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Epoxidation of Crotyl Alcohol Using Ti-Containing Heterogeneous Catalysts: Comments on the Loss of Ti by Leaching

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The leaching of Ti from the redox molecular sieve TS-1 is compared and contrasted with Ti leaching from Ti–Alβ, Ti–MCM-41, and a Ti–xerogel under both batch and continuous flow reaction conditions for the oxidation of crotyl alcohol with hydrogen peroxide. The product distributions for the catalysts are similar, with epoxide being formed initially and, subsequently, the secondary reaction products of the triol and ether diols. Ti leaching is more pronounced under continuous flow conditions and the order of stability is TS-1 > Ti–Alβ > Ti–MCM-41 > Ti–xerogel, for both continuous flow and batch reaction conditions. TS-1 leaching is shown to be caused by the reaction of triol with TS-1 in the presence of hydrogen peroxide. A possible mechanism in which the triol byproduct chelates the Ti and breaks the Ti–O–Si framework bonds, leading in turn to the formation of a Ti species in solution, is proposed. The soluble Ti species is found to be an active homogeneous catalyst giving triol as the major product from crotyl alcohol. Under batch reaction conditions, it is possible that an equilibrium is established between the solution Ti species and Ti on the catalyst surface. This equilibrium is perturbed when continuous flow conditions are used, and this leads to increased Ti leaching. © 2001 Academic Press

Key Words: **epoxidation of allylic alcohols; heterogeneous epoxidation using TS-1; heterogeneous epoxidation using Ti-β; heterogeneous epoxidation using Ti-MCM-41; heterogeneous epoxidation using Ti-xerogel; Ti-leaching.**

INTRODUCTION

Ti-containing materials have been used extensively as oxidation catalysts for both gas phase and liquid phase reactants. The interest in the use of titanium silicates as heterogeneous catalysts was prompted by the discovery that the microporous titanium silicalite TS-1 (1) was effective for the oxidation of hydrocarbons (2–4) and alcohols (5, 6) using hydrogen peroxide as oxidant. Since then, considerable attention has been given to oxidations using wider pore Ti-containing zeolites, e.g., Ti-β (7, 8), and mesoporous Ti-containing MCM-41 (9–12) materials. In addition, titania-silica co-gels, which have nonregular pore structures (13, 14), have been extensively studied for oxidation reactions by Baiker and co-workers. (15, 16). The use of these Ti-containing catalysts for oxidation is, therefore, well established at this time (17), and the range of active catalysts has been extended to include other transition metal-containing microporous and mesoporous materials (18, 19).

Although significant effort has been given to establishing the reactivity of these Ti-containing catalysts, relatively little attention has been given to the stability of these materials under typical reaction conditions. Recently, Sheldon *et al.* (20) have considered the possibility of leaching of metal cations from the framework sites of these catalysts. This leaching is due to solvolysis by polar molecules, either reactants or products, reacting with the metal–oxygen framework, resulting in the removal of the metal into solution. Sheldon *et al.* (20) proposed two types of leaching: (a) the metal may leach but is not active as a homogeneous catalyst and hence there is no interference of the soluble metal complex with the catalyzed reaction of interest, and (b) the metal leaches and provides an active homogeneous oxidation catalyst and, in this case, the observed catalyst activity is a complex mixture of homogeneous and heterogeneous processes. Alternatively, the catalyst structure can be stable under reaction conditions and the reaction can be considered to be wholly heterogeneously catalyzed. However, very low levels of leaching may occur over a long period of time, particularly for catalysts tested under standard batch reaction conditions. Low concentrations of metals in solution can be very active catalysts with a range of oxygen donors. For example, 1–2 ppm of chromium leached from CrAPO-5 was found to be responsible for the oxidation activity of this catalyst (21). Recent studies have addressed this issue, and a large number of redox transition metal microporous and mesoporous catalysts have been shown to leach metals that subsequently

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act as homogeneous catalysts. These include VS-1 (22, 23), VAPO-5 (24, 25), V- and Cr-MCM-41 (26), and CoAPO-5 (27, 28). Although TS-1 is remarkably stable to leaching of Ti, it has been observed during the ammoxidation of cyclohexanone with ammonia and hydrogen peroxide (29) and the epoxidation of propene (30). Purely siliceous MCM-41 materials are very stable at elevated temperatures in air or oxygen; however, even in the presence of low concentrations of water, studies have shown that the mesoporous structure can collapse due to silicate hydrolysis (31–33). Hence, Ti-MCM-41 materials may be expected to be less stable in the presence of hydrogen peroxide than TS-1.

In this paper, we present a detailed study of the relative stability of Ti-containing heterogeneous catalysts for the epoxidation of crotyl alcohol with hydrogen peroxide, under both batch and flow reactor conditions.

EXPERIMENTAL

Synthesis of Materials

Synthesis of TS-1. TS-1(2.4 mol% Ti) was prepared according to the method of Tarramasso *et al.* (1) Tetraethyl orthotitanite (3 g, Aldrich) was added dropwise to tetraethyl orthosilicate (91 g, Merck) and the mixture was stirred for 2 h. To the clear solution, tetrapropylammonium hydroxide (100 g, Alfa, 40% in water, K $<$ 1 ppm, Na $<$ 3 ppm) and deionized water (60 g) were added with stirring at 25°C. The clear gel was stirred at 25°C for 1 h and then heated at 80°C for 5 h to aid hydrolysis; during this procedure, the volume was maintained by addition of deionized water. The resulting solution was heated in a Teflon-lined, stainless steel autoclave at 175°C for 10 days. The crystalline material was recovered by centrifugation, washed with deionized water, dried at 100°C, and calcined in air at 550°C for 24 h.

Synthesis of Ti–Alβ. Ti–Alβ (3.2 mol% Ti) was synthesized by a method similar to that of Camblor *et al.* (34). Aqueous HCl (0.1 M, 4.51 g) was added dropwise to tetraethylorthosilicate (12.5 g, Merck) and stirred (25°C, 40 min). After cooling in ice (15 min) the mixture was added dropwise with stirring to a cooled solution of tetrabutyl orthotitanate (0.65 g, Aldrich) in propan-2-ol (9 g) and stirred for a further period (0°C, 20 min; 25°C, 25 min). Tetraethylammonium hydroxide (9.8 g, 35% in water, Alfa, K $<$ 1 ppm) was added dropwise with stirring until a white solid formed, which was dried (100%, 4 h). Aluminium isopropoxide (0.03 g) and the remainder of the template were added with stirring at 25°C. The resulting solid was placed in a Teflon-lined, stainless steel autoclave and heated at 135°C for 192 h. Ti–Alβ was recovered as a white crystalline solid by centrifugation, dried (100°C, 16 h), and calcined in air (550°C, 24 h).

Synthesis of Ti–MCM-41. Ti–MCM-41 (1.2 mol% Ti) was prepared using a procedure based on the method outlined by Koyano and Tatsumi (35). Tetrabutyl orthotitanate (0.27 g, Aldrich) was added dropwise with stirring to tetraethyl orthosilicate (14.4 g, Merck) at 0°C. Cetyltrimethylammonium hydroxide (62 ml, 25% in water, prepared by ion exchange of cetyltrimethylammonium bromide, BDH), was added dropwise and the mixture was stirred (25°C, 1 h) and then heated (80°C, 4 h) to remove the ethanol. The solution was heated in an autoclave (120°C, 48 h) and the white solid formed was recovered by filtration, washed with deionized water, dried (100°C, 16 h), and heated under nitrogen (550°C, 8 h).

Synthesis of Ti–xerogel. Ti–xerogel (2 mol% Ti) was prepared using a procedure based on that reported by Klein *et al.* (36). Tetraethyl orthosilicate (10.41 g, Merck) was hydrolyzed (0°C, 30 min) by reaction with HCl (1.8 g, 0.05 M) in propan-2-ol (2.5 mol). Tetrabutyl orthotitanate (0.336 g, Aldrich) was added dropwise with vigorous stirring (25°C, 1 h). Aqueous ammonia was added until a gel was formed; this was dried (135°C, 2 h) and calcined (550°C, 24 h).

Catalyst Testing

Catalysts were studied for the epoxidation of crotyl alcohol using the following standard procedures.

Batch reactor. Crotyl alcohol (0.72 g) and aqueous hydrogen peroxide (1.35 g, 30 vol%) were stirred together in methanol (50 ml) in a round-bottomed flask in a thermostatted oil bath at 30°C. The catalyst was added (0.1 g) to initiate the reaction and, at subsequent times, small aliquots were removed, filtered hot through a layer of celite, cooled, centrifuged to remove any catalyst particles, and analyzed using gas chromatography using dimethylsulfone as an internal standard. Ti leaching was determined using ICP-MS analysis. Blank experiments using anatase and silicalite as catalysts showed no product formation under standard reaction conditions. In addition, anatase was observed to be insoluble in the reaction mixture and no Ti leaching was observed.

Continuous flow reactor. Catalysts were pelleted for use in the continuous flow reactor. Silica (5 g, fumed, BDH) was added to the Ti catalyst (1 g) and the mixture pelleted, washed, and sieved to give particles (1–3 mm). Premixed reactants (crotyl alcohol (100 g), aqueous hydrogen peroxide (30% vol, 173 g), dimethylsulfone (5 g, internal standard), and methanol (100 ml)) were fed continuously (0.2 ml/h) to an upflow reactor (15 ml total volume) using a Watson and Marlow multihead 505S pump. Exit samples were stored at 0°C prior to analysis by gas chromatography for product selectivity, pH determination, hydrogen peroxide content, and the concentration of Ti using ICP-MS. The reactor was maintained at 50°C using a thermostatically controlled water bath. A burette was installed at the top of the reactor to monitor oxygen evolution due to hydrogen peroxide decomposition. The premixed reactant solution was regularly monitored to ensure the composition remained constant. The conditions used were as follows:

TS-1,	pellets (4.5g, 100ml), residence time 8.3 h;
Ti–Alβ,	pellets (3.7 g, 7.0 ml), residence time 5.8 h;
Ti–MCM-41,	pellets (4.2 g, 7.0 ml), residence time 5.8 h;
Ti–xerogel,	pellets (3.5 g, 6.0 ml), residence time 5.0 h.

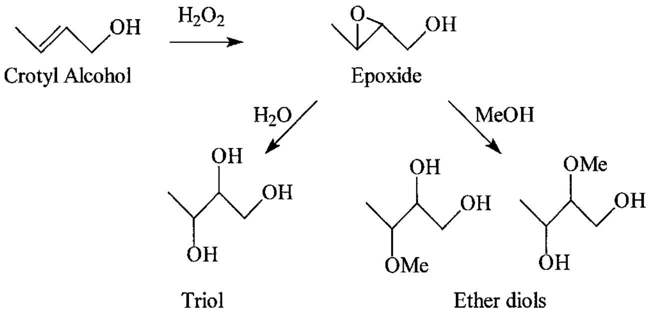
Characterization

Powder X-ray diffraction was carried out on a Siemens D5000 diffractometer using CuK_α radiation using quartz as an internal standard. Infrared spectra were obtained using a Perkin–Elmer system 2000 FTIR spectrometer fitted with a Mir TGS detector. Samples were diluted with KBr (1% sample) and pressed into discs. MAS NMR spectroscopy was carried out using a 400-MHz Chemagenetics CMX-infinity spectrometer with zirconia rotors. DR-UV spectra were obtained with a Cary UV-visible spectrophotometer using boron sulfate as a reference.

RESULTS

Epoxidation of Crotyl Alcohol Using Batch Reactions Conditions

The epoxidation of crotyl alcohol with hydrogen peroxide in methanol solvent was investigated using TS-1, Ti–Alβ, Ti–MCM-41, and Ti–xerogel as catalysts and the results are given in Tables 1–4. For TS-1 (Table 1), initially the epoxide was selectively formed and, at this stage, the pH increased. Subsequently, the epoxide reacted to form ether diols and triol and the pH decreased:



No titanium leaching was observed, within experimental error (<0.5 ppm), throughout the 330-h period of the experiment. For Ti–Alβ (Table 2) again the epoxide is formed selectively in the initial period and an increase in pH is observed. Subsequently, as with TS-1, the epoxide reacts and the triol becomes the dominant product. For Ti–Alβ, some leaching of Ti is observed but, after 190 h reaction, only 0.12% of the total Ti is removed from Ti–Alβ. For Ti–MCM-41 (Table 3), no catalytic activity for the direct formation of epoxide is observed under these reaction conditions but, eventually, triol, diol, and traces of epoxide are formed. Hydrogen peroxide decomposition is observed and some Ti leaching (0.15% of total Ti) after reaction for 170 h. For the Ti-xerogel catalyst (Table 4), a similar reaction profile to TS-1 was observed, except that the catalyst was less active initially. During the initial period, the epoxide is formed selectively and an increase in pH is observed. Subsequently, triol and ether diols are formed and the pH decreases. For the Ti–xerogel, significant leaching of Ti occurs, and 1.5% of the total titaniums is leached during the 234-h reaction period.

TABLE 1

Oxidation of Crotyl Alcohol with Hydrogen Peroxide in Methanol at 50°C under Batch Reaction Conditions Using TS-1 as Catalyst

	Conversion %		Yield %				
Time (h)	Crotyl alcohol	Hydrogen peroxide	Epoxide	Triol	Ether diols	pH	Ti leaching (ppm)
0	0	0	0	0	0	4	0.1
0.8	14.1	25.0	14.1	0	0	5	0.2
2.0	20.6	24.4	20.6	0	0	5.5	0.3
8.3	31.9	44.0	17.7	10.7	3.5	4	0.2
20.4	55.5	35.7	4.3	45.6	5.6	3	tr
68.4	83.0	73.2	0.5	72.5	10.0	1.5	0.3
117.3	90.9	81.0	tr	81.6	9.3	1.5	tr
217.1	89.7	95.8	tr	80.4	9.3	1	tr
290.9	93.8	97.0	tr	83.5	10.3	1	0.5
331.5	97.1	99.4	0.4	86.5	10.2	1	0.6

Epoxidation of Crotyl Alcohol Using Continuous Flow Reaction Conditions

The oxidation of crotyl alcohol with hydrogen peroxide in methanol solvent was investigated for the four catalysts using continuous flow conditions, as stated under the experimental conditions, and the results are given in Figs. 1–4. For TS-1 (Figure 1), initially the epoxide was formed at low conversion but, after 2–3 days time-on-stream, the crotyl

TABLE 2

Oxidation of Crotyl Alcohol with Hydrogen Peroxide in Methanol at 50°C under Batch Reaction Conditions Using Ti–Alβ as Catalyst

	Conversion %		Yield %				
Time (h)	Crotyl alcohol	Hydrogen peroxide	Epoxide	Triol	Ether diols	pH	Ti leaching (ppm)
0	0	0	0	0	0	4.5	0
0.3	5.0	7.0	5.0	0	0	4.5	8.7
1.0	4.1	19.1	4.1	0	0	6	9.7
21.1	58.6	71.9	tr	49.3	9.3	4	14.2
128.7	90.3	97.7	1.2	72.7	16.4	3	22.7
189.6	87.9	98.3	0.8	70.7	16.4	2	26.8

TABLE 3

Oxidation of Crotyl Alcohol with Hydrogen Peroxide in Methanol at 50°C under Batch Reaction Conditions Using Ti–MCM-41 as Catalyst

	Conversion %		Yield %				
Time (h)	Crotyl alcohol	Hydrogen peroxide	Epoxide	Triol	Ether diols	pH	Ti leaching (ppm)
0	0	0	0	0	0	4.5	0
1.7	0	18.1	0	0	0	4.5	2.9
3.4	0	29.8	0	0	0	4.5	3.7
15.4	0	68.7	0	0	0	4.5	10.4
64.0	26.2	88.0	0	23.2	3.0	4	17.2
169.1	83.9	97.0	1.0	67.0	15.9	2	18.0

alcohol conversion increased to 100% and the epoxide selectivity decreased and the triol and ether diols became the dominant products. Interestingly, some leaching of Ti was observed under continuous flow conditions, whereas none was observed under batch reaction conditions. The Ti leaching reached a maximum after ca. 4 days time-on-stream before declining steadily throughout the remainder of the 45-day experiment. Between 2 and 23 days time-on-stream, the reactor effluent became yellow in color, which is indicative of a Ti–peroxy complex in solution.

Ti–Alβ (Fig. 2) shows very similar trends in reactivity and Ti leaching to that of TS-1. However, in the case of Ti–Alβ, some deactivation is observed after ca. 20 days time-on-stream and the Ti leaching is considerably more significant, with a broad maximum occurring at ca. 8 days time-on-stream.

After an initial induction period, Ti–MCM-41 (Fig. 3), formed triol and ether diols as the main products, together with some epoxide. As with Ti–Alβ, decolorization is observed after ca. 20 days reaction time. For Ti–MCM-41, significant Ti-leaching is observed under continuous flow conditions.

TABLE 4

Oxidation of Crotyl Alcohol with Hydrogen Peroxide in Methanol at 50°C under Batch Reaction Conditions Using Ti–Xerogel as Catalyst

	Conversion %		Yield %				
Time (h)	Crotyl alcohol	Hydrogen peroxide	Epoxide	Triol	Ether diols	pH	Ti leaching (ppm)
0	0	0	0	0	0	4.5	0.1
0.9	3.7	1.8	3.7	0	0	5	5.4
1.9	3.6	14.1	3.6	0	0	5	7.2
42.5	12.8	22.7	1.9	9.2	1.7	2	22.7
117.1	52.2	54.6	0	45.0	7.2	1	27.4
234.1	100.0	91.6	0	87.8	12.2	1	165.2

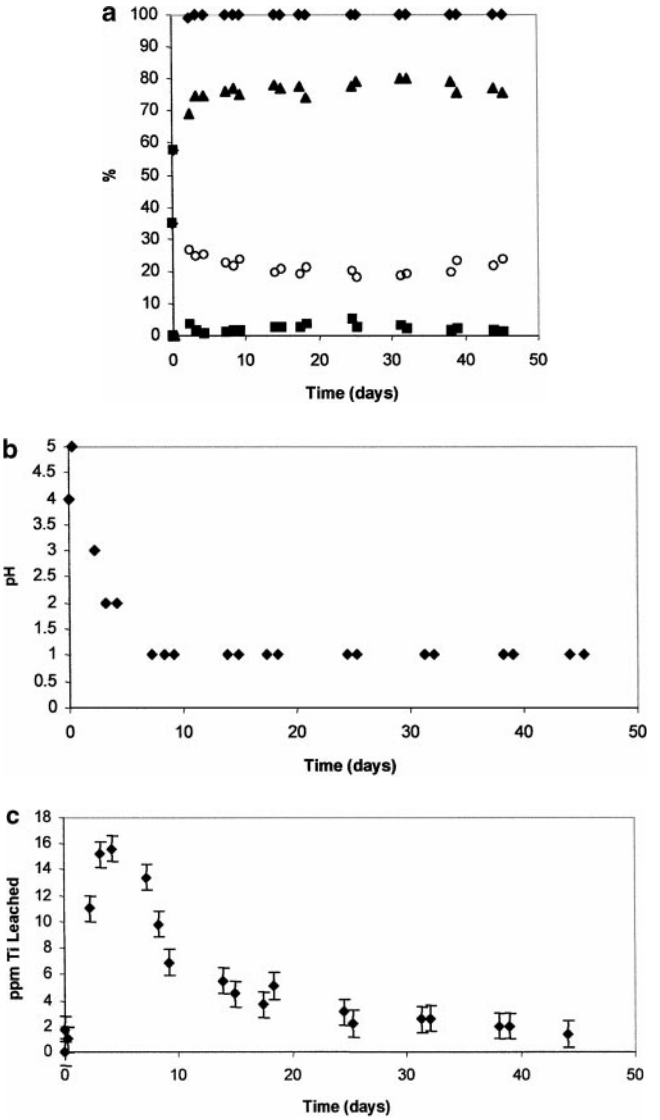


FIG. 1. Reaction of crotyl alcohol with hydrogen peroxide in methanol at 50°C with TS-1 under continuous flow conditions (residence time 8.3 h). (a) Crotyl alcohol conversion and product selectivity: ◆, crotyl alcohol conversion; ■, epoxide; ▲, triol; ○, ether diols, (b) pH, and (c) Ti leaching.

The oxidation of crotyl alcohol with hydrogen peroxide under continuous flow conditions with Ti–xerogel as catalyst also exhibits an initial induction period but, after ca. 2 days, steady conversion is observed with the product being mainly the triol and the ether diols (Fig. 4). After ca. 30 days operation, catalyst deactivation was observed. Ti leaching with the Ti–xerogel under these test conditions was most marked and, interestingly, the conversion of crotyl alcohol appears to correlate with the concentration of Ti in solution.

Ti-Leaching Experiments

TS-1 was used as a test material since, under experimental conditions this material was found to be the most resistant

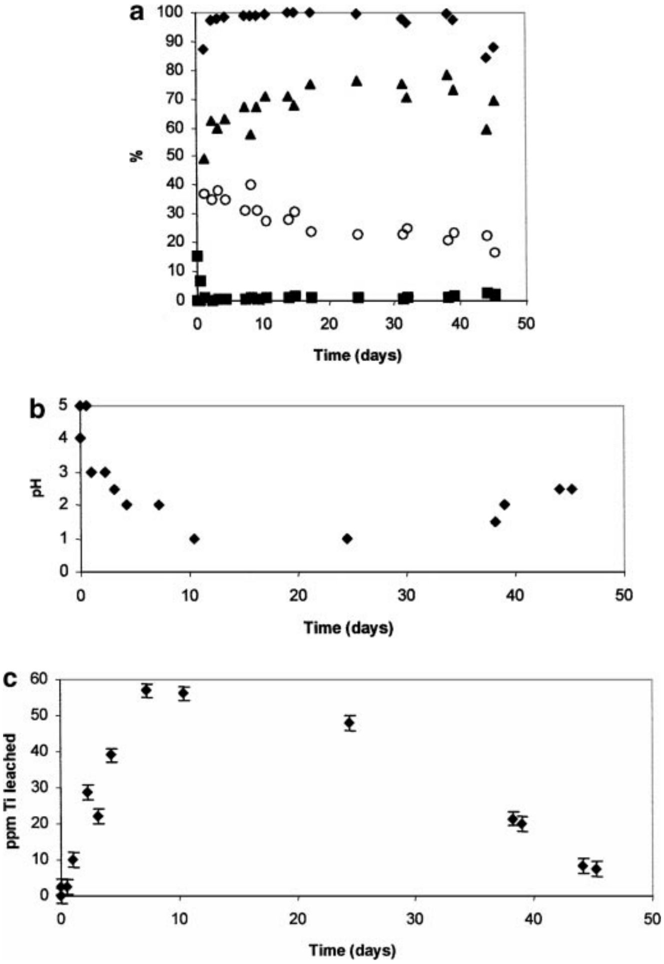


FIG. 2. Reaction of crotyl alcohol with hydrogen peroxide in methanol at 50°C with Ti–Alβ under continuous flow conditions (residence time 5.8 h). (a) Crotyl alcohol conversion and product selectivity: ◆, crotyl alcohol conversion; ■, epoxide; ▲, triol; ○, ether diols, (b) pH, and (c) Ti leaching.

to Ti leaching. A range of reagents was examined to investigate the factors that influence Ti leaching. Reagents were stirred with TS-1 at 50°C for 35 h, using batch reaction conditions. The results in Table 5 show that, for leaching to be observed, a combination of a triol together with hydrogen peroxide is required. Similar experiments with Ti–Alβ indicated that much higher Ti leaching is observed for this material. For example, heating with glycerol and *tert*-butyl hydroperoxide in methanol at 50°C leads to leaching of 0.013% of the Ti from TS-1, but leads to loss of 0.33% of the Ti from Ti–Alβ.

TABLE 5

Ti-Leaching Experiments for TS-1 (Crystallized 2 Days)

Conditions	Ti leaching (%)[a]
Hydrochloric acid (1 M)	0.002
Hydrogen peroxide	0.010
Crotyl alcohol	0.001
2,3 butanediol in methanol	0.005
Glycerol and hydrochloric acid	0.005
Glycerol, hydrochloric acid, and methanol	0.003
Glycerol and *tert*-butylhydroperoxide	0.013
Glycerol, hydrogen peroxide, and methanol	16.2

[a] Fresh TS-1 (2-day crystallization contains 22,060 ppm Ti).

Oxidation Using Titanyl Acetylacetonate

Crotyl alcohol oxidation with hydrogen peroxide was investigated using a solution of titanyl acetylacetonate complex at 50°C (Table 6). This titanium complex was selected as a model for solution Ti species that could be formed in solution due to Ti leaching. For the initial period (ca. 3 h), epoxide selectivity was high but, subsequently, the pH decreased to pH 2.0 after ca. 20 h and ether diols and triol were observed as products. The titanium complex also

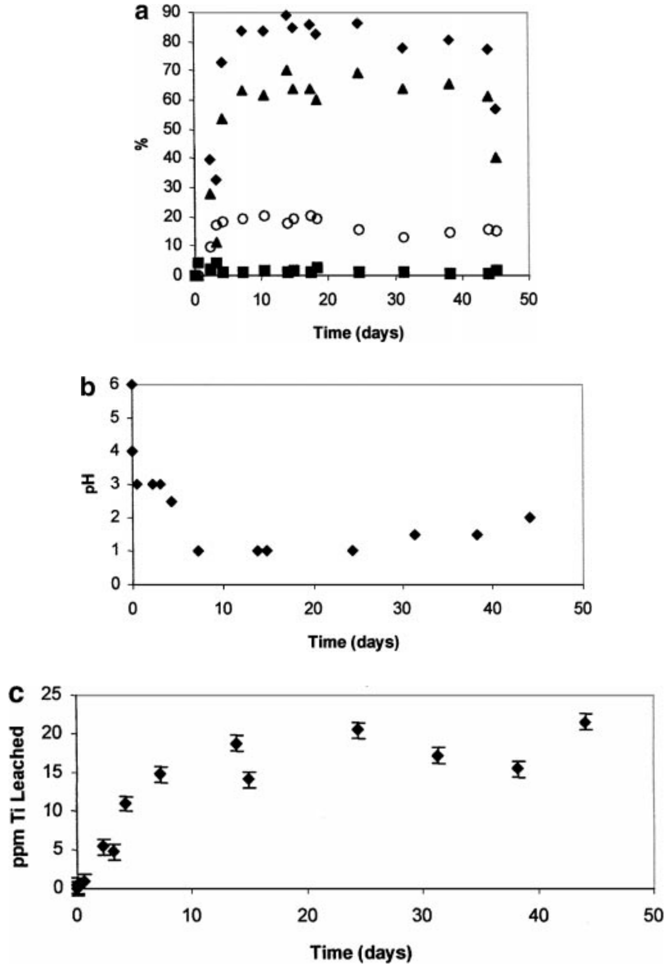


FIG. 3. Reaction of crotyl alcohol with hydrogen peroxide in methanol at 50°C with Ti–MCM-41 under continuous flow conditions (residence time 5.8 h). (a) Crotyl alcohol conversion and product selectivity: ◆, crotyl alcohol conversion; ■, epoxide; ▲, triol; ○, ether diols, (b) pH, and (c) Ti leaching.

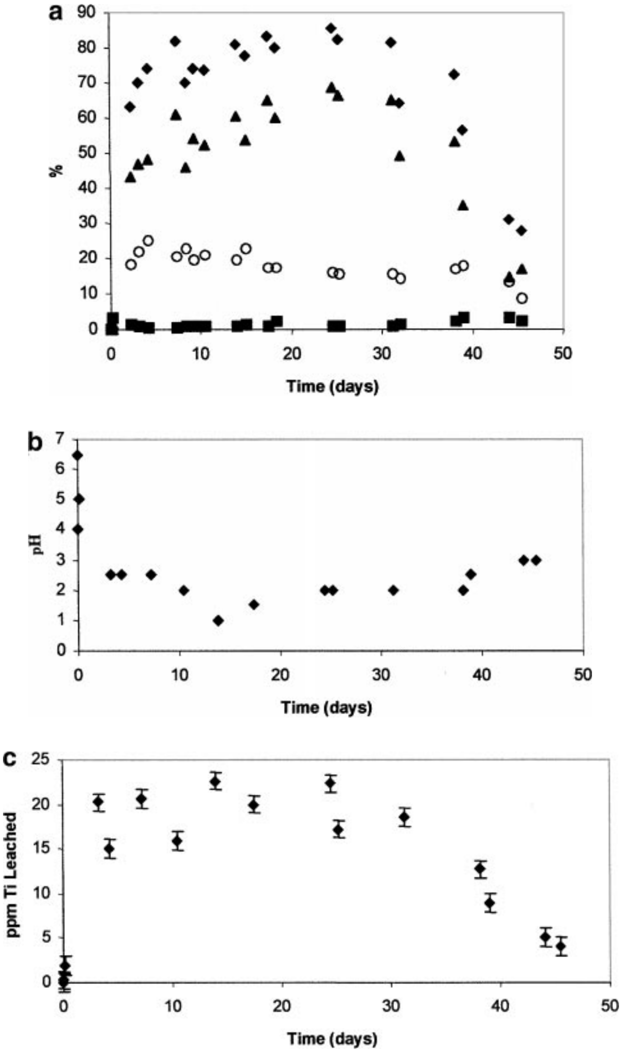


FIG. 4. Reaction of crotyl alcohol with hydrogen peroxide in methanol at 50°C with Ti–xerogel under continuous flow conditions (residence time 5.0 h). (a) Cotyl alcohol conversion and product selectivity: ◆, crotyl alcohol conversion; ■, epoxide; ▲, triol; ○, ether diols, (b) pH, and (c) Ti leaching.

gave decomposition of hydrogen peroxide. From this experiment, it is clear that solution titanium species formed from leaching could play an active role in catalyst testing experiments with these catalysts. To examine this further, filtrates from the reaction mixtures of TS-1 catalyzed experiments were studied. The filtrates from the TS-1 catalyzed reaction were selected since TS-1 demonstrated the highest stability under reaction conditions of the materials examined. Filtrates containing 4 and 25 ppm Ti were reacted with crotyl alcohol and hydrogen peroxide under standard conditions. After 80 h reaction, 55% crotyl alcohol conversion was observed with the 4-ppm Ti filtrate (yields: epoxide 0%, triol 54%, ether diols 1%), and the 25-ppm Ti filtrate gave 89% crotyl alcohol conversion (yields: epoxide 0%, triol 83%, ether diols 6%). These experiments demonstrate the concentration of Ti dissolved in the reaction medium, observed in the experiments with Ti-containing catalysts, could contribute to a homogeneously catalyzed reaction pathway that could be as significant as the heterogeneously catalyzed process. Furthermore, the homogeneous reaction leads exclusively to the formation of triol from the reaction of crotyl alcohol with hydrogen peroxide. Similar experiments using *tert*-butyl hydroperoxide with the titanyl acetylacetonate complex gave only trace levels of product formation and this suggests that this oxidant, and other organic hydroperoxides, may be preferred for the observation of heterogeneously catalyzed reactions with Ti-containing catalysts, other than TS-1.

Catalyst Characterization

Catalysts before and after testing in the continuous flow experiments were selected for study, since these conditions gave the highest levels of Ti leaching.

TS-1. Powder X-ray diffraction of TS-1 before and after catalyst testing showed no change and the diffraction pattern was consistent with literature data (1). Similarly, ^{29}Si MAS NMR spectroscopy showed no differences for fresh and used samples. FT-IR spectroscopy revealed a small difference in the absorption at 963 cm^{-1} for the material used, which is consistent with the loss of Ti from the structure. Transmission electron microscopy showed that the TS-1 crystallites were highly crystalline, but the surface of the crystals was decorated with small (approximately 1 nm) particles considered to be anatase. Raman spectroscopy confirmed the presence of anatase in the sample (Raman shifts: 642, 517, 387 cm^{-1}), but no changes were observed between fresh and used catalysts.

Diffuse reflectance UV spectroscopy of the fresh catalyst shows a major absorption at 208 nm, corresponding to tetrahedral Ti in the silicate framework (Fig. 5). There is also a broad absorption at 290–350 nm corresponding

TABLE 6

Oxidation of Crotyl Alcohol with Hydrogen Peroxide in Methanol under Batch Reaction Conditions Using Titanyl Acetylacetonate as Catalyst at 50°C

	Conversion %		Yield %			
Time (h)	Crotyl alcohol	Hydrogen peroxide	Epoxide	Triol	Ether diols	pH
0	0	0	0	0	0	5
0.9	5.3	8.9	5.3	0	0	3
2.6	4.5	25.9	4.5	0	0	2.5
15.2	57.0	94.9	tr	45.8	11.2	2
26.7	45.7	96.2	tr	34.6	11.0	2
37.9	57.9	97.9	3.9	42.2	11.8	2
110.7	53.0	98.1	1.6	38.0	13.5	2
186.9	64.1	98.7	1.5	47.4	15.1	2

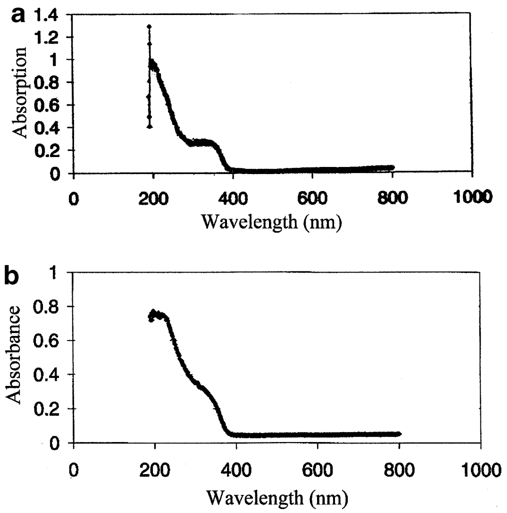


FIG. 5. Diffuse reflectance UV spectra of TS-1 (a) fresh, and (b) after reaction under continuous flow conditions for 45 days.

to extra framework TiO_2 (37). For the used catalyst, the absorption at the lower wavelength decreases in intensity relative to the absorption at the higher wavelength (Fig. 5). This is consistent with loss of framework Ti from the sample. ICP-MS analysis showed that the fresh catalyst contained 2.206 wt.% Ti and the used catalyst contained 2.145 wt.% Ti, indicating that 2.8% of the total Ti present had been leached from the catalyst under continuous flow conditions.

Ti–Alβ. As with the characterization studies for TS-1, powder X-ray diffraction, ^{29}Si-MAS NMR, and Raman spectroscopy showed no differences between fresh and used catalyst samples. FT-IR spectroscopy of the used catalyst showed a decrease in intensity of the absorption at 962 cm^{-1}, which is consistent with Ti loss from the structures. ICP-MS analysis confirmed that significant Ti leaching occurred under continuous flow conditions. The fresh catalyst contained 2.200 wt.% Ti and the used catalyst contained 1.204 wt.% Ti, indicating that 45.2% of the total titanium had been leached from the catalyst.

Ti–MCM-41. Powder X-ray diffraction, ^{29}Si-MAS NMR, and Raman spectroscopy showed no differences between fresh and used samples. FT-IR spectroscopy showed that the absorption at 967 cm^{-1} was absent in the used material. ICP-MS analysis confirmed that significant Ti leaching occurred under continuous flow conditions. The fresh catalyst contained 1.200 wt.% Ti and the used catalyst contained 0.674 wt.% Ti, indicating that 43.8% of the total Ti present had been leached from the catalyst.

Ti–xerogel. FT-IR spectroscopy of the Ti–xerogel sample following use showed that the absorption at 947 cm^{-1} was no longer present. ICP-MS analysis of the catalysts confirmed significant Ti leaching was caused by reaction under continuous flow conditions. The fresh catalyst contained 1.053 wt.% Ti and the used catalyst contained 0.403 wt.% Ti, indicating that 61.8% of the total Ti present was leached during reaction.

DISCUSSION

The reaction profiles for the oxidation of crotyl alcohol under batch reaction conditions using hydrogen peroxide for all the samples show that, although the epoxide can be formed initially, the secondary products of triol and ether diols dominate possibly due to ring-opening reactions of the oxirane, as we have previously discussed (38). The secondary products of triol and ether diols also dominate as products under continuous flow conditions. The formation of these secondary products is associated with a decrease in pH and this is observed for both the batch and continuous flow reaction conditions. Crotyl alcohol was selected as the substrate as it exhibits low reactivity with respect to epoxidation, compared with simple alkenes, and hence the formation of secondary products relative to the formation of the primary epoxide product can be readily studied.

This study demonstrates that Ti leaching can be relatively facile for the reaction of Ti-containing catalysts. Furthermore, solutions containing 4 and 25 ppm Ti have been shown to be effective homogeneous catalysts leading to the formation of triols and ether diols for the reaction of crotyl alcohol with hydrogen. This was confirmed by experiments using titanyl acetylacetonate as a model compound. Ti leaching from TS-1 was investigated for a range of solvent combinations, but leaching was observed only when TS-1 was stirred in the presence of a triol and hydrogen peroxide. It is, therefore, apparent that trace levels of triols could lead to Ti leaching for other oxidation reactions and that the effect will be autocatalytic, since the soluble Ti complex formed will catalyze the formation of further triols. However, this study confirms the stability of TS-1 under most reaction conditions.

For TS-1 and Ti–Alβ, it is considered unlikely that the nonframework Ti, as observed by electron microscopy and Raman spectroscopy, is the source of the leached Ti. In addition, for Ti–MCM-41 and Ti–xerogel, TiO_2 was observed not to be present in the fresh samples. First, model experiments using anatase showed that it is insoluble in the reaction mixture under these conditions. Second, the FT-IR spectra show the loss of the absorption at 963 cm^{-1}, which is consistent with loss of Ti from framework sites in the zeolite structure. We consider that the titanium that is removed from TS-1, and also from Ti–Alβ, during reaction with crotyl alcohol and hydrogen peroxide, originates from defect sites in the framework where the framework is not perfectly coordinated to four -OSi group. These defects have been proposed by Lamberti *et al.* (39) However, an alternative titanium species in TS-1, $Ti(OSi)_2(OH)_2$, has been proposed by Sinclair and Catlow (40) and, if present, this may also be removed under reaction conditions.

A key observation from this study is that Ti leaching under continuous flow conditions is considerably more pronounced than under batch reaction conditions. For example, under batch reaction conditions, leaching of only 0.6 ppm Ti from TS-1 was observed after 13 days, whereas under continuous flow conditions at an equivalent experimental time, a steady leaching of approximately 5 ppm Ti was observed. Leaching of Ti from TS-1, and the other Ti-containing catalysts, may be decreased under batch reaction conditions due to either (i) adsorption of organic molecules onto the surface (41) or (ii) an equilibrium being established between Ti in solution and Ti adsorbed on the surface of the catalyst. It is known that reversible hydrolysis of Ti–O–Si bonds can take place to form Ti–OH and Si–OH (42). Both of these processes would be expected to be perturbed by the use of continuous flow conditions.

With Ti–xerogel, Ti leaching is observed at the beginning of the reaction, in agreement with previous literature (43). Ti–xerogels are known to be rapidly deactivated by reaction with water due to hydrolysis of Ti–O–Si bonds. The leached Ti can then form Ti–O–Ti bonds by condensation reactions or form a soluble yellow titanium peroxo species (44).

Catalyst deactivation is observed under continuous flow conditions with Ti–Alβ, Ti-MCM-41, and the Ti–xerogel catalyst. Previous studies with Ti–xerogels have suggested that dimerization and polymerization of the epoxide product and/or the alkene could lead to deactivation. However, in the present study, the deactivation observed using continuous flow conditions is considered to be related to the extensive loss of Ti from the catalysts. For the materials tested, the order of stability is TS-1 > Ti–Alβ > Ti–MCM-41 > Ti–xerogel under both batch and continuous flow condition. For TS-1 under batch conditions, the Ti leaching is negligible, and it is found that both triol and hydrogen peroxide are required to observe Ti leaching. For Ti–MCM-41 and Ti–xerogels, Ti leaching in the presence of just hydrogen peroxide is possible. The decreased leaching of the well-defined structure TS-1 compared with the less well-defined structures of Ti–MCM-41 and Ti–xerogel may be due to the higher defect concentration expected for these materials. This is consistent with the much higher Ti leaching observed with Ti–Alβ relative to TS-1, since zeolite β structures are known to contain a high concentration of defects.

It is interesting to comment on the mechanism by which titanium is removed from the framework sites of TS-1 by reaction with a triol in the presence of hydrogen peroxide. UV-visible spectroscopy has shown that TS-1 contains four coordinate Ti^{4+} in the absence of water (45). Exposure of TS-1 to water and water hydrogen peroxide mixtures leads to the Ti^{4+} becoming six coordinate, retaining three Ti–O–Si bonds within the microporous structure. The retention of the three Ti–O–Si bonds is considered to anchor the Ti firmly within the catalyst structure. We propose that when this site is exposed to a triol, further Ti–O–Si bonds are hydrolyzed/broken and this then leads to the loss of Ti from the structure. With TS-1, interaction with a triol, a potential tridentate ligand, is required to cause Ti loss, and a diol or ether diol does not cause this effect. With the more defective structures of Ti–Alβ, Ti–MCM-41, and Ti-xerogels, a similar Ti leaching mechanism can be expected to operate, except that the effect can be observed in the absence of tridentate ligand.

A key result of the comparison of batch and flow reaction conditions is that Ti leaching is minimized by using controlled batch reaction conditions. This may be of significance with respect to the utilization of these materials as catalysts in the fine chemicals industry.

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