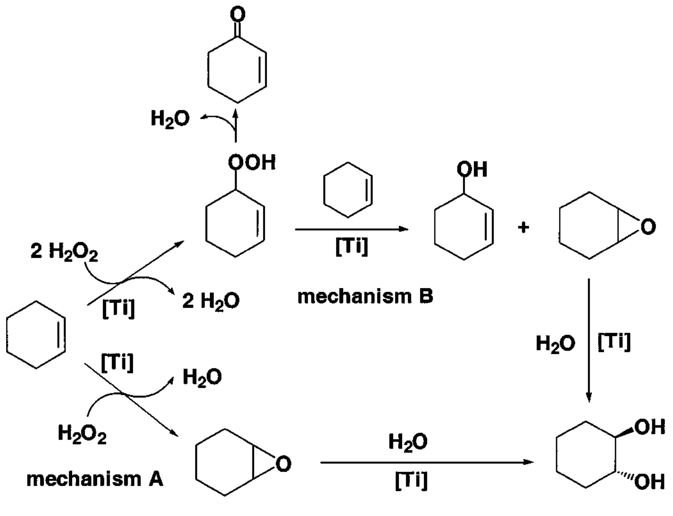
[f] The amount of catalyst and reagents were adjusted to obtain the reported H_2O_2/Ti ratio without modification of the concentrations.

RESULTS AND DISCUSSION

Effect of Catalyst and Reaction Conditions on the Conversion of H_2O_2

The first question about the effect of titanium catalysts in the epoxidation is their role in the productive conversion of hydrogen peroxide. If we consider the stoichiometry of the different oxidation reactions (Scheme 1), each cyclohexenyl hydroperoxide (**chhp**) molecule requires the conversion of two molecules of hydrogen peroxide in the radical pathway. Indications of the participation of this mechanism have been obtained by the effect of hydroquinone on the selectivity (20). Given that one molecule of 2-cyclohexenol (**chexol**) and one of cyclohexene oxide (**epox**) are produced from each molecule of **chhp**, only one H_2O_2 molecule is required for each. 2-Cyclohexenone was not detected by NMR spectroscopy in the crude after reaction, so all the ketone detected by gas chromatography comes from the decomposition of **chhp**. The formation of **epox** by direct epoxidation requires only one molecule of H_2O_2. As *trans*-1,2-cyclohexanediol (**diol**) comes directly from **epox** hydrolysis, the consumption of hydrogen peroxide is again one molecule per molecule of **diol**. So the productive conversion of H_2O_2 was calculated as **epox** + **diol** + **chexol** + 2 × **chhp**.

We tried to adjust the Ti content of the solids (see Table 1) and the reaction conditions to have similar H_2O_2/Ti ratios and study the effect of end-capping, change of titanium ligand, and dispersion of titanium. The main results are collected in Table 2 and Fig. 1. As can be seen, the reaction is



SCHEME 1

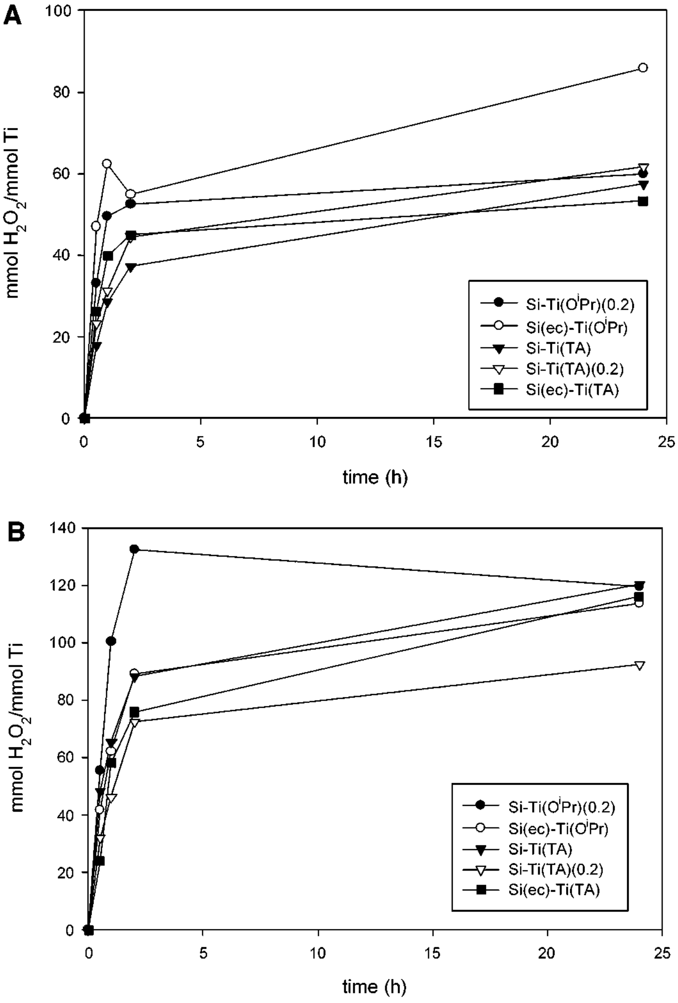


FIG. 1. Conversion of H_2O_2 (mmol/mmol of Ti) with (A) fresh and (B) recovered catalysts.

fast and most of the hydrogen peroxide is consumed in the first 2–3 h.

When H_2O_2/Ti ratio is low (*ca.* 12) there are no differences between the fresh catalysts (entries 2, 4, 6, and 8) and the TOF is nearly the same in all cases. It is noteworthy that the high conversion is due to the titanium centers, given that the same amount of silica gives rise to a much lower conversion (entry 1). The relatively high amount of titanium accounts for the very fast reaction, and a much higher H_2O_2/Ti ratio was then used (entries 10–21). In these new conditions important differences were detected.

The change of ligand from isopropoxy to tartaric acid groups reduces the activity (entries 10, 12, 16, and 18), probably due to the presence of coordinating carboxylic groups, which makes more difficult the approach of hydrogen peroxide to the titanium centers. This result shows an opposite effect to that reported for polar groups present in titania–silica xerogels in the epoxidation with TBHP (22). The possible unproductive conversion of H_2O_2 can be discarded by the similar final TON values obtained with both catalysts. A higher dispersion of Ti has a positive effect on the activity, showing that some interactions between the sites may exist in the case of solids with 1 mmol of Ti/g. In fact, high dispersion is considered as one of the most important factors for the high efficiency of the titanium supported by ion beam implantation (19).

Finally, the silanization of the silanol groups has a positive influence on the catalytic activity (entries 12, 14, 18, and 20). This effect is more evident for the catalysts with isopropoxy groups, where the activity per site is significantly higher in the silanized catalyst ($\mathrm{TOF} = 94\ \mathrm{h}^{-1}$) than in the nonsilanized one ($\mathrm{TOF} = 66\ \mathrm{h}^{-1}$). A similar effect was observed for Ti–MCM-41 (9) and organically modified mixed oxides (10, 11). However, related centers supported on silsesquioxane models show the reversed behavior for the epoxidation with alkyl hydroperoxides (23), which can be attributed to steric problems.

The catalysts were reused twice and the results of the third reaction are also gathered in Table 2. In these cases the H_2O_2/Ti ratios are not so accurate as in the first reaction, given that the titanium analysis was carried out after the reaction, but the results are in any case illustrative of the catalytic activity. All the catalysts lose part of the titanium (Table 1), between 12 and 46% of the initial amount, which means an average of 4 to 15% in each reaction. However, the real loss is lower than that indicated by the analysis because of the gain in carbon content due to adsorption of products or coke. A simple calculation shows that between 350 and 1870 molecules of H_2O_2 are required to leach an atom of Ti, depending on the catalyst, and these figures are 3 times higher if we consider H_2O_2 and water altogether. Another important point is the contribution of the leached species to the reaction results. Some experiments of filtration in the reaction conditions had shown the truly heterogeneous character of Si–Ti(O^{i}Pr) using low H_2O_2/Ti ratio (20). This kind of experiment was repeated with high H_2O_2/Ti ratio and again no conversion was detected in the filtrate, demonstrating that the leached titanium species are not active, either for H_2O_2 conversion or for cyclohexene epoxidation.

In spite of the loss of titanium, in the recycled catalysts the remaining centers present similar activity to those in the freshly prepared ones. Even in some cases, the centers in the recovered catalysts are clearly more active, as happens in Si–Ti(O^{i}Pr)(0.2) or Si–Ti(TA). Then, low-active species seem to be leached from the surface, as demonstrated in the experiment of filtration in the reaction conditions with Si–Ti(O^{i}Pr) (20). The modification of the active sites, with loss or exchange of the organic ligands, may also account for this change in catalytic activity.

Consumption of H_2O_2 by Different Mechanisms

As discussed above, the hydrogen peroxide can be consumed either in the direct epoxidation of cyclohexene or in the radical pathway by generation of **chhp** and subsequent use of this hydroperoxide in the epoxidation reaction. So an estimation of the consumption of hydrogen peroxide through both mechanisms can be made by

$$\text{conv (radical)} = 2 \times \mathbf{chhp} + 2 \times \mathbf{chexol}$$

$$\text{conv (direct)} = \mathbf{epox} + \mathbf{diol} - \mathbf{chexol}.$$

In some cases the data at short reaction times do not fit well, probably due to the adsorption of some of the products, but a general picture can be drawn from Fig. 2. The contribution of the direct mechanism of epoxidation to the final conversion of H_2O_2 is shown in Table 2. At low H_2O_2/Ti ratio, the final contribution of direct epoxidation is around 40% of the H_2O_2 conversion. The only exception is Si–Ti(O^{i}Pr)(ec), with a contribution of only 12%. This behavior is completely different in the third reaction, where a much lower amount of H_2O_2 is converted through the direct pathway.

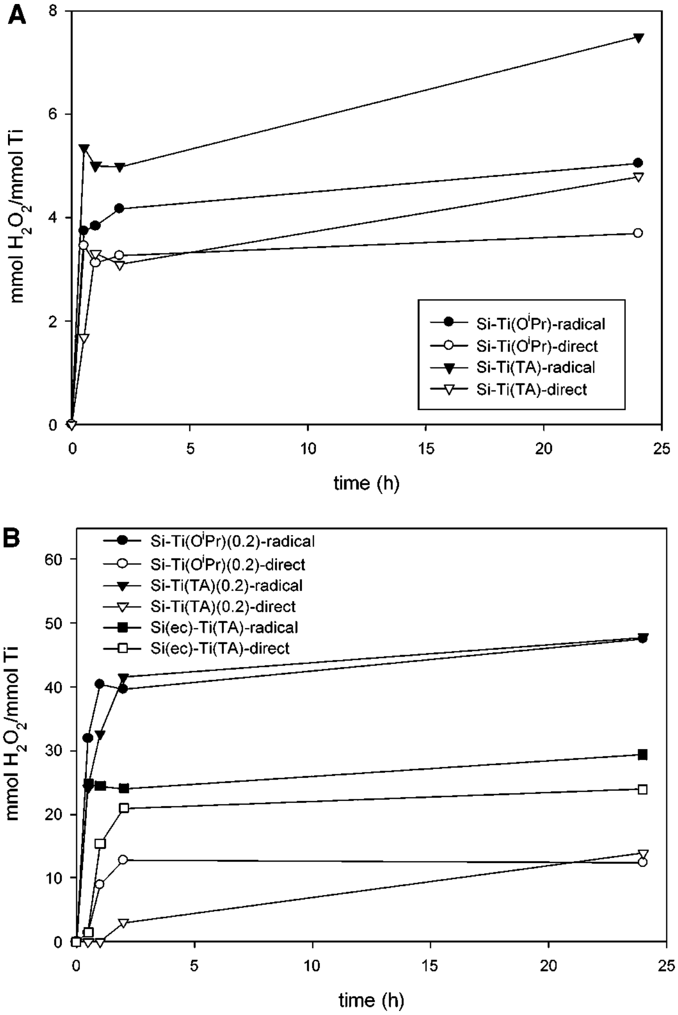


FIG. 2. Conversion of H_2O_2 (mmol/mmol of Ti) through the radical (filled symbols) and the direct (open symbols) mechanisms: (A) $H_2O_2/\text{Ti} = 12$ and (B) $H_2O_2/\text{Ti} = 60$–80.

On the other hand, in the reactions with a higher H_2O_2/Ti ratio, the contribution of the radical mechanism is in general much more important. As expected, a decrease in the catalyst concentration has a stronger effect on the nonradical direct epoxidation than on the radical conversion of hydrogen peroxide. This effect is reflected in the final results, where the contribution of the direct epoxidation is reduced to values ranging between 20 and 30%. The only exception is the Si(ec)–Ti(TA) catalyst, which leads to a similar relative result irrespective of the conditions. However, this good behavior is not maintained after recovery and the contribution of the direct epoxidation are again lower, around only 10%.

In any case, the increase in the hydrophobic character of the surface has not the positive effect on the C=C attack described by Kochkar and Figueras for the xerogels (11) and by Bu and Rhee for Ti–MCM-41 (9d).

Epoxidation through Both Mechanisms

Although we have analyzed in the preceding part the consumption of H_2O_2 through both mechanisms, the primary product of the radical pathway is **chhp**. Therefore, the epoxide is produced in a second reaction, which is also titanium-catalyzed. The analysis of the composition of the reaction mixtures shows the relative activity of the different catalysts for the epoxidation of cyclohexene with the two oxidants present in the medium, hydrogen peroxide and **chhp** (Table 3).

The reactions carried out with low excess of H_2O_2 (entries 1–4) show an important initial contribution of the direct epoxidation (Fig. 3). In fact, more than 80% of the epoxidation takes place initially through the direct mechanism. Only in the case of Si–Ti(TA) this contribution diminishes to 68%. However, the consumption of H_2O_2 at short reaction times allows the **chhp**-mediated epoxidation to proceed, reducing the final contribution to 60%. The only exception is the reaction with Si–Ti(O^{i}Pr)(ec). This catalyst leads to low final selectivity, again in contrast with previous work (9d, 11), and moreover a significant amount of nonconverted **chhp** remains, showing deactivation for the **chhp**-mediated epoxidation. It is also noteworthy that high initial activity is detrimental for the final TON, given that higher activity seems to correspond to faster deactivation.

The situation for the reaction with high H_2O_2/Ti ratio is very different (entries 5–16). Si–Ti(O^{i}Pr) shows lower activity for epoxidation than in the conditions of low H_2O_2/Ti ratio. In spite of this, the contribution of the direct epoxidation is also 60%. The dispersion of Ti (entry 7) has a positive effect on activity but negative effect on the final selectivity. The effect of the silanization (entry 9) is clearly

TABLE 3

Activity of the Different Catalysts To Yield Epoxidation Products

				mmol of (**epox** + **diol**)/mmol of Ti					
Entry	Catalyst	Run	H_2O_2/Ti[a]	Initial (h^{-1})[b]	% mech. A[c]	Final	% mech. A[c]	Remaining **chhp**[d]	**epox/diol**
1	Si–Ti(O^iPr)	1	11.7	8.40	82	5.92	61	0.28	5/95
2	Si–Ti(O^iPr)(ec)	1	12.4	7.66	82	6.39	29	2.02	25/75
3	Si–Ti(TA)	1	12.6	4.94	68	7.70	62	0.83	0/100
4	Si–Ti(TA)(0.2)	1	11.4	2.98	86	8.10	60	0.33	11/89
5	Si–Ti(O^iPr)	1	60.0	4.1	61	17.7	60	9.8	29/71
6		3	86.7	1.0	0	3.6	0	27.9	44/56
7	Si–Ti(O^iPr)(0.2)	1	52.1	12.9	70	31.2	40	5.0	52/48
8		3	96.1	10.4	0	39.5	15	23.1	78/22
9	Si(ec)–Ti(O^iPr)	1	73.5	10.5	20	33.1	27	14.1	76/24
10		3	83.3	6.8	0	29.4	2	27.7	73/27
11	Si–Ti(TA)	1	63.0	5.5	55	25.3	63	11.4	22/78
12		3	111.6	11.5	0	52.8	26	14.2	41/59
13	Si–Ti(TA)(0.2)	1	56.8	4.1	37	31.6	44	6.1	56/44
14		3	78.1	10.8	0	36.8	23	13.7	65/35
15	Si(ec)–Ti(TA)	1	62.5	19.6	78	37.3	64	1.3	51/49
16		3	83.3	6.0	0	32.5	19	28.6	81/19

[a] In the 3rd run the ratio was calculated with the titanium analysis after the reaction.
[b] Estimated from yields at the early stage of the reaction.
[c] 100 × (**epox** + **diol** − **chexol)/(epox** + **diol**).
[d] mmol of **chhp**/mmol of Ti in the final reaction mixture.

negative, mainly in the early stage of the reaction. The catalysts modifiedwith tartaric acid (entries 11 and 13) show activity similar to that of Si–Ti(O^iPr). In this case no positive effect of the dispersion is observed. However, the selectivity to epoxidation products shows the same dependence with the dispersion as in the catalysts with isopropoxy groups. In this case the silanization has a very positive effect (entry 15) on both catalytic activity and selectivity. Moreover, Si(ec)–Ti(TA) shows the best yield among the freshly prepared catalysts and also the lowest amount of nonconverted **chhp**.

The recovered catalysts show different behavior. In all cases initial activity for direct epoxidation is suppressed. Direct epoxidation shows only a small contribution (0–14%) to the final yield in epoxidation products. The initial activity is reduced in the case of the catalysts with high activity as prepared, namely, those with isopropoxy groups and Si(ec)–Ti(TA). In contrast, the activity is increased for the catalysts modified with tartaric acid. The final TON values for epoxidation are similar for all the catalysts, fresh and reused, in the range 30–40, with only Si–Ti(TA) as a positive exception and Si–Ti(O^iPr) as a negative one. Moreover, the amount of nonconverted **chhp** is always higher with the reused catalysts than with the fresh ones. So as a conclusion, we can say that the remaining Ti centers after two reactions

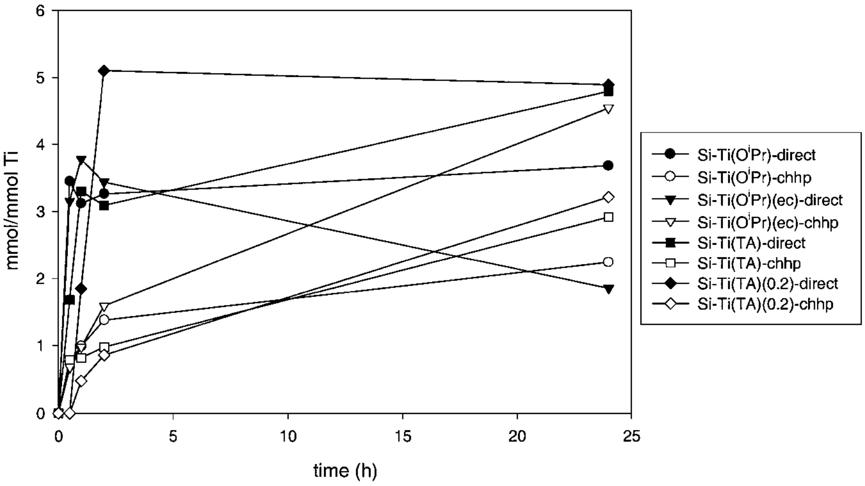


FIG. 3. Epoxidation (mmol of **ep** + **diol**/mmol of Ti) by direct mechanism (filled symbols) or with **chhp** (open symbols).

are still active in the epoxidation of cyclohexene with alkyl hydroperoxides (**chhp** in this case), but the nature of the sites has changed and their activity for the direct epoxidation with diluted H_2O_2 is greatly reduced or in some cases even suppressed.

Activity for Epoxide Hydrolysis

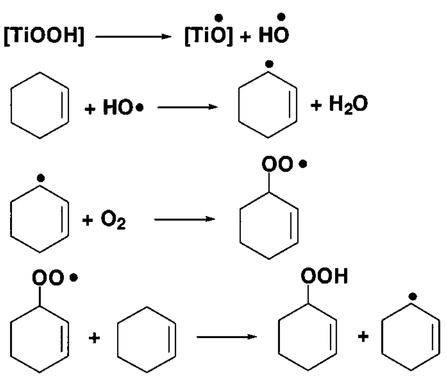
In all cases, part of the epoxide suffers hydrolysis with opening to diol. The role of titanium centers in this reaction is clear from the lack of activity of pure silica in the same conditions. However, not all the sites behave in the same way, as can be seen in Table 3.

In conditions of low H_2O_2/Ti ratio, the hydrolysis is extensive with Si–Ti(O^{i}Pr). Silanization has a positive effect (entry 2), but yet 75% of epoxide is hydrolyzed. The catalyst modified with tartaric acid produces the complete hydrolysis of the epoxide (entry 3) and dispersion (or low loading of titanium on silica) has also a slightly positive effect (entry 4).

An increase in the H_2O_2/Ti ratio, with the increase also in the water/Ti ratio, produces a decrease in the diol proportion (entries 5–16). Again, the silanization is positive in the catalysts with isopropoxy groups (entries 7 and 9), with only 24% hydrolysis with Si(ec)–Ti(O^{i}Pr). The treatment with tartaric acid does not modify the activity for hydrolysis, although a positive effect of dispersion is again observed. The effect of silanization is in this case negligible (entries 13 and 15). The recovered catalysts show in general lower activity for hydrolysis. The low value of 19% hydrolysis obtained with recovered Si(ec)–Ti(TA) is remarkable. Again, the recovered catalysts show a change in behavior, which suggests the change in the structure of the active sites. In any case, the Lewis acidity of the sites (responsible for the hydrolysis) and the activity for direct epoxidation seem to be related.

Role of the Atmospheric Oxygen

It is worthy to note that in many cases the final TON for H_2O_2 conversion is higher than the initial H_2O_2/Ti ratio (see Table 2), showing the participation of the atmospheric molecular oxygen in the oxidation process. In fact, it has been proposed (14) that the propagation step of the radical pathway takes place through the attack of the allylic radical to the molecular oxygen, with generation of a peroxy radical (Scheme 2). In view of this, the reactions with conversions higher than 100% (entries 12, 14, and 18) were repeated under an Ar atmosphere, thus with exclusion of atmospheric oxygen. In those cases the H_2O_2 conversion is lower than 100% (97, 84, and 95%, respectively). The analysis of the product distribution of these reactions shows that the contribution of the direct mechanism is similar to those reactions carried out under atmospheric conditions, between 10 and 20%. The yields in epoxidation products are only slightly lower under an inert atmosphere and the contributions of both mechanisms are almost identical.



SCHEME 2

This little effect of the atmospheric oxygen is not unexpected taking into account the tendency of hydrogen peroxide to decompose into water and oxygen at the reaction temperature. Thus, the main contribution of the molecular oxygen comes from the oxygen produced by the uncatalyzed hydrogen peroxide decomposition, which is much more difficult to prevent, and the fact that reactions are carried out without inert atmosphere does not invalidate the conclusions of this study.

Insight into the Nature of the Active Sites

The first question about the nature of the sites is the coverage of the silica surface. Excessive Ti density would indicate the presence of dimers, with a structure closely related to that proposed for Al species (24) (Fig. 4A). It has been described that the surface density of hydroxyl groups for silicas is 4.6 OH/nm^2 (25), with a distribution of 1.4 and 3.2 OH/nm^2 for isolated and hydrogen-bridged hydroxyls, respectively. These figures have been recently confirmed for Merck 60 silica (26), with only slight variations. Thus, for silica with 475 m^2/g, the total amount of hydroxyl groups will be 3.63 mmol/g, with 1.10 mmol/g of isolated and 2.53 mmol/g of hydrogen-bridged hydroxyls. It has also been described that hexamethyldisilazane reacts only with isolated OH groups (27). The analysis of Si(ec) shows 3.25 mmol of C/g, which corresponds to 1.08 mmol/g

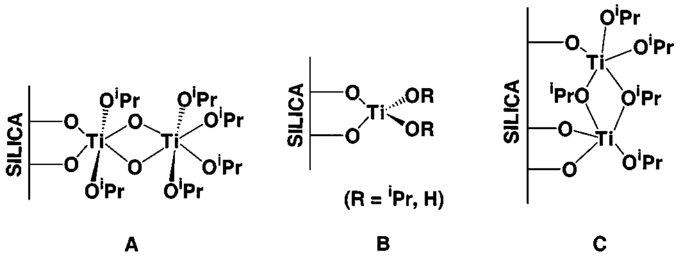


FIGURE 4

of trimethylsilyl groups. Considering the increase in weight of silica due to silanization, the density of $SiMe_3$ groups will be 1.48 $SiMe_3/nm^2$, in good agreement with the density of isolated hydroxyls. On the other hand, Si–Ti(O^iPr) has a titanium content of 1.07 mmol/g, corresponding to a density of 1.64 Ti/nm^2, with the same consideration for the gain in weight, in agreement with structure B in Fig. 4. Although we cannot assure that all the titanium species form two bonds with the silica surface, the EXAFS data seem to indicate it (28), and the Ti content also suggests that all the bridged hydroxyls (3.28 according to Ti density) have reacted. Only the carbon content is not in agreement with this hypothesis, and it seems to indicate the presence of a mixture of species with $Ti(OH)_2$, Ti(OH)(O^iPr), and $Ti(O^iPr)_2$ groups, leading to an average of one isopropoxy group per titanium.

This structure is in disagreement with that proposed from stoichiometric considerations by Scott and co-workers (29), formed by dimers (Fig. 4C), whose pentacoordinated titanium atoms do not fit well with our EXAFS data (28). The lower density of hydroxyl groups in Degussa aerosil (2.6 OH/nm^2) used in that work and the lower temperature for the surface functionalization can account for this disagreement.

The solids have been studied by IR spectroscopy. In the preceding paper (20) the presence of isopropyl groups in Si–Ti(O^iPr) was confirmed by the bands at 1466–1452 and 1385–1375 cm^{-1}. In the case of Si(ec) the methyl groups in $SiMe_3$ show bands at 1443 and 1413 cm^{-1} (Fig. 5), clearly different from those of the isopropyl groups. To detect the bands corresponding to Si–O–Si and Si–O–Ti vibrations (30), wafers diluted with KBr were prepared and the spectra recorded (Fig. 6). Two facts make the estimation of the titanium dispersion difficult, the presence of a band at 960 cm^{-1} in the starting Merck silica and the low titanium content, with the corresponding low intensity of the Si–O–Ti band at 949 cm^{-1}.

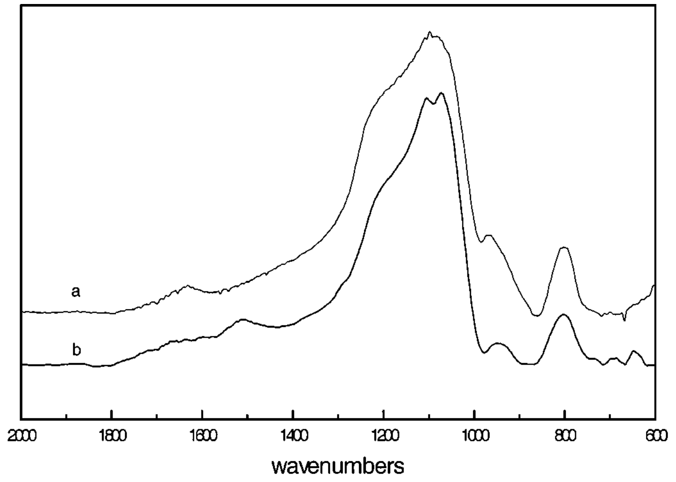


FIG. 6. IR spectra of (a) silica and (b) Si–Ti(O^iPr).

In Si–Ti(TA) the IR spectrum shows a large band corresponding to the carbonyl groups (20). The lower amount of tartaric acid in Si(ec)–Ti(TA) allows us to draw some conclusions from the spectrum (Fig. 7). In spite of this lower amount, the carbonyl band is again large and now the maximum is more clearly in the zone 1600–1650 cm^{-1}, far from the position in tartaric acid at 1735 cm^{-1}. The band in the solid agrees with the presence of tartrate anion, both in position and width. As an example, sodium tartrate shows the carbonyl band at 1611 cm^{-1}. Thus, the structure of the titanium sites must be different from that proposed in Ref. (20), with a probable formation of titanium tartrate supported on silica.

In Figs. 5 and 7 the spectra of the used catalysts are also shown. In the case of Si–Ti(O^iPr) the intense bands

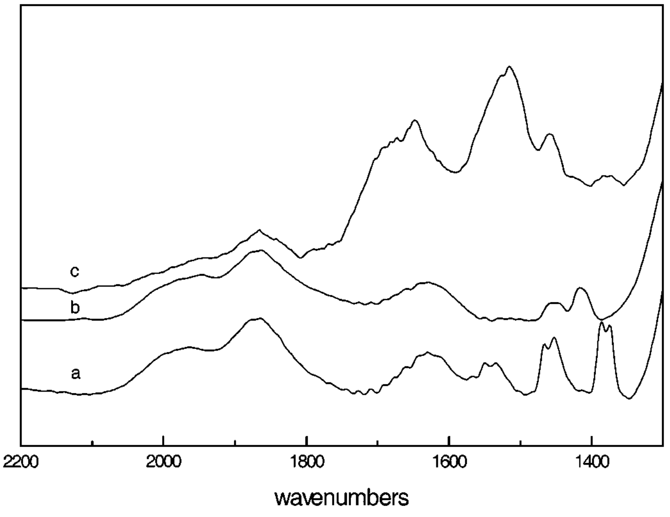


FIG. 5. IR spectra of (a) Si–Ti(O^iPr), (b) Si(ec) and, (c) used Si–Ti(O^iPr).

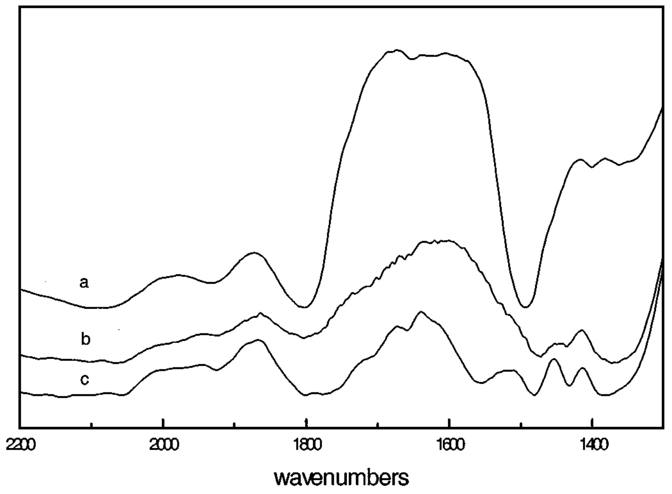


FIG. 7. IR spectra of (a) Si–Ti(TA), (b) Si(ec)–Ti(TA), and (c) used Si(ec)–Ti(TA).

TABLE 4

Reactivation of Si–Ti(O^{i}Pr)

Treatment	Conv. H_2O_2 TOF (h^{-1})	Conv. H_2O_2 TON	Epoxidation[a]	% Mech. A	Remaining **chhp**	**epox/diol**
Fresh	14.4	8.7	5.9	61	0.3	5/95
Soxhlet toluene	19.8	20.0	7.0	0	2.4	100/0
Soxhlet ^{i}PrOH	24.2	19.7	2.7	0	6.1	100/0

[a] mmol of (**epox** + **diol**)/mmol of Ti.

in the range 1450–1700 cm^{-1} (Fig. 5) demonstrate the adsorption of some by-products . The two more prominent bands are present at 1645 and 1516 cm^{-1}. These bands are in the zone attributed to C=O and C=C stretching for α, β-unsaturated ketones adsorbed on strong Lewis acid sites. Similar bands in the ranges 1638–1687 and 1552–1589 cm^{-1} are detected for mesityl oxide adsorbed on aluminum species supported on silica (31). The cyclohexenone adsorption may be responsible for these bands, and the dehydration of cyclohexenyl hydroperoxide on the acid sites of the titanium catalysts may account for the formation of the ketone. Its strong adsorption explains its absence in the reaction mixture.

The IR spectrum of the used Si(ec)–Ti(TA) (Fig. 7) shows a much lower amount of tartrate than the freshly prepared catalyst. The width and position of the carbonyl band seem to confirm the anionic nature of the tartaric on the surface. In contrast with the gain in carbon content (Table 1) no adsorption of by-products is detected in this case. This absence of strong adsorption on a silylated solid shows the important role of the silanol groups in the acidity of the solid.

Reactivation of Si–Ti(O^{i}Pr)

Given the possible deactivation of Si–Ti(O^{i}Pr) by strong adsorption of organic molecules, two different treatments have been tried to reactivate it: Soxhlet extraction for 72 h with a solvent, nonpolar toluene or polar isopropanol. In both cases there exist leaching of titanium, given that the resulting solids have 0.60 mmol of Ti/g. The fact that even toluene is able to produce this leaching seems to indicate that part of the titanium species after reaction is only adsorbed onto the silica surface and prolonged treatment with a solvent enables them to be extracted to the liquid phase.

Both regenerated solids were studied by IR spectroscopy and both presented the same type of spectrum. A broad band centered at 1650 cm^{-1} remains after Soxhlet extraction, whereas the band at 1516 cm^{-1} completely disappears. This behavior shows that there are at least two adsorbed species on the used catalyst, one weakly adsorbed (probably containing titanium), which can be eliminated with a solvent, and another one strongly adsorbed, which remains on the solid after the treatment.

Both treatments have effects on the performance of the catalyst (Table 4), but none of them are able to regenerate the fresh catalyst. In fact, the extracted catalysts are more active for the conversion of H_2O_2. For the epoxidation the extraction with toluene is more efficient, showing that the adsorption of organic molecules of low polarity is a significant cause of deactivation. In contrast, treatment with isopropanol leads to a catalyst less active for epoxidation. The higher activity of the solid extracted with toluene is confirmed by the lower amount of remaining **chhp**, whereas the amount is much higher in the case of the solid extracted with isopropanol. However, the activity for direct epoxidation is not recovered at all, and the epoxidation takes place only through the radical mechanism. Finally, the recovered solids are not active for the hydrolysis of the epoxide, in contrast with the fresh catalyst. It is difficult to explain the increase in the epoxidation activity without increasing also the Lewis acidity of the solid. The leaching of titanium continues in the subsequent reaction, leading to 0.55 mmol of Ti/g, showing that all the species can be leached and the extension of leaching is probably a question of equilibrium.

Study of Recovery with Cyclooctene

One hypothesis about deactivation is the adsorption of by-products, which can be produced from the epoxidation products or by side reactions of the radical pathway. The assessment of one of these possibilities can be obtained from the reaction with cyclooctene, which only proceeds by direct mechanism. Data are gathered in Table 5. As can be seen, initial activity of the catalyst is reduced after recovering, but even in the third reaction the epoxidation takes place and the final TON is similar or even higher than that in the first run. Another interesting point is the almost complete absence of leaching after three reactions, with a titanium content of 0.97 mmol/g compared to the initial 1.07 mmol/g or the content of 0.74 mmol/g after three reactions with cyclohexene in the same conditions. In the case of TS-1 the role of polyhydroxilated molecules in the leaching of titanium has very recently been pointed out (32). In our case this role can be played by **diol**, which is not produced in the epoxidation of cyclooctene.

TABLE 5

Reactions of Epoxidation of Cyclooctene with Si–Ti(O^{i}Pr)[a]

Run	TOF (h^{-1})	TON[b]
1	21.0	16.0
2	9.0	21.2
3	7.1	18.9
4[c]	14.8	18.4

[a] Ratio H_2O_2/Ti = 60. Only epoxide was obtained.
[b] After 24 h.
[c] After three reactions with cyclohexene.

The total suppression of the direct epoxidation in the case of cyclohexene after recovery can be due only to a reduction in the reaction rate, making it the more favorable the radical pathway, less sensitive to deactivation. A deactivated catalyst from Si–Ti(O^{i}Pr) after reaction with cyclohexene, which promoted only **chhp**-mediated epoxidation, was used in the epoxidation of cyclooctene. In that case (Table 5) the catalyst was nearly as active as the fresh one, showing that the activity for the direct epoxidation is not suppressed but only reduced to a level low enough to shift the mechanism to the radical pathway.

CONCLUSIONS

Titanium derivatives supported on silica are active catalysts for the epoxidation of alkenes with diluted aqueous hydrogen peroxide. The epoxidation of cyclooctene demonstrates the high stability of this system, reusable at least three times with a decrease in the initial activity but higher final TON. In the case of cyclohexene, the easy formation of the cyclohexenyl radical allows the reaction to proceed through two competitive mechanisms. The direct epoxidation takes place to a considerable extent with the fresh catalysts, although its contribution is in general reduced with the increase in H_2O_2/Ti ratio. Moreover, the presence of the diol or other by-products contributes to the leaching of titanium, which is much lower with the more selective cyclooctene. Silanization of the silica surface or exchange of isopropoxy groups by tartaric acid have little influence on the catalytic behavior in these conditions, although simultaneous variation of both has a positive effect on the selectivity. The change in nature of the catalytic sites after reaction has as a consequence the reduction in catalytic activity of the recycled catalysts for the direct epoxidation, although they convert hydrogen peroxide with the same or higher efficiency. Thus, the recycled catalysts only epoxidize cyclohexene through the radical pathway, by formation of cyclohexenyl hydroperoxide. The original nature of the catalytic sites is not easily regenerated and further studies are in progress to try to improve the results, both in selectivity and reusability of this system.

ACKNOWLEDGMENT

This work was made possible by the generous financial support of the C.I.C.Y.T. (Project MAT99-1176).

REFERENCES

1. (a) Clerici, M. G., Bellusi, G., and Romano, U., *J. Catal.* **129**, 159 (1991). (b) Clerici, M. G., and Ingallina, P., *J. Catal.* **140**, 71 (1993).
2. (a) Corma, A., Esteve, P., Martínez, A., and Valencia, S., *J. Catal.* **152**, 18 (1995). (b) Jappar, N., Xia, Q., and Tatsumi, T., *J. Catal.* **180**, 132 (1998).
3. (a) Blasco, T., Corma, A., Navarro, M. T., and Pérez Pariente, J., *J. Catal.* **156**, 65 (1995). (b) Chen, L. Y., Chuah, G. K., and Jaenicke, S., *Catal. Lett.* **50**, 107 (1998). (c) Díaz-Cabañas, M. J., Villaescusa, L. A., and Camblor, M. A., *Chem. Commun.* 761 (2000).
4. Hutter, R., Mallat, T., and Baiker, A., *J. Catal.* **153**, 177 (1995).
5. Corma, A., Diaz, U., Domine, M. E., and Fornés, V., *J. Am. Chem. Soc.* **122**, 2804 (2000).
6. Murugavel, R., and Roesky, H. W., *Angew. Chem. Int. Ed. Engl.* **36**, 477 (1997).
7. Langhendries, G., De Vos, D. E., Baron, G. V., and Jacobs, P. A., *J. Catal.* **187**, 453 (1999).
8. Blasco, T., Camblor, M. A., Corma, A., Esteve, P., Martínez, A., Prieto, C., and Valencia, S., *Chem. Commun.* 2367 (1996).
9. (a) Tatsumi, T., Koyano, K. A., and Igarashi, N., *Chem. Commun.* 325 (1998). (b) Corma, A., Domine, M., Gaona, J. A., Jordá, J. L., Navarro, M. T., Rey, F., Pérez-Pariente, J., Tsuji, J., McCulloch, B., and Nemeth, L. T., *Chem. Commun.* 2211 (1998). (c) D'Amore, M. B., and Schwarz, S., *Chem. Commun.* 121 (1999). (d) Bu, J., and Rhee, H.-K., *Catal. Lett.* **65**, 141 (2000).
10. Klein, S., and Maier, W. F., *Angew. Chem. Int. Ed. Engl.* **35**, 2230 (1996).
11. Kochkar, H., and Figueras, F., *J. Catal.* **171**, 420 (1997).
12. (a) Wulff, H. P., U.S. Patent 3,923,843 (1975). (b) Wulff, H. P., and Wattimena, F., U.S. Patent 4,021,454 (1977).
13. (a) Fraile, J. M., García, J. I., Mayoral, J. A., de Ménorval, L. C., and Rachdi, F., *J. Chem. Soc. Chem. Commun.* 539 (1995). (b) Cativiela, C., Fraile, J. M., García, J. I., and Mayoral, J. A., *J. Mol. Catal. A* **112**, 259 (1996).
14. Jorda, E., Tuel, A., Teissier, R., and Kervennal, J., *J. Catal.* **175**, 93 (1998).
15. (a) Holmes, S. A., Quignard, F., Choplin, A., Teissier, R., and Kervennal, J., *J. Catal.* **176**, 173 (1998). (b) Holmes, S. A., Quignard, F., Choplin, A., Teissier, R., and Kervennal, J., *J. Catal.* **176**, 182 (1998).
16. (a) Maschmeyer, T., Rey, F., Sankar, G., and Thomas, J. M., *Nature* (*London*) **378**, 159 (1995). (b) Morey, M. S., O'Brien, S., Schwarz, S., and Stucky, G. D., *Chem. Mater.* **12**, 898 (2000).
17. Kriesel, J. W., and Tilley, T. D., *Chem. Mater.* **12**, 1171 (2000).
18. Alder, K. I., and Sherrington, D. C., *J. Mater. Chem.* **10**, 1103 (2000).
19. (a) Yang, Q., Li, C., Yuan, S., Li, J., Ying, P., Xin, Q., and Shi, W., *J. Catal.* **183**, 128 (1999). (b) Yang, Q., Li, C., Wang, S., Lu, J., Ying, P., Xin, Q., and Shi, W., *Stud. Surf. Sci. Catal.* **130**, 221 (2000).
20. Fraile, J. M., García, J. I., Mayoral, J. A., and Vispe, E., *J. Catal.* **189**, 40 (2000).
21. (a) de Frutos, P., and Campos-Martín, J. M., WO 9948884 (1999). (b) Capel-Sánchez, M. C., Campos-Martín, J. M., Fierro, J. L. G., de Frutos, M. P., and Padilla-Polo, A., *Chem. Commun.* 855 (2000).

22. Müller, C. A., Schneider, M., Mallat, T., and Baiker, A., *J. Catal.* **189**, 221 (2000).
23. (a) Klunduk, M. C., Maschmeyer, T., Thomas, J. M., and Johnson, B. F. G., *Chem. Eur. J.* **5**, 1481 (1999). (b) Crocker, M., Herold, R. H. M., Orpen, A. G., and Overgaag, M. T. A., *J. Chem. Soc. Dalton Trans.* 3791 (1999).
24. Fraile, J. M., García, J. I., Mayoral, J. A., and Pires, E., *J. Mol. Catal. A* **119**, 95 (1997).
25. Armistead, C. G., Tyler, A. J., Hambleton, F. H., Mitchell, S. A., and Hockey, J. A., *J. Phys. Chem.* **73**, 3947 (1969).
26. Schrijnemakers, K., Van Der Voort, P., and Vansant, E. F., *Phys. Chem. Chem. Phys.* **1**, 2569 (1999).
27. Blitz, J. P., Meverden, C. C., and Diebel, R. E., III, *Langmuir* **14**, 1122 (1998).
28. Fraile, J. M., García, J., Mayoral, J. A., Proietti, M. G., and Sánchez, M. C., *J. Phys. Chem.* **100**, 19484 (1996).
29. Bouh, A. O., Rice, G. L., and Scott, S. L., *J. Am. Chem. Soc.* **121**, 7201 (1999).
30. Müller, C. A., Maciejewski, M., Mallat, T., and Baiker, A., *J. Catal.* **184**, 280 (1999).
31. Fraile, J. M., García, J. I., Mayoral, J. A., Pires, E., Salvatella, L., and Ten, M., *J. Phys. Chem. B* **103**, 1664 (1999).
32. Davies, L., McMorn, P., Bethell, D., Bulman Page, P. C., King, F., Hancock, F. E., and Hutchings, G. J., *Chem. Commun.* 1807 (2000).