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Silica-Supported Titanium Derivatives as Catalysts for the Epoxidation of Alkenes with Hydrogen Peroxide: A New Way to Tuneable Catalytic Activity through Ligand Exchange

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Titanium tetraisopropoxide supported on silica [Si–Ti(O^{i}Pr)] is an efficient catalyst for the epoxidation of alkenes, cyclooctene, and cyclohexene with 30% hydrogen peroxide at 80°C. In the case of cyclohexene, allylic oxidation is also produced through a radical mechanism and the epoxide undergoes hydrolysis to the *trans*-diol due to the acidity of the catalyst and the presence of water. The catalyst can be recycled with very low titanium leaching and has a slightly lower catalytic activity after two cycles. These best results are obtained when an alkene/H_2O_2 ratio = 20 is used. Lowering this ratio up to 5 has a detrimental effect on the final yield but does not affect the epoxidation/allylic selectivity. Further decrease to alkene/H_2O_2 = 1 leads to very low activity and selectivity. This catalyst bears isopropoxy groups that can be substituted by nonfunctionalized and functionalized diols. Such a process modifies the activity and selectivity of the catalyst, showing that it is possible to modulate the performance of this kind of titanium catalyst by changing the environment of the catalytic sites. The substitution with ethylene glycol improves the performance of the recovered catalyst. The catalyst prepared by treating the original Si–Ti(O^{i}Pr) with tartaric acid [Si–Ti(TA)] gives rise to high overall oxidation yields, with 97% selectivity in H_2O_2 and an epoxidation/allylic oxidation ratio around 65/35. Moreover, it is very stable during at least three cycles. End-capping of the silica surface has a positive effect on the epoxide hydrolysis but not on the epoxidation/allylic oxidation selectivity, in contrast with previously described results. The lower functionalization of the silylated solids noticeably increases the turnover numbers. Filtration experiments in the reaction conditions have shown that Si–Ti(O^{i}Pr) and Si(ec)–Ti(TA) are truly heterogeneous catalysts, with no contribution of the leached species. However, Si–Ti(TA) leads to leaching of active species, although an important part of them remains on the solid after three filtrations, and the contribution to the activity of homogeneous and heterogeneous species is nearly the same. © 2000 Academic Press

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

INTRODUCTION

Oxidations can be carried out with many different oxidants, but from an economic point of view there are two oxidants of choice, molecular oxygen and dilute hydrogen peroxide, given their availability, low price, ease of handling, and absence of toxic waste (1). Thus, a lot of research is currently in progress to try to find active catalysts for different oxidation reactions with these oxidants. Epoxides are among the most versatile synthetic intermediates and, consequently, a large part of that research concerns epoxidation reactions.

The ability of titanium silicalites to catalyze the epoxidation of olefins with dilute hydrogen peroxide (2) was a great success with small olefins but the microporosity of these materials precludes the epoxidation of bigger molecules such as cyclohexene. Thus, considerable effort has been focused on the incorporation of titanium atoms into the structure of zeolites with larger pores, such as beta (3), or even in mesoporous crystalline silicas, such as MCM-41 (4, 5). However, in all these cases the selectivity in hydrogen peroxide is decreased with respect to TS-1 and hydrolysis (and alcoholysis) of the epoxide also reduces the selectivity to the epoxide.

The good results obtained with TS-1 have been attributed to the hydrophobic character of this zeolite, which keeps water far from the catalytic sites and precludes the hydrolysis of the epoxides and the deactivation of the catalyst (6). With this hypothesis, some efforts have been aimed at increasing the hydrophobic character of larger pore zeolites. In that way, the synthesis of a Ti-beta in a fluoride medium (7) or the silylation of the silanol groups in MCM-41 (8) have shown a positive effect on the activity of those catalysts.

Titania–silica mixed xerogels have been proposed as an alternative to the Ti-zeolites. The hydrophobic character of the surface has been changed by synthesis with variable ratios of aryl- or alkyltrialkoxysilanes and this has led to a

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significant effect on both the activity and the selectivity of epoxidation reactions (9–11).

Silica-supported titanium materials have been prepared by treatment of silica with TiF_4 (12) or tetraneopentyltitanium (13). Both solids are catalysts for the epoxidation of cyclohexene with 70% hydrogen peroxide. The results depend on the titanium loading and the postsynthesis treatment of the material. More importantly, these results show that hydrophilic silicas can be used as supports for titanium species that are active for the epoxidation of alkenes with hydrogen peroxide.

We have described silica-supported $Ti(O^iPr)_4$ as an excellent catalyst for epoxidation with alkyl hydroperoxides (14). In this paper we describe the use of this solid in the epoxidation with hydrogen peroxide. We have also explored the strategy of modification of the environment of titanium centers by replacement of the isopropoxy groups present in the catalyst by diols and the changes in catalytic performance associated with this modification.

EXPERIMENTAL

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(O^iPr) was prepared by treatment of silica (Merck 60) with $Ti(O^iPr)_4$ in toluene under reflux as described in Ref. 14.

Si–Ti(EG) was prepared by treatment of Si–Ti(O^iPr) (1 g) with ethylene glycol (80.6 mg, 1.3 mmol) in anhydrous toluene (25 mL) under reflux in an Ar atmosphere for 6 h. Fifteen milliliters of solvent was then distilled off and the reaction mixture was cooled to room temperature. The solid was separated by filtration, washed with anhydrous toluene and dichloromethane, and dried under vacuum. Si–Ti(DET) was prepared by treatment of Si–Ti(O^iPr) with diethyl L-tartrate following the same procedure. Si–Ti(TA) was prepared by treatment of Si–Ti(O^iPr) with L-tartaric acid following the same procedure but, in this case, butyl acetate was used as a solvent instead of toluene.

Si(ec) was prepared by treatment of silica (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 off, washed with ethanol, water, ethanol, and ether, and dried under vacuum. Si(ec)–T(O^iPr) was prepared by treatment of Si(ec) (5 g) with $Ti(O^iPr)_4$ (1.5 mmol) in anhydrous toluene (25 mL) under reflux in an Ar atmosphere for 48 h (14). Si(ec)–Ti(TA) was prepared by treatment of Si(ec)–Ti(O^iPr) (1 g) with L-tartaric acid (0.5 mmol) as described above.

Characterization of the Catalysts

Titanium analyses were carried out by plasma emission spectroscopy on a Perkin-Elmer Plasma 40 emission spectrometer. Carbon analyses were carried out using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer. Self-supported wafers were treated under vacuum ($<10^{-5}$ Torr) at 140°C in a cell equipped with NaCl windows. UV spectra were recorded on a Unicam UV4 spectrometer.

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 (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 (FID from Hewlett-Packard 5890 II, helium as a carrier, 20 p.s.i.; cross-linked methyl silicone column, 25 m × 0.2 mm × 0.33 μm; oven temperature program: 45°C (4 min), 25°C/min, 250°C (2 min); retention times: internal standard 2.9 min, cyclohexene 3.5 min, cyclohexene oxide 6.5 min, 2-cyclohexenol 6.9 min, 2-cyclohexenone 7.3 min, *trans*-1,2-cyclohexanediol 8.7 min). The products were detected in the reaction mixture by ^1H NMR spectroscopy, identified in the chromatogram by comparison with authentic samples and calibrated against the internal standard. After 24 h the catalyst was filtered off, washed with dichloromethane (5×5 mL), dried under vacuum, and reused under the same conditions. The H_2O_2 content in the final solution was analyzed by iodometric titration.

A number of experiments were carried out in which filtration at the reaction temperature was performed. Si–Ti(O^iPr) was added to a reaction mixture under the conditions described above but after 7 min the mixture was quickly filtered at 80°C. The liquid phase was allowed to react at 80°C and monitored by GC. The solid was reused in the same way and the new liquid phase reaction was again monitored. Finally the recovered solid was used as a catalyst in a normal reaction and compared with the freshly prepared catalyst. Si(ec)–Ti(TA) was also used in two filtration experiments. Si–Ti(TA) was used in the same way but three filtration cycles instead of two were carried out.

RESULTS AND DISCUSSION

Epoxidation Reactions with Si–Ti(O^iPr)

The first aim of this work was to test the performance of Si–Ti(O^iPr), already described as a good epoxidation catalyst with TBHP (14), in epoxidation reactions with 30% hydrogen peroxide. Characterization of this catalyst had been carried out by MAS-NMR (14) and X-ray absorption

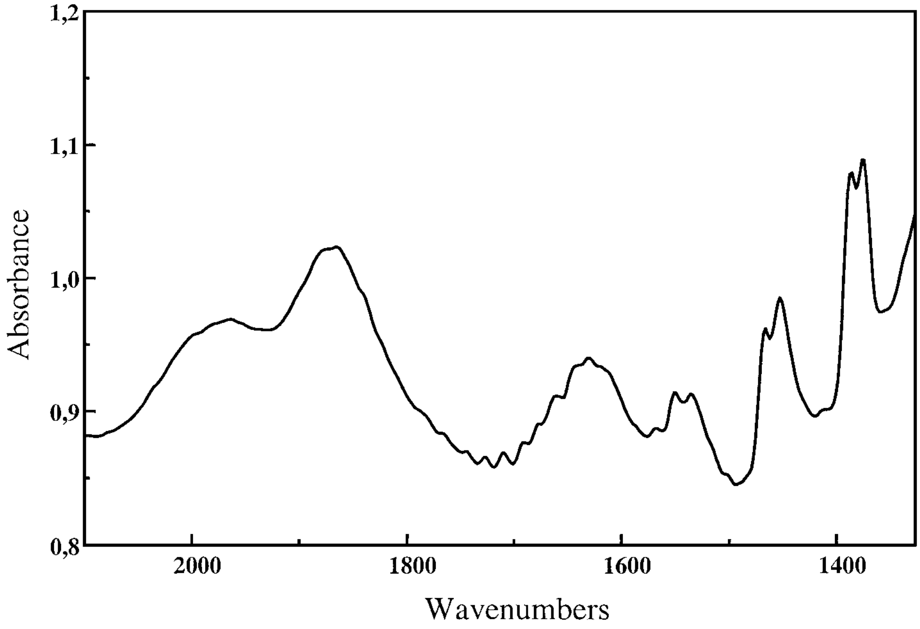


FIG. 1. IR spectrum of Si–Ti(O^{i}Pr).

spectroscopy (15). The main conclusions were that the only titanium atoms present on the solid were tetrahedral, without anatase impurities and the presence of isopropoxy groups. This characterization was completed with both IR and UV spectroscopy. The IR spectrum (Fig. 1) shows bands at 1466 and 1452 cm^{-1}, corresponding to $\delta(CH_3)$ asymm, and also bands at 1385 and 1375 cm^{-1}, which are typical of isopropyl groups [$\delta(CH_3)$ symm]. The UV spectrum shows the absence of absorption above 300 nm, confirming the absence of anatase on this solid.

The results of the epoxidation (Table 1) show that Si–Ti(O^{i}Pr) is able to catalyze epoxidation reactions with dilute hydrogen peroxide in spite of the hydrophilicity of the silica (6). First, the cyclooctene leads only to the epoxide, as already described (10). Thus this alkene is not truly representative and gives very little information about the reaction mechanism and the catalytic performance. Therefore we used cyclohexene in the rest of this work, given that it leads to two side reactions, allylic oxidation and hydrolysis of the epoxide (Scheme 1).

TABLE 1

Results of the Epoxidation Reactions with 30% H_2O_2

			% Yield[a]								
Alkene	Catalyst	*t* (h)	Epoxide	Diol	Alcohol	Ketone[b]	Overall[c]	TON[d]	% Select. H_2O_2[e]	Epoxide/Diol	Epoxidation/ Allylic ox.[f]
Cyclooctene	Si–Ti(O^{i}Pr)	1	25	0	0	0	25	—	—	100/0	100/0
		24	36	0	0	0	36	4.2	36	100/0	100/0
Cyclohexene	—	24	4	2	2	(8)	(16)	—	23	67/33	37/63
	SiO_2	24	4	2	4	(34)	(44)	—	78	67/33	16/84
	Si–Ti(O^{i}Pr)	1	23	12	9	(8)	(52)	—	—	66/34	—
		24	2	49	19	3	73	8.8	75	5/95	70/30
	Si–Ti(O^{i}Pr)	1	14	6	3	(2)	(25)	—	—	70/30	—
	(hydroquin.[g])	24	0	27	6	1	34	4.2	36	0/100	79/21

[a] Referred to the maximum.

[b] This value corresponds to ketone and cyclohexenyl hydroperoxide. We considered that values in brackets are mainly hydroperoxide, whereas the final values of the reactions with titanium were mainly ketone.

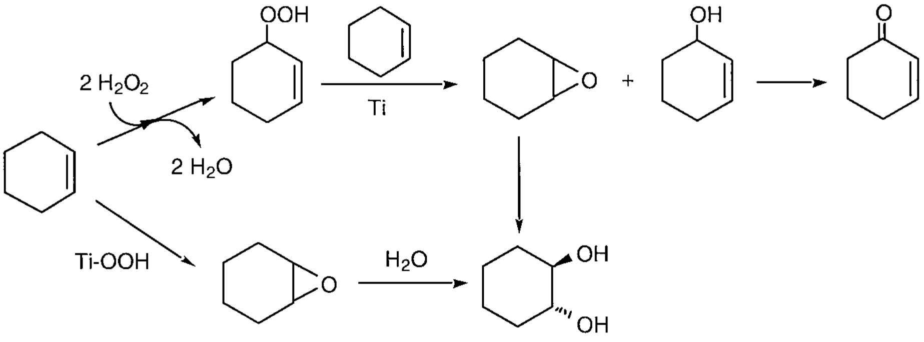
[c] Values in brackets are not exact because of the presence of noncalibrated cyclohexenyl hydroperoxide.

[d] mmol products/mmol Ti.

[e] Selectivity to oxidation products.

[f] (Epoxide + diol)/(alcohol + ketone).

[g] 0.3 mmol hydroquinone/mmol Ti.



SCHEME 1

In the absence of catalyst the reaction is very slow and leads mainly to allylic oxidation products. The presence of silica accelerates the allylic oxidation, which is detrimental for the reaction with Si–Ti(O^{i}Pr). In spite of this problem, the use of Si–Ti(O^{i}Pr) gives rise to a good selectivity in terms of epoxidation/allylic oxidation (70/30), with the yields of epoxide and diol taken as epoxidation and the yields of 2-cyclohexenol (alcohol) and 2-cyclohexenone (ketone) as allylic oxidation.

The epoxide can be produced by two different mechanisms (12), direct epoxidation with titanium hydroperoxide and radical formation of cyclohexenyl hydroperoxide, which subsequently acts as an oxidant. The existence of this mechanism is confirmed by the decrease in the apparent yield of ketone at longer reaction times, given that the cyclohexenyl hydroperoxide decomposes during GC analysis to give the ketone (12). In this second mechanism the amounts of epoxide and 2-cyclohexenol obtained are the same, so a larger amount of epoxide shows that the direct epoxidation also takes place. In our case, the 70% selectivity to epoxidation should correspond to 40% by direct epoxidation and 30% by the cyclohexenyl hydroperoxide pathway. In order to confirm the radical mechanism of the allylic oxidation, hydroquinone was added to a repeat reaction mixture. The result of this modification was a lower overall yield with a higher selectivity (79/21), which confirms the radical mechanism. Another possible mechanism could be the oxidation of the solvent to TBHP and its use as an oxidant. However, TBHP was not detected in any of the reactions, even in a blank test reaction in the absence of alkene, whereas this oxidant had been observed by GC in previous work (14).

In spite of the lower epoxidation/allylic oxidation selectivity, the use of cyclohexene increases the selectivity in H_2O_2 in comparison with cyclooctene. This could be due to the impossibility of the radical pathway with cyclooctene, which leads to a nonproductive decomposition of hydrogen peroxide through this mechanism. The extent of this decomposition is reduced with cyclohexene given that the radical pathway has a productive end in cyclohexenyl hydroperoxide.

Another remarkable conclusion is the higher activity of Si–Ti(O^{i}Pr) in comparison with other silica-supported titanium catalysts (12, 13) in that these other solids were not active with 30% H_2O_2 and required the use of 70% H_2O_2 and higher reaction temperatures (90–115°C). Although the turnover numbers are rather low, because of the low H_2O_2/Ti ratio used, the reaction is very fast at the beginning and the TOF values calculated in the first 30 min are around 25 h^{-1} for total conversion of cyclohexene and 13 h^{-1} for epoxidation products (see Fig. 4). These values are comparable to some others reported in the literature (5).

The epoxide hydrolysis is a subsequent reaction that takes place due to the presence of water and the acidity

TABLE 2

Results of the Epoxidation of Cyclohexene with 30% H_2O_2 Using Si–Ti(O^{i}Pr) as a Catalyst

		% Yield[a]								
Run	t (h)	Epoxide	Diol	Alcohol	Ketone[b]	Overall[c]	TON[d]	% Select. H_2O_2[e]	Epoxide/Diol	Epoxidation/ Allylic ox.[f]
1	1	23	12	9	(8)	(52)	—	—	66/34	—
	24	2	49	19	3	73	8.8	75	5/95	70/30
2	1	14	13	7	(10)	(44)	—	—	52/48	—
	24	2	40	28	5	75	9.2	79	4/96	55/45
3	1	8	5	5	(5)	(23)	—	—	62/38	—
	24	2	13	15	2	32	4.4	34	13/87	47/53

[a–f] As in Table 1.

TABLE 3

Analysis of Si–Ti(O^{i}Pr)

Run	C (mmol/g)	Ti (mmol/g)	C/Ti
0	3.46	1.07	3.24
1	5.32	—[a]	—[a]
2	5.67	—[a]	—[a]
3	6.29	0.96	6.55

[a] The titanium content was not determined because of the lack of sample.

of the catalyst. This hydrolysis is more significant in the case of Si–Ti(O^{i}Pr) than with silica, showing that the titanium sites are also responsible for the acidic character of this solid.

An additional important question concerns the reusability of this catalyst. The solid was in fact reused twice after filtration, washing and drying. The results are gathered in Table 2 and the corresponding analyses in Table 3. As can be seen, the catalyst loses part of its activity for the direct epoxidation after the first run, leading to a lower epoxidation/allylic oxidation selectivity, which is even lower in the third run. However, this loss of activity does not have a parallel titanium leaching, which is lower than 10% taking into account the gain in weight shown by the carbon analysis. Several factors could account for the deactivation and the main ones are the adsorption of some products or byproducts on the titanium sites, which would also explain the gain in carbon content, or the replacement of isopropoxy groups by other groups associated with greater steric hindrance, such as *tert*-butoxy from the solvent or the alcohols formed in the reaction, which would be also in agreement with the gain in carbon content. Such deactivation had also been reported for other solids such as Ti-MCM-41 (5) and silica-supported titanium (12). In both cases significant titanium leaching was also observed, and even reached a level of more than 90% in the freshly prepared catalyst with 30% H_2O_2 (12). Our results represent a marked improvement in stability in comparison with related silica-supported catalysts.

The effect of the reaction conditions was also studied. Given that all the reactions described were carried out with a large excess of alkene (20/1), the alkene/hydrogen peroxide ratio was diminished. The results are shown in Fig. 2. The ratio can be reduced to 10/1 with only a slightly lower final yield, but with a ratio of 5/1 the reaction stops after 1 h and then only epoxide hydrolysis takes place. In spite of this, the epoxidation/allylic oxidation selectivity remains constant. This is not the case with a ratio of 1/1, given that the yield is very low and no direct epoxidation takes place, as shown by the 50/50 epoxidation/allylic oxidation selectivity. The effect of temperature is also very important. At 50°C the reaction is slower and the epoxidation/allylic oxidation selectivity is lower. The yield of apparent cyclohexenone does not diminish with time, showing that the activity for the epoxidation with cyclohexenyl hydroperoxide is lower. Therefore, the rate of the radical reaction is influenced to a lesser extent by temperature.

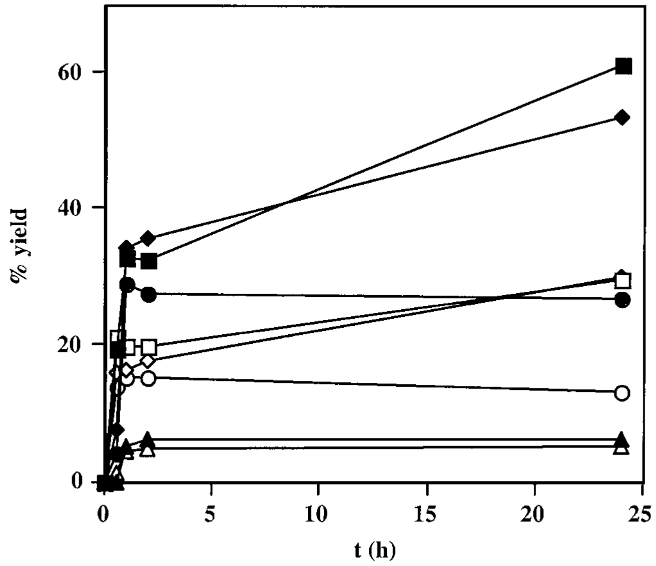


FIG. 2. Yield of epoxidation (filled symbols) and allylic oxidation (open symbols) with different alkene/H_2O_2 ratios: (■) 20/1, (◆) 10/1, (●) 5/1, (▲) 1/1.

Increase of the Hydrophobic Character of Silica by End-Capping

The first attempt to obtain better results involved the end-capping of silica prior to the grafting of titanium. It has been described (7–11) that a decrease in the hydrophilicity of the silica surface has a positive effect on the activity of the solid. The treatment of silica was carried out with hexamethyldisilazane. In this way the vicinal silanol groups mainly remain intact (16), so the distribution of the titanium species on the surface should be more uniform. With this aim in mind, a smaller amount of Ti(O^{i}Pr)$_4$ was used for grafting. In fact, the Ti content in Si(ec)–Ti(O^{i}Pr) (Table 4) is much lower than in Si–Ti(O^{i}Pr) and the C/Ti ratio, taking into account the C content in Si(ec), is near the expected value for a species with two isopropoxy groups. The results for the epoxidation of cyclohexene are shown in Table 5. As can be seen, this catalyst leads to much higher

TABLE 4

Analysis of the End-Capped Solids

Solid	C (mmol/g)	Ti (mmol/g)	C/Ti[a]
Si(ec)	3.25	—	—
Si(ec)–Ti(O^{i}Pr)	4.16	0.17	5.4
Si(ec)–Ti(TA)	4.63	0.20	6.9

[a] The carbon content was considered as C_{sample}–$C_{Si(ec)}$.

TABLE 5

Results of the Epoxidation of Cyclohexene with 30% H_2O_2 Using Si(ec)–Ti(O^{i}Pr) as a Catalyst

Run	t (h)	% Yield[a] Epoxide	Diol	Alcohol	Ketone[b]	Overall[c]	TON[d]	% Select. H_2O_2[e]	Epoxide/Diol	Epoxidation/ Allylic ox.[f]
1	1	18	0	7	(17)	(42)	—	—	100/0	—
	24	35	22	35	5	97	73.5	101	60/40	59/41
2	1	8	3	11	(31)	(53)	—	—	72/28	—
	24	33	13	38	9	93	73.5	100	70/30	49/51

[a–f] As in Table 1.

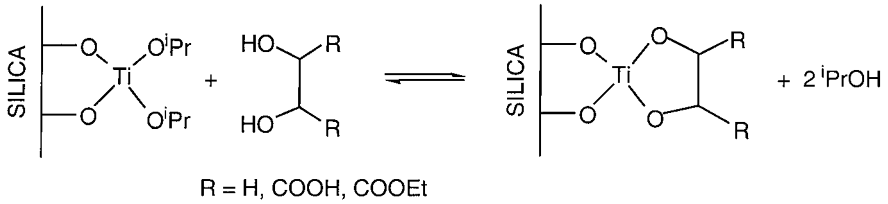
turnover numbers than Si–Ti(O^{i}Pr) due to the lower Ti content. The conditions used in this case were more similar to those reported in the literature (11, 13). The final yields show that the selectivity in hydrogen peroxide is complete, demonstrating that its nonproductive decomposition has been minimized. In contrast with previously described results (8a), the epoxidation/allylic oxidation selectivity is not better with the end-capped catalyst. Interestingly, the extent of epoxide hydrolysis is greatly reduced and after 24 h only 40% of the epoxide had been converted to diol. This result can be explained by the role of the silanol groups in the acidic properties of the solid. It is most likely that the silanol groups are polarized by the presence of the titanium centers favoring the epoxide hydrolysis. Alternatively, in the case of the end-capped catalyst, the hydrophobicity of the surface would keep the water molecules away from the acid sites, disfavoring the epoxide hydrolysis.

With regard to the recovery of the catalyst, this solid is very stable given the hydrogen peroxide conversion. However, the lower yield of epoxidation products and the large amount of cyclohexenone detected (cyclohexenyl hydroperoxide) after 1 h show that the activity for epoxidation is greatly reduced. As a consequence, the epoxidation/allylic oxidation selectivity is lower in the recovered catalyst (50/50), indicating that the direct epoxidation is almost completely suppressed. In conclusion, the end-capping has not, in this case, led to the positive effect described for other titanium catalysts (8a).

Modification of Si–Ti(O^{i}Pr) with Ethylene Glycol: Catalytic Activity

Although hydrophobicity is considered to be the main reason for the good catalytic performance of several solids (6, 17), all research efforts have been driven toward the modification of the siliceous surface in zeolites or silica-based catalysts rather than to the modification of the titanium environment. This trend has occurred in spite of the fact that the character of the environment in the immediate vicinity of the titanium should not be less important than the silica modification. One possible advantage of our catalyst is the presence of isopropoxy groups on the titanium centers, which are exchangeable by other groups and can lead to modification of the environment of the catalytic sites. This strategy has already been applied to this kind of catalyst in the oxidation of sulfides to sulfoxides with hydrogen peroxide (18), leading to more selective catalysts. This kind of modification is not possible when the titanium is included in the three-dimensional structure of the solid, such as in a zeolite or a mixed oxide for example. Our first idea involved the replacement with ethylene glycol (EG). The first problem in this approach was to be sure that the exchange had taken place, because the diol could be adsorbed not only on the titanium sites but also on the silica surface. Moreover, it is very difficult to distinguish spectroscopically between Ti-diol and diol-on-silica species. For this reason three reference points were taken, the loss of isopropanol during the preparation of the new solids, the carbon analysis, and the modification in catalytic activity and selectivity.

The preparation was carried out following the method used in the liquid phase, i.e., with the use of toluene as a solvent and the distillation of the toluene/isopropanol azeotrope in order to shift the equilibrium to the substituted form (Scheme 2). Isopropanol was detected in the distillate by GC and the amount detected was in good agreement with the carbon content in the Si–Ti(O^{i}Pr) catalyst. The analysis (Table 6) shows that Si–Ti(EG) has a C/Ti ratio higher than the expected value. This may be explained by



SCHEME 2

TABLE 6

Analysis of Si–Ti(EG)

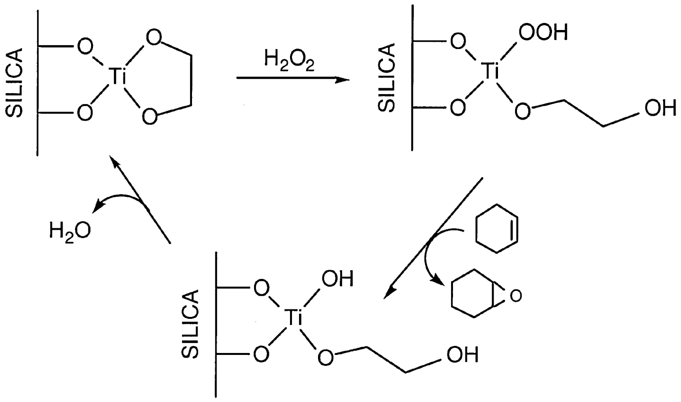
Run	C (mmol/g)	Ti (mmol/g)	C/Ti
0	3.44	1.14	3.02
1	5.07	—[a]	—[a]
2	4.92	—[a]	—[a]
3	5.83	1.10	5.30

[a] The titanium content was not determined because of the lack of sample.

a partial adsorption of ethylene glycol on the surface. It is important to note that there is no titanium leaching during this process.

The exchange with EG gives rise to a catalyst that is slightly less active and selective than Si–Ti(O^{i}Pr) in the first run (Table 7) but is much more stable, as shown by the results of the third run. Both yield and selectivity are almost the same and the epoxide hydrolysis is slightly reduced. However, analysis after the different runs (Table 6) shows that the carbon content increases, mainly after the first run as with Si–Ti(O^{i}Pr), but this adsorption does not affect the catalytic performance. So, in spite of the similar analysis, the adsorption on Si–Ti(O^{i}Pr) after the first run must be, at least in part, on the titanium sites, whereas in the case of Si–Ti(EG) the presence of a chelate complex must enhance the stability of this species, which helps to maintain the catalytic activity. It therefore seems clear that the titanium centers have been modified.

This catalyst seems to be more stable than other titanium catalysts, either bearing the titanium centers in the three-dimensional structure of the solid (5) or grafted on a support (12), as shown by the absence of titanium leaching after three runs (Table 6). In our case, the presence of a weak Ti–O(C) bond may drive the attack of hydrogen peroxide to this point, whereas the stronger Ti–O(Si) bonds remain intact. In Si–Ti(EG) only one bond of the chelate has to be broken (Scheme 3) to form the Ti–OOH active species and, after the oxidation process, the chelate can be formed again because of its high stability. Therefore, the formation of a titanium-diol chelate is a simple method of increasing the stability of the titanium centers on the silica surface.



SCHEME 3

Modification of Si–Ti(O^{i}Pr) with Tartaric Acid Derivatives: Catalytic Activity

After the study with a nonfunctionalized diol we tried a new strategy based on the introduction of functionalized diols, similar to that performed in the case of sulfide oxidation (18). We chose tartaric acid derivatives because of their availability and we selected tartaric acid (TA) and diethyl tartrate (DET) as model compounds with groups of a different nature. The exchange method for these diols was the same as described above but, given that tartaric acid was not soluble in toluene, we used butyl acetate and in this case the distillate was not an azeotrope but a mixture of butyl acetate and isopropanol.

The modification of the solid was again followed by analysis of isopropanol in the distillate, carbon analysis (Table 8), and assessment of catalytic activity. However, the nature of these new ligands allowed us to detect them by IR spectroscopy. Self-supported wafers of the new solids treated under vacuum were analyzed and a very broad carbonyl band was apparent in both solids (Fig. 3), which provided additional evidence for the exchange of ligands.

TABLE 7

Results of the Epoxidation of Cyclohexene with 30% H_2O_2 Using Si–Ti(EG) as a Catalyst

		% Yield[a]								
Run	t (h)	Epoxide	Diol	Alcohol	Ketone[b]	Overall[c]	TON[d]	% Select. H_2O_2[e]	Epoxide/Diol	Epoxidation/ Allylic ox.[f]
1	1	18	8	9	(9)	(44)	—	—	69/31	—
	24	2	39	25	5	71	8.3	76	5/95	58/42
2	1	17	7	7	(11)	(42)	—	—	71/29	—
	24	4	36	26	4	70	7.9	72	10/90	58/42
3	1	17	9	8	(9)	(43)	—	—	65/35	—
	24	8	35	28	3	74	8.5	75	19/81	58/42

[a–f] As in Table 1.

TABLE 8

Analysis of Si–Ti(TA) and Si–Ti(DET)

Catalyst	Run	C (mmol/g)	Ti (mmol/g)	C/Ti
Si–Ti(TA)	0	5.09	0.99	5.14
	1	5.22	—[a]	—[a]
	2	4.62	—[a]	—[a]
	3	5.24	0.98	5.35
Si–Ti(DET)	0	4.82	1.13	4.26
	1	6.87	—[a]	—[a]
	2	6.42	—[a]	—[a]
	3	9.81	0.87	11.27

[a] The titanium content was not determined because of the lack of sample.

The results of the cyclohexene epoxidation are gathered in Table 9. The yield of epoxidation products obtained with Si–Ti(TA) was higher than that obtained with Si–Ti(O^{i}Pr) or Si–Ti(EG), and was associated with a reasonable epoxidation/allylic oxidation selectivity (67/33). More importantly, this catalyst keeps its catalytic activity after two runs, with the best selectivities found with recycled catalysts (epoxidation/allylic oxidation = 60/40). The catalyst is also very stable, as shown by the analyses (Table 8), given that neither carbon nor titanium contents are modified after three runs. Its higher catalytic activity was shown in the epoxidation of cyclooctene, which is faster than with Si–Ti(O^{i}Pr), but again the selectivity in H_2O_2 falls to 37%. The higher catalytic activity might be due to a new reaction mechanism. The presence of carboxylic acid groups near the titanium centers might favor the oxidation to peroxycarboxylic acid groups, and these might be responsible for part of the epoxidation reaction. Another possible explanation is the more hydrophilic character of the titanium environment in Si–Ti(TA). In this case the effect should be similar to the modification of the silica surface, given that the balance Ti-hydrophilicity/silica-hydrophobicity changes in the same way by modification of one of the variables.

On the other hand, Si–Ti(DET) has a behavior similar to Si–Ti(EG), but the yield rises in the third run. However, the selectivity remains rather low and there is some titanium leaching and significant adsorption of by-products.

These results show the possibility of modifying the catalytic centers with chiral diols, opening the way to the preparation of enantioselective heterogeneous catalysts.

Simultaneous Modification of Ti Centers and silica surface

With the previous conclusions in mind it remained to assess the effect of the simultaneous modification of the hydrophilic/hydrophobic character of both the titanium centers and the silica surface. Si(ec)–Ti(TA) was prepared by treatment of Si(ec)–Ti(O^{i}Pr) with L-tartaric acid and the analysis of this system is shown in Table 4. The C/Ti ratio is higher than the expected value, which may be due to some adsorption of tartaric acid. The results of the cyclohexene epoxidation are gathered in Table 10. The catalytic performance is good, with high TON due to the low functionalization of the catalyst, as it happened with Si(ec)–Ti(O^{i}Pr). In this case the calculated TOF is around 32 h^{-1},

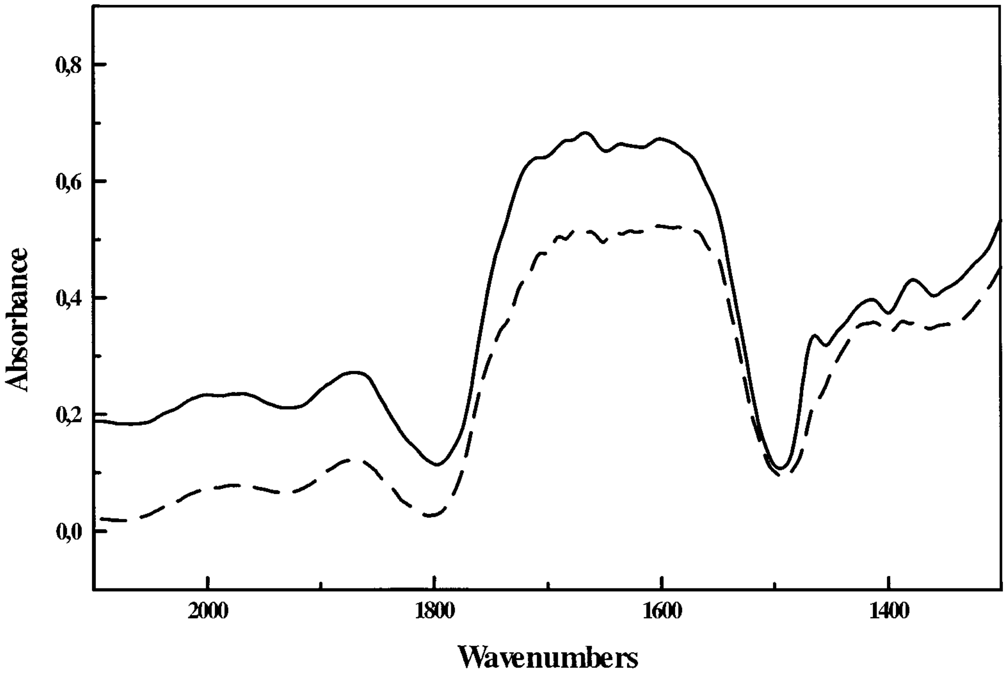


FIG. 3. IR spectra of Si–Ti(TA) (continuous line) and Si–Ti(DET) (dotted line).

TABLE 9

Results of the Epoxidation of Cyclohexene with 30% H_2O_2 Using Si–Ti(TA) or Si–Ti(DET) as a Catalyst

			% Yield[a]								
Catalyst	Run	*t* (h)	Epoxide	Diol	Alcohol	Ketone[b]	Overall[c]	TON[d]	% Select. H_2O_2[e]	Epoxide/Diol	Epoxidation/ Allylic ox.[f]
Si–Ti(TA)	1	1	13	19	7	(13)	(52)	—	—	41/59	—
		24	0	61	23	7	91	12.2	97	0/100	67/33
	2	1	18	18	8	(10)	(54)	—	—	50/50	—
		24	1	56	27	6	91	12.2	97	2/98	63/37
	3	1	16	22	7	(8)	(53)	—	—	42/58	—
		24	2	47	27	5	81	10.7	85	4/96	60/40
	Cyclooctene	1	31	0	0	0	31	—	—	100/0	100/0
		24	37	0	0	0	37	4.7	37	100/0	100/0
Si–Ti(DET)	1	1	14	3	7	(12)	(36)	—	—	82/18	—
		24	2	37	28	4	71	8.4	76	5/95	55/45
	2	1	18	11	10	(5)	(44)	—	—	62/38	—
		24	10	25	32	3	70	8.1	73	29/71	50/50
	3	1	19	0	8	(6)	(33)	—	—	100/0	—
		24	23	22	32	5	83	12.6	88	51/49	54/46

[a–f] As in Table 1.

slightly higher than that obtained with Si(ec)–Ti(O^{i}Pr). The epoxidation/allylic oxidation selectivity is the best that was obtained with this kind of catalyst (72/28). Moreover, the hydrolysis to diol is reduced to 50% after 24 h, in spite of the presence of tartaric acid groups. As a consequence, this solid is the catalyst with the highest epoxide selectivity described in this work.

However, the recovered Si(ec)–Ti(TA) shows different properties. A new peak is observed in the GC analysis, which is the main product, together with the ketone peak after a short reaction time. The evaporation of the solvent from one sample and ^{1}H NMR analysis of the crude material showed that the product was cyclohexenyl hydroperoxide, which was not completely decomposed in the injector. Therefore, when the amount of hydroperoxide in the mixture is large, both ketone (from the decomposition) and hydroperoxide are detected by GC. In Table 10 both products have been listed together in the ketone column, in order to maintain the format of the table, in spite of the fact that the analyzed product is cyclohexenyl hydroperoxide. This fact shows that after one run Si(ec)–Ti(TA) is deactivated for epoxidation with cyclohexenyl hydroperoxide, given that this is the main product after 1 h. After 24 h the amount of hydroperoxide is still high and the H_2O_2 selectivity is higher than 100%, which can be attributed to the involvement of atmospheric O_2 (12). If the hydroperoxide is not included, the epoxidation/allylic oxidation selectivity is 62/38, a value very close to those obtained with the rest of the catalysts. This fact shows that the activity for the direct epoxidation with H_2O_2 is reduced to the same extent as the activity for epoxidation with hydroperoxide, probably because the mechanism is analogous.

The nature of this deactivation, similar to that observed with Si(ec)–Ti(O^{i}Pr), is not easy to explain and further work is needed to elucidate whether the end-capping or the lower titanium content is responsible for this behavior.

TABLE 10

Results of the Epoxidation of Cyclohexene with 30% H_2O_2 Using Si(ec)–Ti(TA) as a Catalyst

		% Yield[a]								
Run	*t* (h)	Epoxide	Diol	Alcohol	Ketone[b]	Overall[c]	TON[d]	% Select. H_2O_2[e]	Epoxide/Diol	Epoxidation/ Allylic ox.[f]
1	1	21	11	7	(13)	(52)	—	—	66/34	—
	24	31	29	21	2	83	53.1	85	51/49	72/28
2	1	8	0	6	(26)	(40)	—	—	100/0	—
	24	34	15	30	(24)	(103)	79.4	127	69/31	(48/52)[g]
3	1	5	0	8	(28)	(41)	—	—	100/0	—
	24	32	7	32	(34)	(105)	86.9	139	82/18	(37/63)[h]

[a–f] As in Table 1.

[g] If cyclohexenyl hydroperoxide is not included, epoxidation/allylic = 62/38.

[h] If cyclohexenyl hydroperoxide is not included, epoxidation/allylic = 55/45.

Studies of Filtration at the Reaction Temperature

Finally, a question remains regarding the homogeneous or heterogeneous character of this process. Recently it has been proposed that filtration at the reaction temperature and execution of the reaction in the liquid phase can be used to resolve this question (17, 19). We carried out this kind of experiment with Si–Ti(O^{i}Pr), Si–Ti(TA), and Si(ec)–Ti(TA).

First of all, it was necessary to choose a time for filtration, which was set at 7 min in order to obtain a low yield that could increase if the reaction took place in the liquid phase. The filtration was carried out quickly at 80°C through a hot filter and the solution was collected in a cooled flask in order to stop any further reaction. The liquid phase was subsequently heated again at 80°C and the reaction monitored by GC. The recovered Si–Ti(O^{i}Pr) was treated in the usual way and a second reaction in the liquid phase was also carried out. The solid recovered in this second filtration was used as a catalyst in a new reaction and its results compared with the freshly prepared catalyst (Fig. 4). As can be seen, the epoxidation stopped after the filtration and only a low yield was obtained from the noncatalyzed reaction (Table 1). The amount of cyclohexenone, or more likely cyclohexenyl hydroperoxide, slowly increases in contrast to the decrease observed in the catalyzed reaction. This result shows that some leaching may exist but the species in solution is not active for epoxidation, even for epoxidation with alkyl hydroperoxides, but only for the allylic oxidation. After the second filtration the results are nearly the same and the recovered solid behaves in the same way as the freshly prepared catalyst. The existence of leaching was confirmed by analysis of the recovered solid, which had 0.87 mmol Ti/g. We can therefore conclude that the epoxidation reaction takes place on the surface of the solid catalyst, whereas allylic oxidation can take place both on the solid and in the liquid phase, where a small part of nonactive titanium is leached.

The results of an analogous experiment with Si–Ti(TA) are shown in Fig. 5. In this case the behavior is very different from that of Si–Ti(O^{i}Pr). After the first filtration the liquid phase had catalytic activity, as shown by the yield in epoxidation products (epoxide and diol). However, the behavior with regard to cyclohexenyl hydroperoxide is different, given that in solution its yield does not diminish. A second filtration led to a solution that was less active than the first one, but the still significant activity prompted us to carry out a third filtration. The third solution was no longer active and we then tested the recovered solid. This was even more active than the freshly prepared catalyst, given that the yields of epoxidation and allylic oxidation were higher in spite of its lower Ti content (0.62 mmol/g). Thus, two different active titanium species seem to coexist on the surface, one able to pass to the liquid phase under the reaction conditions and the other well-grafted to the silica surface. The nongrafted species might be produced in the treatment of Si–Ti(O^{i}Pr) with tartaric acid, but this species is strongly adsorbed on the surface at room temperature, as shown by the fact that it is not lost under the normal reaction procedure. So both homogeneous and heterogeneous catalysis play a role and the two species have similar contribution to catalytic activity under the normal reaction conditions. It can be speculated that titanium species grafted through

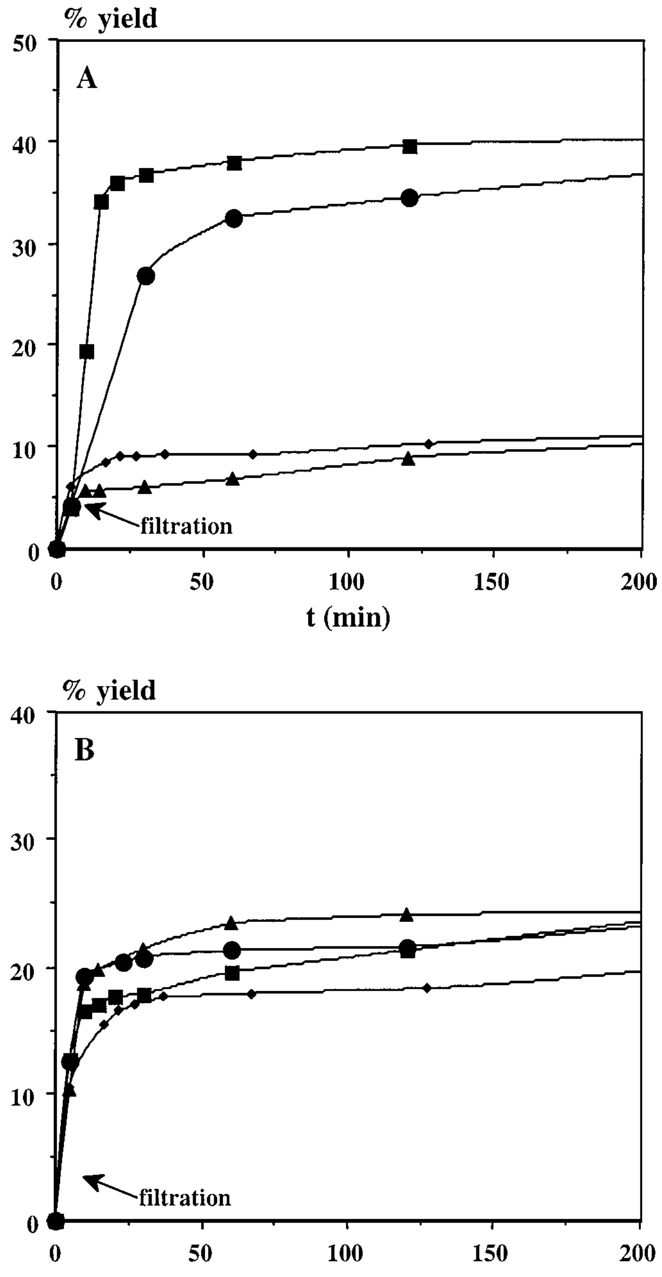


FIG. 4. Filtration of Si–Ti(O^{i}Pr) under the following reaction conditions: (A) epoxidation, (B) allylic oxidation. (■) Freshly prepared catalyst, (◆) solution after the first filtration, (▲) solution after the second filtration, (●) recovered solid.

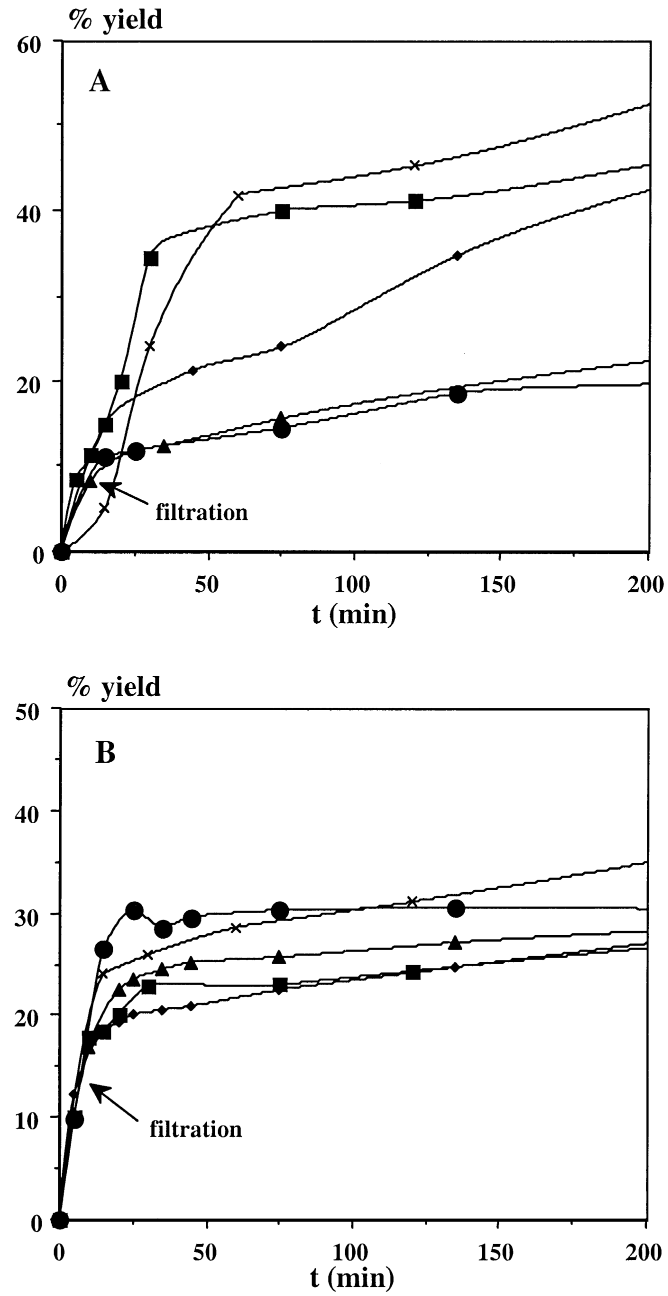


FIG. 5. Filtration of Si–Ti(TA) under the following reaction conditions: (A) epoxidation, (B) allylic oxidation. (■) Freshly prepared catalyst, (◆) solution after the first filtration, (▲) solution after the second filtration, (●) solution after the third filtration, (✕) recovered solid.

two covalent bonds to the silica surface are more stable than those species with only one bond. If this hypothesis were correct, the end-capped silica with vicinal silanol groups would lead to a more stable catalyst, even after treatment with tartaric acid.

In an attempt to confirm this hypothesis the filtration experiment with Si(ec)–Ti(TA) was also carried out and the results are shown in Fig. 6. The solution after the first filtration has no activity for expoxidation, in contrast to Si–Ti(TA), but higher activity for allylic oxidation than the original solid. The solution after the second filtration experiment again did not show any activity. These results confirm that titanium leaching occurs only in species that are active for allylic oxidation, as happened with Si–Ti(O^{i}Pr), and the epoxidation reaction is truly heterogeneous. However, the behavior of the recovered solid is different from that

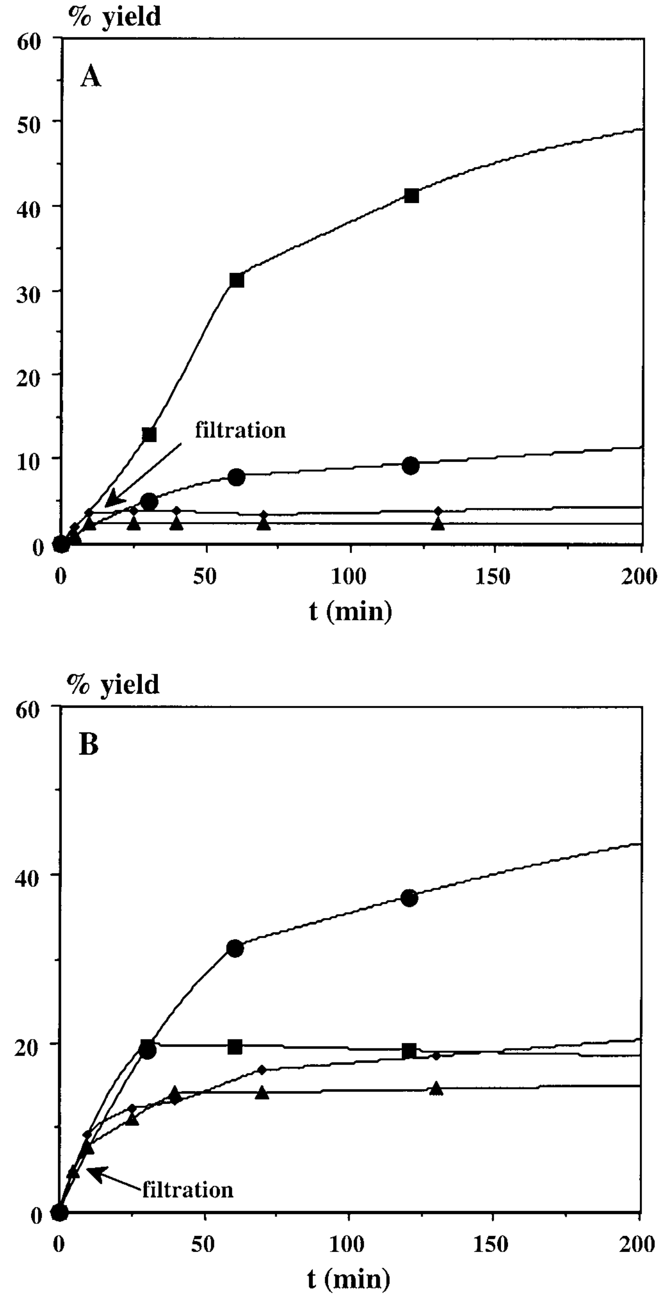


FIG. 6. Filtration of Si(ec)–Ti(TA) under the following reaction conditions: (A) epoxidation, (B) allylic oxidation. (■) Freshly prepared catalyst, (◆) solution after the first filtration, (▲) solution after the second filtration, (●) recovered solid.

observed with Si–Ti(O^{i}Pr). This solid shows lower activity for epoxidation and higher activity for allylic oxidation than the original solid, as happened with the catalyst recovered after one reaction (Table 10). This change seems to indicate an important modification of the titanium centers after treatment with hydrogen peroxide, a change that is not observed in the catalysts with a higher titanium charge and without end-capping.

Further work is currently in progress in order to increase the stability of the catalysts against titanium leaching and deactivation and to determine the origin of the modifications observed in the recycled catalysts.

CONCLUSIONS

Silica-supported titanium catalysts prepared with Ti(O^{i}Pr)$_4$ are active in the epoxidation of alkenes with 30% H_2O_2 at 80°C. In the case of cyclooctene only epoxide is obtained. With cyclohexene a mixture of products from epoxidation, hydrolysis of the epoxide, and allylic oxidation is obtained. Allylic oxidation has a radical mechanism and generates cyclohexenyl hydroperoxide as a primary product. The epoxidation takes place at the titanium sites through two mechanisms; direct reaction with H_2O_2 and epoxidation with the generated hydroperoxide. Hydrolysis of the epoxide is a secondary reaction, which is catalyzed by acidic sites that are mainly the titanium centers. The reaction conditions used in this work leads to low TON because of the high functionalization of the solids. However, the calculated TOF is similar to that reported in the literature for Ti-MCM-41. A limitation of this catalysts is the need for a high alkene/H_2O_2 ratio (>10) and lower ratios reduce the yield and even the epoxidation/allylic selectivity when equimolecular amounts are used. The presence of isopropoxy groups opens the way for the modification of the environment of the titanium by exchange with diols. Ethylene glycol leads to a more stable catalyst, probably by formation of a chelate. The use of tartaric acid derivatives also modifies the catalytic activity. In fact, the solid with L-tartaric acid is more active (91% yield, 67/33 epoxidation/allylic oxidation ratio), which might be due to the existence of another mechanism, consisting of the oxidation of carboxylic acid groups to peroxycarboxylic acid groups, or to the increase in hydrophilicity of the titanium centers. The increase in the hydrophobic character of the silica surface alone does not have a significant influence on the selectivity, but the lower Ti content makes the TON increase. The combination of this increase in hydrophobic character with the treatment with tartaric acid leads to the best catalyst described in this work, which has both high activity and epoxidation/allylic oxidation selectivity (72/28). Moreover, the epoxide hydrolysis is noticeably reduced. However, the recovered catalyst is less active for epoxidation, as shown by the large amount of cyclohexenyl hydroperoxide remaining after 24 h. The experiments involving filtration under the reaction conditions show that the epoxidation reaction is truly heterogeneous in the case of Si–Ti(O^{i}Pr) and Si(ec)–Ti(TA), but the latter deactivates by the action of hydrogen peroxide. In contrast, with Si–Ti(TA) the reaction takes place in both the homogeneous and the heterogeneous phase with similar contribution of the two kinds of species. These results show that not only the modification of the silica surface but also the change in the titanium environment affect the results in epoxidation reactions with 30% H_2O_2 and the stability of the catalyst. This work also opens the way for the use of these solids as chiral heterogeneous catalysts.

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