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Studies on the Catalytic Oxidation of Alkanes and Alkenes by Titanium Silicates

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Titanium containing, aluminum-free ZSM-5 (TS-1) and amorphous TiO_2–SiO_2 coprecipitate are investigated as catalysts for the selective oxidation of alkanes and alkenes using a variety of oxidants at temperatures below 100°C. Comparisons between the activities of TS-1 and the TiO_2–SiO_2 coprecipitate for alkane oxidation and alkene epoxidation using nonaqueous H_2O_2 indicate that the absence of water is crucial for the catalytic activity of silica-supported titanium. Due to the hydrophobicity of TS-1, the concentration of water surrounding the titanium is maintained at a low value, and thus TS-1 can be used as an oxidation catalyst with aqueous H_2O_2 as oxidant. Alkyl hydroperoxides are active as oxidants for alkene epoxidation on the TiO_2–SiO_2 coprecipitate but not for alkane oxidation reactions on both TS-1 and the TiO_2-SiO_2 coprecipitate. A plausible explanation for the above results is provided. The presence of stereoscrambling without any "radical clock" rearrangement during alkane oxidation on TS-1 indicates that the radicals formed may have a very short life-time, or their movements are restricted such that no rearrangement can occur. A proposal for the mechanism of alkane oxidation on TS-1 is given and compared to a mechanism suggested for alkene epoxidation on TS-1 and the TiO_2-SiO_2 coprecipitate. © 1994 Academic Press, Inc.

INTRODUCTION

Titanium substituted ZSM-5 (TS-1) is able to catalyze a wide spectrum of selective oxidation reactions that include aromatic hydroxylations, alkane oxidations, and alkene epoxidations (1–8). These conversions are performed using dilute aqueous hydrogen peroxide (40% aqueous H_2O_2 or less) as an oxidant and produce water as the by-product. Additionally, the reactions are operated at relatively low temperatures (<100°C) and pressures (~1 atm). Due to the outstanding catalytic activity and selectivity of TS-1, this catalyst has been used commercially in Italy for the production of catechol and hydroquinone from phenol (1).

Numerous studies investigating the nature of the titanium environment in TS-1 have been recently reported. Based on the unit cell expansion, the titanium atoms in TS-1 are believed to be incorporated in the zeolite framework (9, 10). Additionally, Boccuti *et al.* (11) claim by UV–vis spectroscopy that the titanium sites in TS-1 are tetrahedrally coordinated (TiO_4) contrary to the previously proposed titanyl structure (Ti=O) (1). Furthermore, Pei *et al.* (12) show by EXAFS experiments that the titanium sites in TS-1 are tetrahedrally coordinated. Further EXAFS studies on the nature of titanium in Ti–Al-β suggest that the coordination number of titanium varies depending upon whether the samples are as-made, calcined, hydrated, or dehydrated (13) and this is likely to be the case for TS-1 as well. The XPS data of TS-1 show an identical binding energy to that of Ti(IV) in TiO_2-SiO_2 glasses suggesting that the oxidation state of titanium in TS-1 is +4 (14, 15).

It has been reported that the oxidation of alkanes on TS-1 occurs only at secondary and tertiary carbons without any activation at primary C–H bonds (7, 16). It has also been shown that TS-1 can differentiate linear from branched and cyclic alkanes (16). The selectivity has been attributed to the transport restrictions that inhibit branched/cyclic molecules from passing through the pores and this implies that the catalytic reaction occurs inside the zeolite pores. Although no extensive mechanistic study has been performed for alkane oxidation on TS-1, it has been postulated that the oxidation proceeds through a homolytic mechanism that gives rise to radical intermediates (7). Nevertheless, better knowledge of the mechanism of alkane oxidation on TS-1 is needed in order to understand the limitations of this catalyst, e.g., no terminal activation, and the conditions necessary for a titanium atom to be an active catalyst for alkane oxidation, e.g., why is TiO_2–SiO_2 not active for alkane activation?

In this work, we investigate TS-1 and amorphous TiO_2–SiO_2 as catalysts for the selective oxidation of *n*-octane using aqueous H_2O_2 and organic hydroperoxides as the oxidants at temperatures below 100°C. For compar-

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ison, similar experiments have been conducted on the epoxidation of 1-hexene. The mechanism of alkane activation on TS-1 is further investigated by determining the stereoselectivity of this catalyst for *cis*- and *trans*-1,3-dimethylcyclopentane oxidations and by studying the "radical clock" rearrangement of ethyl cyclopropane and iso-propyl cyclopropane during the oxidation reaction. A proposal for the mechanism of alkane hydroxylation is given and compared to a mechanism suggested for olefin epoxidation.

EXPERIMENTAL

Samples

TS-1 was synthesized following the preparation method reported in the patent literature (9). Tetraethylorthotitanate (TEOT) (Johnson Matthey), tetraethylorthosilicate (TEOS) (Aldrich), tetrapropylammonium hydroxide (TPAOH) (1 *M*, Johnson Matthey), and distillated deionized water were mixed, forming a clear solution with the following composition:

$$\mathrm{TEOS:TEOT:TPAOH:H_2O} = 1:0.03:0.4:20$$

This solution was heated in Teflon-lined autoclaves at 175°C for 10 days. The product was recovered by filtration. Prior to catalytic tests, the material was calcined in air at 550°C for 8 h to remove the organic species occluded in the pores of TS-1. The Si/Ti ratio of this sample is 70.

Sodium exchanged TS-1 (Na–TS-1) was prepared by mixing 1 g TS-1 (calcined) with 100 ml of 1.0 *M* NaOH solution at 25°C for 24 h.

TiO_2–SiO_2 coprecipitate (type III, no. 2) was obtained from W. R. Grace. Before catalytic tests, it was dried in air at 200°C for 24 h. The Si/Ti ratio of this sample is 56.

TiO_2 anatase (~5 μm) was obtained from Aldrich and the nanophase TiO_2 anatase (~6 nm) was synthesized by the method reported in Ref. 17.

The titanium peroxo-derivative was prepared by mixing 1 g TS-1 with 5 ml aqueous H_2O_2 for 1 minute. The sample was then filtered and dried for 4 h at room temperature.

Analysis

A X-ray powder diffraction (XRD) pattern of TS-1 was collected on a Scintag XDS-2000 diffractometer equipped with a liquid-nitrogen-cooled Germanium solid-state detector using CuK_α radiation. The Fourier transform infrared (FTIR) spectrum was obtained on a Nicolet System 800 spectrometer (KBr beamsplitter and DTGS detector) using the KBr pellet technique (~2.5 wt% TS-1). The Raman spectrum of TS-1 was recorded on the Nicolet Raman accessory for the FTIR system described above (CaF_2 beamsplitter and a liquid-nitrogen-cooled germanium detector). The diffuse reflectance UV (DR-UV) spectrum of TS-1 was obtained on a spectrometer system constructed from an EG&G PAR diode array (1024 element Si) detector and a high-radiance Oriel deuterium lamp. The spectrum was ratioed to a reference spectrum obtained from powdered MgO. Adsorption capacities of various organic molecules were determined with a McBain–Bakr balance. The nitrogen adsorption isotherms were collected at 77 K on an Omnisorp 100 analyzer. Temperature programmed desorption experiment was performed in a flow type, fixed-bed reactor connected to a Dycor M200M quadrupole gas analyzer. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Catalytic Reactions

Epoxidation of 1-hexene using aqueous and anhydrous H_2O_2. The epoxidation of 1-hexene with aqueous H_2O_2 as oxidant was carried out using 20 mg TS-1, 5 mmol 1-hexene, 2 mmol H_2O_2 (30% in H_2O, stabilized) (Mallinkrodt), and 3 ml methyl ethyl ketone (MEK) (Mallinkrodt) as the solvent. The reaction was conducted at 50°C for 2 h with vigorous stirring in a 10 ml glass reactor immersed in a constant temperature bath. For the TiO_2–SiO_2 coprecipitate, 0.2 g of catalyst was used, and the reaction was carried out at 50°C for 4 h. The epoxidation of 1-hexene was also performed using anhydrous H_2O_2 and the procedure was the same as listed above except 2 mmol of H_2O_2 was provided from an anhydrous H_2O_2 solution (7.8% in MEK, prepared by adding anhydrous $MgSO_4$ to 30% aqueous H_2O_2 in MEK solution). The amount of solvent was reduced so that the total amount of the solution was the same as with the reaction using aqueous H_2O_2. Anhydrous $MgSO_4$ (25 mg) was added to the solution as a water adsorbent.

Epoxidation of 1-hexene using alkyl hydroperoxides. A procedure similar to that listed above for the epoxidation with anhydrous H_2O_2 was used for the epoxidation at nonaqueous conditions with 2 mmol of alkyl hydroperoxide used as the oxidant rather than aqueous H_2O_2. The oxidants were *tert*-butyl hydroperoxide (TBHP) (5.5 *M* in 2,2,4-trimethylpentane) (Aldrich) and *n*-butyl hydroperoxide (NBHP) (synthesized by the method reported in Ref. 18). Anhydrous $MgSO_4$ (25 mg) was introduced into the solution as a water adsorbent. The reaction was conducted for 4 h at 50°C with vigorous stirring in a 10 ml glass reactor.

Oxidation of alkanes using aqueous and anhydrous H_2O_2. The oxidations of *n*-octane (Aldrich), ethyl cyclopropane, iso-propylcyclopropane (Wiley Organics), *cis*-1,3-dimethylcyclopentane (Pfaltz and Bauer) and *trans*-1,3-dimethylcyclopentane (Wiley Organics) were performed in a 10 ml glass reactor immersed in a constant temperature oil bath. The reaction mixture would typically contain 20 mg TS-1, 0.5 ml alkane, 2.9 mmol H_2O_2 (30% in H_2O, stabilized), and 0.5 ml MEK as the solvent. The reactions were conducted at 80°C for 24 h with vigorous stirring except for *n*-octane, where the reaction was carried out for 4 h. With the TiO_2-SiO_2 coprecipitate, 50 mg of catalyst was used, and the reaction was performed at 80°C for 4 h. The procedure for the oxidation of *n*-octane using anhydrous H_2O_2 was the same as the outline above for epoxidation except that 2.9 mmol of H_2O_2 (7.8% in MEK) was used. As with the epoxidation reaction, the amount of solvent was reduced so that the total amount of solution was the same as when using aqueous H_2O_2. Finally, 25 mg of anhydrous $MgSO_4$ was added into the solution as a water adsorbent.

Oxidation of n-octane using alkyl hydroperoxides. The procedure was similar to that used for the oxidation of *n*-octane with nonaqueous H_2O_2 except that 2.9 mmol alkyl hydroperoxide was employed as the oxidant.

Oxidation of aromatics. The oxidation of benzene, toluene, ethyl benzene, *para*-xylene and 4-methyl ethylbenzene (Aldrich) were also conducted in a 10 ml glass reactor immersed in a constant temperature oil bath. The reaction mixture would typically contain 20 mg catalyst, 0.5 ml aromatics, 2.9 mmol H_2O_2 (30% in H_2O, stabilized), and 0.5 ml MEK as the solvent. The reactions were run for 6 h at 80°C with vigorous agitation.

Solvolysis of cis-2,3-epoxybutane. A typical procedure for the solvolysis of *cis*-2,3-epoxybutane in methanol involved contacting 20 mg catalyst with 0.1 ml *cis*-2,3-epoxybutane, 0.05 ml H_2O_2 (30% in H_2O, stabilized) or 0.1 ml TBHP (5.5 *M* in 2,2,4-trimethylpentane), and 5 ml methanol as solvent in a 10 ml glass reactor at 30°C for 4 h. Both TS-1 and the TiO_2–SiO_2 coprecipitate were used as catalysts.

In all cases mesitylene was used as an internal standard for gas chromatography analysis. Prior to analysis, the product mixtures were diluted with acetone in order to obtain a single, homogeneous phase. The products were analyzed on a HP 5890 Series II gas chromatography equipped with a 25 m HP-FFAP (polar) capillary column. For the detection of *cis*- and *trans*-1,3-dimethylcyclopentane reaction products, a 50 m long β-cyclodextrin capillary column was used. Hydrogen peroxide conversions were measured by titration with 0.1 *N* $Ce(SO_4)_2$ using ferroin as indicator. Hydrogen peroxide efficiency was calculated by dividing the amount of H_2O_2 converted to form the alcohols and ketones (1 mol of H_2O_2/mol of alcohol formed and 2 mol of H_2O_2/mol of ketone formed) by the amount of H_2O_2 consumed during the reaction.

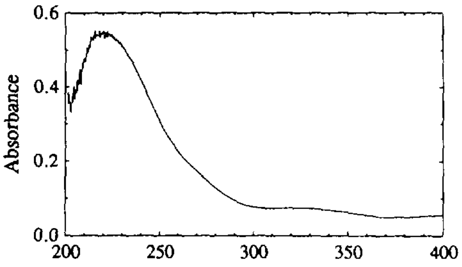


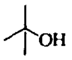
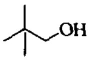
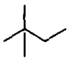
FIG. 1. DR–UV spectrum of TS-1.

RESULTS AND DISCUSSION

To ascertain whether the TS-1 sample prepared here has the same physicochemical and catalytic properties as reported previously (19, 20), the sample was extensively characterized. XRD data show that the material is highly crystalline and does not contain other crystalline phases. Both the IR and the Raman spectra of this sample exhibit an absorption band at 960 cm^{-1} that is characteristic of TS-1 (20, 21). The Raman spectrum (4000–200 cm^{-1}) also reveals that no TiO_2 anatase is present in the sample. In addition to Raman spectroscopy, ultraviolet diffuse reflectance (DR–UV) spectroscopy has been used to probe the existence of framework and nonframework titanium (11, 20, 22, 23). It has been reported that DR–UV spectroscopy is one order of magnitude more sensitive than the Raman spectroscopy for detecting nonframework titanium. The DR–UV spectrum for the TS-1 sample is shown in Fig. 1. The band at 220 nm has been assigned to isolated framework titanium in tetrahedral coordination (11). A very small band appears between 300 and 350 nm that suggests the presence of nonframework titanium species (bands at approximately 312 nm have been assigned to anatase (24)). From the results of DR–UV and Raman spectroscopy, the amount of the nonframework titanium is very small and must be very close to the limiting concentration that can be detected using DR–UV spectroscopy (has been reported to be ~0.03 wt% for anatase (22)). Nitrogen adsorption data are very similar to that obtained with pure-silica ZSM-5, both in the relative pressure for adsorption and the final capacity. These data indicate that the amount of extra-framework titanium species presence in the sample is very small. *n*-Octane oxidation and 1-hexene epoxidation were performed on this catalyst at 80 and 50°C, respectively. The epoxidation of 1-hexene gives only 1,2-epoxy hexane while the oxidation of *n*-octane yields a mixture of 2-, 3-, and 4-octanols and octanones without any terminal alcohol being detected, as has been reported previously (7, 8, 16, 20). The conversions of 1-hexene and *n*-octane were 7 and 15%, respectively, while the hydrogen peroxide efficiencies were 64

TABLE 1

Adsorption Capacities of TS-1 for Several Organic Molecules at Room Temperature

Molecule	Adsorption Capacity* (g/g zeolite)
	0.117
	0.057
	0.033

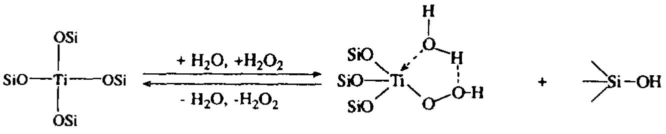
* $P/P_0 \approx 0.3$.

and 32%, respectively. Since the conversions and the hydrogen peroxide efficiencies are dependent upon all the reaction conditions, e.g. temperature, solvent type (16), no direct comparison with data from the open literature could be made. Because of this, *n*-octane was reacted at the exact condition used by Clerici (16). Here, we obtained *n*-octane conversion of 18% with a hydrogen peroxide efficiency of 55% as compared to Clerici's conversion of 21% with a hydrogen peroxide efficiency of 63%. Thus, the combined physical characterizations and preliminary catalytic tests show that the TS-1 sample prepared here is of high quality.

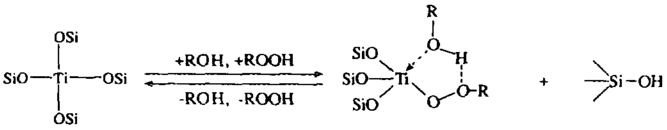
It has been shown that anhydrous TBHP can not be used as oxidant for alkane activation with TS-1 (16). To verify that it is not due to the inability of TBHP to enter TS-1 pores, the adsorption capacity of TS-1 for several molecules similar in size to TBHP was measured (we did not wish to use the data for the adsorption of TBHP directly in case there is some type of chemisorption occurring). The results are tabulated in Table 1. All the molecules tested adsorb into TS-1. Therefore, TBHP should be able to adsorb into the pores of TS-1. Thus, the lack of activity must not be due to the ability of TBHP to enter the interior of the TS-1 crystals. The hypothesis is supported by the lack of activity of TS-1 when NBHP, for which there is no doubt that it can enter TS-1 pores, is used as the oxidant for *n*-octane oxidation. This result is also in agreement with the fact that TS-1 catalyzes the reaction between *tert*-butyl alcohol and H_2O_2 to form *tert*-butyl hydroperoxide (25).

In Scheme 1, we propose a plausible reason why alkylhydroperoxides are not active as oxidants. When aqueous hydrogen peroxide is in contact with TS-1, Clerici (16) has postulated that a Ti-peroxo complex is formed. Physicochemical characterizations (XRD, IR, UV, TGA, and TPD) and catalytic tests for acidity imply the presence of a titanium peroxo derivative as shown in Scheme 1a (26).

a. Aqueous H_2O_2 is used as oxidant (adapted from Ref. 16)



b. ROOH is used as oxidant



SCHEME 1. Possible interaction between TS-1 and aqueous H_2O_2 or ROOH.

It is known that titanium (IV) interacts readily with an organic hydroperoxide forming a Ti-alkylperoxo complex (27). Thus, the titanium in TS-1 will most likely interact with organic hydroperoxides unless the position of the active titanium in TS-1 does not allow for the formation of a Ti-alkylperoxo complex due to steric effects. We believe this is unlikely especially when using NBHP. Hence, we postulate that when organic hydroperoxide is used as the oxidant for reactions with TS-1, a Ti-alkylperoxo complex as shown in Scheme 1b is formed. Since the complex is located in the intracrystalline void space of TS-1 the alkyl group of the complex could block the reactants from approaching the active titanium sites. Consequently, no activity is possible for either the alkane hydroxylation or olefin epoxidation reactions.

In an attempt to verify the above postulate, both the olefin epoxidation and alkane oxidation reactions were conducted on dry TiO_2–SiO_2 coprecipitate using an alkyl hydroperoxide as the oxidant. The IR spectrum of the TiO_2–SiO_2 coprecipitate shows a band at ~960 cm^{-1} like that observed on TS-1. Moreover, this material can be used as a precursor for the synthesis of TS-1 (28). Hence, some of the titanium on the TiO_2–SiO_2 coprecipitate is most likely in a similar coordination state to the titanium on TS-1. Since this material is not microporous, the reaction will occur at the surface of the catalyst. Steric restrictions arising from the alkyl group on the Ti-alkylperoxo complex are less likely to occur than inside the TS-1 pores. Table 2 shows the results from the olefin epoxidation using the TiO_2–SiO_2 coprecipitate catalyst. Although the TiO_2–SiO_2 coprecipitate used here is not optimized for the epoxidation reaction (as compared to the commercial Shell catalyst (29)), it shows some activity for 1-hexene epoxidation with either TBHP or NBHP as the oxidant. Thus, TBHP and NBHP must interact with the titanium in the TiO_2–SiO_2 coprecipitate most likely giving an alkyl peroxide. On the other hand, no catalytic activity is observed for alkane activation.

It has been claimed that the Ti-hydroperoxo complex

TABLE 2

Epoxidation of 1-Hexene on TiO_2–SiO_2 Coprecipitate Using Alkyl Hydroperoxides as the Oxidants

Oxidant	Conversion (%)	Hydroperoxide eff. (%)
tert-Butyl hydroperoxide	0.7	3.6
n-Butyl hydroperoxide	1.3	5.1
tert-Butyl hydroperoxide (without catalyst)	0.1	0.6

Note. Reaction condition: 200 mg dried TiO_2–SiO_2 coprecipitate, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol alkyl hydroperoxide, 3 ml MEK, 80°C, for 4 h.

(Scheme 1a) has a higher acidity than the pure TS-1 (16). As reported earlier, the presence of acidity by this complex was evaluated by studying the acid-catalyzed solvolysis of *cis*-2,3-epoxybutane to 2-methoxy-3-butanol in methanol. To minimize the amount of H_2O_2 consumed by side reactions with the accompanying formation of organic by-products, we performed this reaction at 30°C in methanol. Figure 2 compares the reactivity of TS-1 for the solvolysis of *cis*-2,3-epoxybutane in the presence and absence of H_2O_2 or TBHP. Similar to that reported previously (16), the effectiveness of TS-1 for the solvolysis of *cis*-2,3-epoxybutane is greatly improved by the presence of H_2O_2. The increase in activity is attributed to the presence a stable five-membered cyclic structure (Scheme 1a) which enhances the acidity. Conversely, the presence of TBHP does not have any significant effect on the hydrolysis reaction suggesting that if the Ti-alkylperoxo complex (Scheme 1b) is formed, it is less acidic than the Ti-hydroperoxo complex (Scheme 1a). These results also imply that the presence of the acidity is not related to the silanol group that is speculated to appear upon the formation of the Ti-hydroperoxo or Ti-alkylperoxo complex. (The presence of this silanol group and its effect on the catalytic behavior of TS-1 is discussed below.) Similar experiments were performed on the TiO_2–SiO_2 coprecipitate (Fig. 3). As with TS-1, the activity of the TiO_2–SiO_2 coprecipitate for the solvolysis of *cis*-2,3-epoxybutane is greatly enhanced by the presence of H_2O_2 but not by TBHP suggesting that the lack of acidity on the Ti-alkylperoxo complex is not related to steric restrictions inside the TS-1 pores. Comparison between the activity of the two catalysts indicates that TS-1 is much more reactive than TiO_2–SiO_2 coprecipitate for the solvolysis reaction. This may be attributed to a smaller number of titanium sites involved in the reaction on the TiO_2–SiO_2 coprecipitate when compared to TS-1. Based on the difference in acidity between the Ti-alkylperoxo complex and Ti-hydroperoxo complex, it is likely that the acidity of the Ti-hydroperoxo complex is important for the abstraction of hydrogen that occurs in alkane activation. Hence, organic hydroperoxides are active as oxidants for olefin epoxidation on silica-supported titanium (29) but not for alkane oxidation presumably because no hydrogen abstraction is necessary for epoxidation.

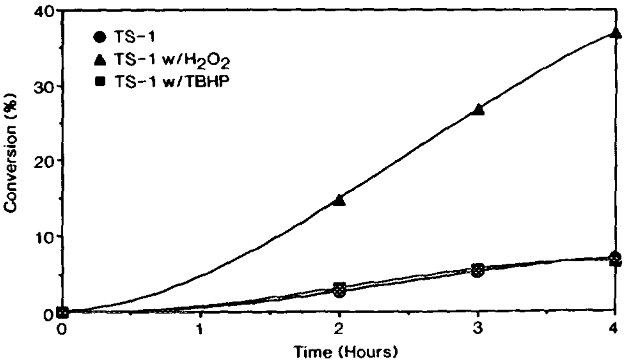


FIG. 2. Solvolysis of *cis*-2,3-epoxybutane on TS-1.

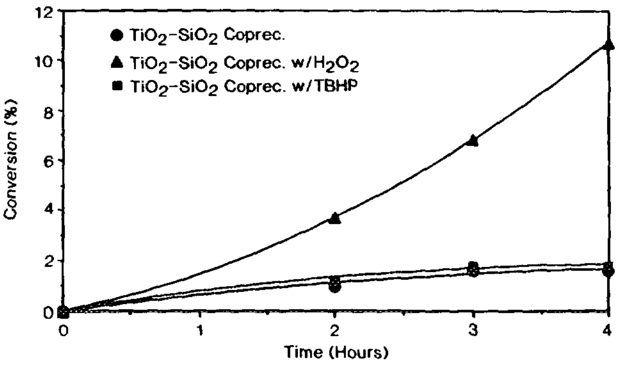


FIG. 3. Solvolysis of *cis*-2,3-epoxybutane on the TiO_2–SiO_2 coprecipitate.

To understand the effect of water on the catalytic activity of TS-1 and the TiO_2–SiO_2 coprecipitate, anhydrous hydrogen peroxide in MEK (less than 1% water) was used as the oxidant for alkane oxidation and alkene epoxidation. For all cases, anhydrous $MgSO_4$ was added into the reaction medium to adsorb the water formed from H_2O_2 decomposition (from catalytic reaction or thermal decomposition). With TS-1, similar catalytic activities are observed for both alkane oxidation and alkene epoxidation whether aqueous H_2O_2 or anhydrous H_2O_2 is used as the oxidant (see Table 3). However, with the TiO_2–SiO_2 coprecipitate, activity is observed (with the same product distribution as the one on TS-1) only when anhydrous H_2O_2 is used as the oxidant (Table 3). Since the TiO_2–SiO_2 coprecipitate is hydrophilic (contains 50 wt% H_2O when it is exposed to humid air), its surface will preferentially adsorb water instead of the organics. The importance of the absence of H_2O for the epoxidation of olefins is well

TABLE 3

Epoxidation of 1-Hexene and Oxidation of *n*-Octane with TS-1 and the TiO_2–SiO_2 Coprecipitate Using Aqueous and Anhydrous H_2O_2

Oxidant	TiO_2–SiO_2 coprecipitate Conv. (%)		TS-1 Conv. (%)	
	Conv. (%)	H_2O_2 eff. (%)	Conv. (%)	H_2O_2 eff. (%)
n-Octane oxidation				
Anhydrous H_2O_2[a]	2.71	4.37	16	30
Aqueous H_2O_2[b]	0.14	0.24	15	32
1-Hexene epoxidation				
Anhydrous H_2O_2[c]	1.86	8.58	8	68
Aqueous H_2O_2[d]	0.24	0.53	7	64

[a] Reaction condition: 50 mg dried TiO_2–SiO_2 coprecipitate or 20 mg TS-1, 25 mg $MgSO_4$, 3 mmol n-octane, 2.9 mmol H_2O_2 (7.8% in MEK) 80°C, for 4 h, stirred in a glass reactor.

[b] Reaction condition: 50 mg dried TiO_2–SiO_2 coprecipitate or 20 mg TS-1, 25 mg $MgSO_4$, 3 mmol *n*-octane, 2.9 mmol H_2O_2 in (30% in H_2O), and 1 ml MEK 80°C, for 4 h, stirred in a glass reactor.

[c] Reaction condition: 0.2 g dried TiO_2–SiO_2 coprecipitate or 25 mg TS-1, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol H_2O_2, (7.8% in MEK), 2 ml MEK, 50°C, for 4 h, stirred in a glass reactor.

[d] Reaction condition: 0.2 g dried TiO_2–SiO_2 coprecipitate or 25 mg TS-1, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol H_2O_2, (30% in H_2O), 3 ml MEK, 50°C, for 4 h, stirred in a glass reactor.

TABLE 4

H_2O_2 Decomposition on TS-1, TiO_2–SiO_2 Coprecipitate, Anatase, and Pure-Silica ZSM-5

Catalyst	H_2O_2 conv. (%) (40°C)	H_2O_2 conv. (%) (80°C)
Blank[a]	1.6	9.5
Pure-silica ZSM-5[a]	3.5	10.3
TiO_2–SiO_2 coprec.[a]	10.7	54.0
TS-1 (uncalcined)[a]	1.6	45.5
TS-1[a]	13.7	87.5
Anatase (~5 μm)	14.4	n.d.
Anatase (~6 nm)	70.1	n.d.
TS-1 + *n*-octane[b]	n.d.	99.1
TS-1 + toluene[b]	n.d.	49.2

Note. n.d. not determined.

[a] Reaction condition: 20 mg catalyst, 2.9 mmol H_2O_2 (30% in H_2O), 1.0 ml MEK stirred for 12 h in a glass reactor.

[b] Reaction condition: 20 mg catalyst, 2.9 mmol H_2O_2 (30% in H_2O), 0.5 ml MEK and 0.5 ml *n*-octane/toluene stirred for 12 h, in a glass reactor.

known for the Shell catalyst in the formation of propylene oxide (29) and for the Sharpless asymmetric epoxidation (30). Since TS-1 is hydrophobic, the titanium active sites are effectively screened from bulk water and thus allow for the use of aqueous H_2O as an oxidant. Moreover, this hypothesis is in perfect agreement with the recent paper by Tatsumi *et al.* showing that only alkenes with a hydrophilic group, e.g., unsaturated alcohols, can be adsorbed and oxidized on the TiO_2–SiO_2 coprecipitate using aqueous H_2O_2 as the oxidant due to the hydrophilicity of this material (31).

The results for the decomposition of H_2O_2 on the TiO_2–SiO_2 coprecipitate, pure-silica ZSM-5, calcined TS-1, and uncalcined TS-1 are listed in Table 4. In the absence of titanium, less than 4% of the H_2O_2 is decomposed after 12 h of reaction at 40°C. The presence of titanium (as in TiO_2–SiO_2 coprecipiate and TS-1) accelerates the decomposition of H_2O_2 in agreement with previously reported results (20). This is especially true for the nanophase anatase. Anatase has been reported to catalyze the decomposition of H_2O_2 to water and oxygen (20) and both the samples used here do so as well; conversion increases for the higher surface area anatase (nanophase) as expected. As the temperature is increased to 80°C, the decomposition of H_2O_2 increases for all the catalysts tested especially for TS-1. A temperature-programmed-desorption experiment on TS-1 contacted with H_2O_2 shows that oxygen is formed at approximately 50°C (measured by mass spectroscopy). This result suggests that TS-1 becomes an active catalyst for the decomposition of H_2O_2 above ~50°C. This threshold temperature may also be related to the temperature at which TS-1 becomes active for alkane oxidation (unlike epoxidation, TS-1 is not active for alkane oxidation at room temperature). The presence of an oxidizable substrate, e.g., *n*-octane, increases the conversion of H_2O_2 since in this case two competing reactions occur, the decomposition of H_2O_2 and the oxyfunctionalization of the substrate. However, when aromatics, e.g., toluene, *para*-xylene, are presence as the oxidizable substrate, the H_2O_2 conversion decreases. It is likely that the aromatic molecules are blocking the H_2O_2 molecules from reacting inside the TS-1 pores since the H_2O_2 conversion for TS-1 when aromatics are presence in the reaction mixture is similar to that of the uncalcined TS-1.

In order to understand further the mechanism of alkane activation on TS-1, the regioselectivity pattern of oxidizing a series of substrates was investigated. It has been reported that only monooxyfunctionalization of alkanes are observed (7, 16, 20). Moreover hydroxylation of alkanes on TS-1 occurs preferentially at the tertiary and secondary positions without noticeable amounts of terminal oxygenated products. Table 5 shows the catalytic activity of TS-1 for the oxidation of various aromatic compounds. These data are in agreement with those reported previously (16, 32). The results show that for toluene and *para*-xylene, no activation occurs at the methyl group although this methyl group (benzylic carbon) has the weakest C–H bond. The lack of activity at the terminal position must therefore be inherent in the reaction mecha-

TABLE 5

Oxidation of Aromatics by TS-1

Substrates	Products	Conversion (%)	Selectivity (%)	H_2O_2 conv. (%)
Benzene	phenol	4.0	—	47
Ethylbenzene	acetophenone	5.8	56	69
	1-phenylethanol		4	
	ethylphenols		40	
Toluene	cresols	3.8	—	49
Para-xylene	2,5-dimethylphenol	2.5	—	59
4-methyl-ethylbenzene	1-ethanol-4-methyl benzene	2.5	29	58
	1-ethanone-4-methyl benzene		40	
	2-methyl-5-ethylphenol		31	

Note. Reaction condition: 20 mg TS-1, 0.5 ml aromatic substrates, 2.9 mmol H_2O_2 (30% in water), 0.5 ml MEK as solvent, 80°C for 12 h in a glass reactor.

nism of TS-1 and not solely due to the differences among the activation energies. For ethylbenzene, activation occurs both at the benzylic carbon and the benzene ring. Reaction using both *n*-octane and benzene in the same mixture shows that both substrates are functionalized; i.e., no significant preference for either benzene or *n*-octane is observed (Table 6). The activity for both *para*-xylene and 4-methyl-ethylbenzene is lower than that of the other molecules investigated and this can be attributed to the lower diffusivity of *para*-xylene and 4-methyl-ethylbenzene in TS-1 (Table 5).

Comparison of the selectivities obtained for oxyfunctionalization with TS-1 to other oxidation catalysts reveals that the regioselectivity pattern of TS-1 is similar to that of vanadium (V) peroxo complexes (e.g., $[VO(O_2)(Pic)_2]^-A^+L\{A^+ = H^+, PPh_4^+; L = H_2O$, hexamethylphosphoric triamide; Pic = pyridine-2-carboxylate}) (33). Both catalysts do not activate terminal C–H bonds. However, for the latter system, stereoscrambling occurs for both alkane oxidation and alkene epoxidation. The mechanism for both reactions is believed to proceed through radical intermediates and the active species is tentatively attributed to a V^{IV}–OO· radical which adds to double bonds and aromatic nuclei or abstracts hydrogen atoms from alkanes to give carbon radical intermediates. Thus, we speculate that the mechanism of TS-1 for alkane oxidation is similar to that of vanadium (V) peroxo complexes catalyst but not for alkene epoxidation since no stereoscrambling is observed for alkene epoxidation on TS-1 (34, 35).

TABLE 6

Reactions of *n*-Octane and Benzene on TS-1

Substrate	Conversion[a] (%)	
	Benzene	*n*-Octane
Benzene[b]	3.7	—
n-Octane[c]	—	19.0
Benzene + *n*-octane[d]	1.5	15.6

[a] Conversion is based on the substrates.

[b] Reaction condition: 20 mg catalyst, 0.5 ml benzene, 2.9 mmol H_2O_2 (30% in H_2O), 1 ml MEK, 80°C, stirred for 6 h in a glass reactor.

[c] Reaction condition: 20 mg catalyst, 0.5 ml *n*-octane, 2.9 mmol H_2O_2 (30% in H_2O), 1 ml MEK, 80°C, stirred for 6 h in a glass reactor.

[d] Reaction condition: 20 mg catalyst, 0.5 ml benzene and 0.5 ml *n*-octane, 2.9 mmol H_2O_2 (30% in H_2O), 1 ml MEK, 80°C, stirred for 6 h in a glass reactor.

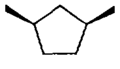
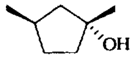
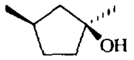
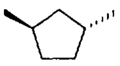
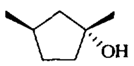
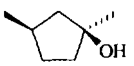
The color change of TS-1 from white to yellow upon contact with aqueous hydrogen peroxide suggests the formation of titanium peroxo derivatives which is supported by the results from UV–vis spectroscopy (36). To test whether this peroxo derivative is the active species, the following experiment was performed. TS-1 was contacted with aqueous hydrogen peroxide and the color changed to yellow. After drying at room temperature for approximately 4 h, the TS-1 sample, which was still yellow, was contacted with MEK and *n*-octane at 80°C without any oxidant present in the solution. During the reaction, the color gradually faded and eventually disappeared after 2 h of reaction. Analysis of the products indicates that alcohols and ketones were formed in the reaction. This result shows that a titanium peroxo derivative is active as the oxidant for alkane oxidation suggesting that either it is the active species or the precursor to the active species, in agreement with the generally accepted concepts (1, 7, 32, 37, 38).

As mentioned earlier, the reaction for olefin epoxidation proceeds without any stereoscrambling, e.g., *cis*-epoxide is formed only from *cis*-olefin (34, 35). Additionally, it has been postulated that oxidation of alkanes and epoxidation of olefins on TS-1 proceed through different pathways (20). Table 7 reports the results revealing the stereoselectivity of TS-1 in an alkane activation. It is shown that reacting *cis*-1,3-dimethylcyclopentane yields both *cis*- and *trans*-1,3-dimethylcyclopentanol. The same products are obtained when *trans*-1,3-dimethylcyclopentane is used as the reactant. The stereoscrambling suggests that alkane oxidation on TS-1 proceeds through a radical mechanism, in agreement with the previously postulated mechanism (7).

The unimolecular rearrangements of radical intermediates have been widely used as a tool to study the mechanisms of reactions that proceed through radical intermediates (39). This mehod is widely known as the "radical clock" technique. In this technique, the production of rearranged products indicates that a radical intermediate with a longer lifetime than the time required for radical rearrangement is formed in the reaction pathway. Usu-

TABLE 7

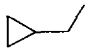
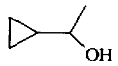
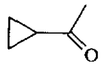
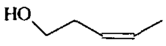
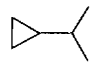
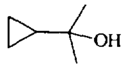
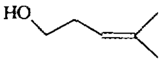
Stereoselectivity Pattern of TS-1 for *cis*- and *trans*-1,3-Dimethylcyclopentane

Substrate	Conv. (%)	Products	Ratio (%)
	6		53
			47
	4		49
			51

Note. Reaction conditions: 20 mg catalyst, 0.5 ml substrate, 2.9 mmol H_2O_2 (30% in H_2O), 0.5 ml MEK, stirred at 80°C, for 24 h in a glass reactor.

TABLE 8

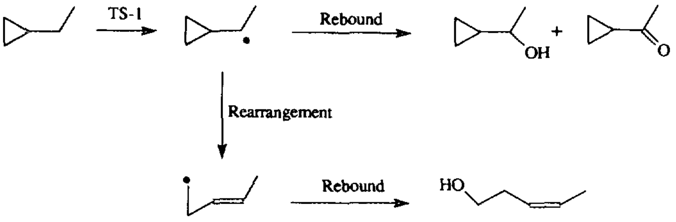
"Radical Clock" Study on TS-1

Reactant	Product	Selectivity (%)	Conversion (%)
		27	15.6
		73	
		0	
	Others	0	
		50	3.2
		0	
	Others	50	

Note. Reaction conditions: 20 mg catalyst, 0.5 ml substrate, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, stirred at 80°C for 24 h in a glass reactor.

ally, molecules with especially fast radical rearrangements are used so that competing reactions will not intercept the first-formed radical before rearrangement. Here, two hydrocarbon substrates, ethylcyclopropane and iso-propylcyclopropane (with a reactive secondary and tertiary carbon, respectively), were employed as probes in the oxidation catalyzed by TS-1. At 80°C, the ring opening reaction for these two molecules has a rate constant (k_r) of 3.2×10^8 and 3.7×10^8 s^{-1}, respectively (calculated from the data in Ref. 40). For each case, if a free radical is formed in the reaction pathway, it could either rebound to form the unrearranged product or ring-open to afford the rearranged products as depicted in Scheme 2 for ethylcyclopropane depending on the lifetime of the radical intermediates.

Table 8 shows the results from the 'radical clock' experiments. Analysis of the products reveals that ethylcyclopropane is converted only to 1-cyclopropylethanol and 1-cyclopropylethanone without any rearrangement products being detected. Additionally, iso-propylcyclopropane is converted to 1-cyclopropylisopropanol and another product (which most likely is from the cracking of the alcohol and not from the further reaction of the rearrangement product), however, no species due to rearrangement are detected. Moreover, other possible products such as olefins, epoxides and oligomers that may be formed from further reactions of the rearrangement products are not detected either. These observations combined with the results from the stereoselectivity of TS-1 toward *cis*- and *trans*-1,3-dimethylcyclopentane oxidation suggest that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur. A similar observation has been reported for the stereoselectivity pattern of the methane monooxygenase enzyme for alkane activation in which stereoscrambling occurs but no "radical clock" rearrangement is detected (41, 42).



SCHEME 2. "Radical clock" technique.

It has been shown that sodium has a significant effect on the catalytic activity of TS-1 (19). Further study on the effect of sodium on the catalytic activity of TS-1 indicates that TS-1 exchanged with sodium hydroxide (Na-TS-1) is inactive for both alkane oxidation and alkene epoxidation (Table 9). Unlike TS-1, Na-TS-1 does not change color upon contact with aqueous H_2O_2 suggesting that a titanium hydroperoxo complex similar to that as the one on TS-1 is not present. The IR spectrum of the Na-TS-1 shows that the band at 960 cm^{-1} is shifted and

TABLE 9

Catalytic Activity of Sodium Exchange TS-1 (Na–TS-1) for *n*-Octane Oxidation

Catalyst	Si/Ti	Si/Na	Conversion (%)
TS-1	70	797	15
Na-TS-1	70	21	~1

Note. Reaction conditions: 20 mg catalyst, 0.5 ml substrate, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, stirred at 80°C for 4 h in a glass reactor.

converted into a shoulder at ~985 cm^{-1} as shown in Fig. 4. The IR band at 960 cm^{-1} was originally assigned to the stretching vibration of $Si\text{–}O^{\delta-} \ldots Ti^{\delta+}$ (11). However, more recently, Camblor *et al.* (13) have reported that this band is better assigned to the stretching vibration of the $Si\text{–}O^-$ groups where H^+, tetraethylammonium$^+$ and/or Na^+ can act as the countercations. This assignment is in agreement with the fact that the IR band of the calcined sample is different than that of the uncalcined one and also consistent with the shifting of the IR band for Na-TS-1. Moreover, it also suggests that sodium exchange on TS-1 occurs at the silanol group as illustrated in Scheme 3. The absence of catalytic activity on Na-TS-1 suggest that the presence of a silanol group in the neighborhood of titanium is necessary for both alkane oxidation and alkene epoxidation activity.

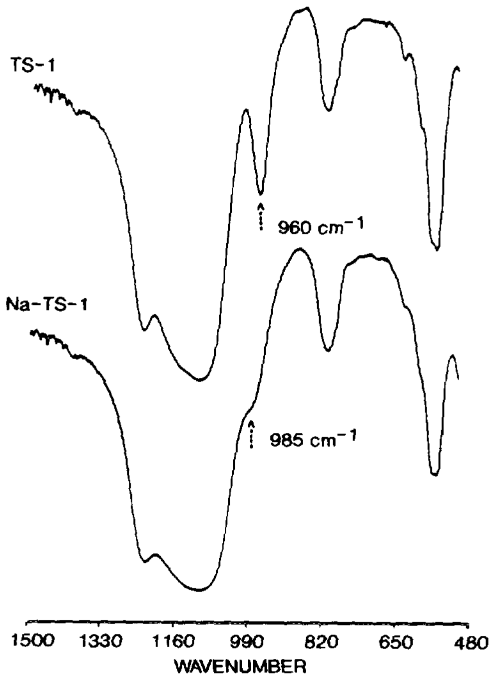
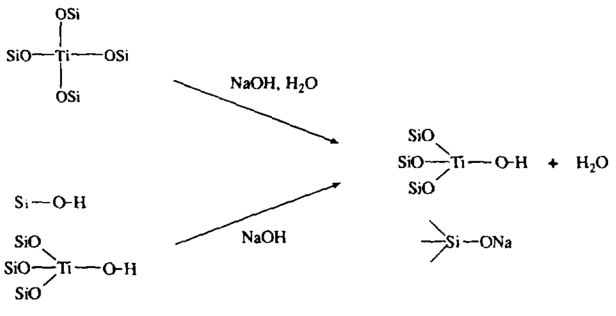
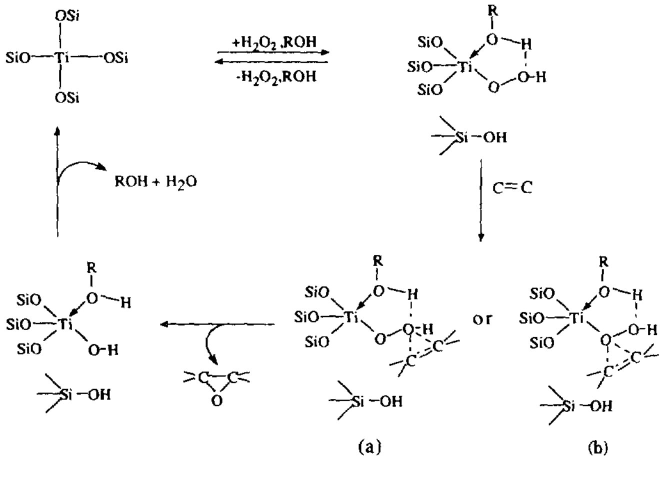


FIG. 4. IR spectra of TS-1 and sodium exchange TS-1 (Na-TS-1).

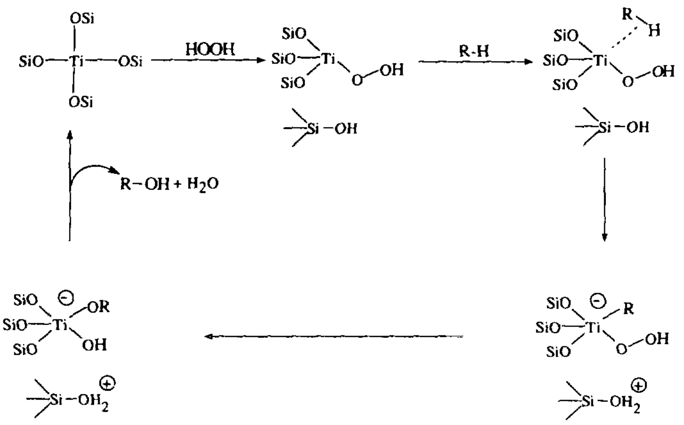


SCHEME 3. TS-1 exchanged with NaOH.

Clerici and Ingallina (43) have postulated that epoxidation on TS-1 proceeds through a heterolytic peracid-like mechanism and that the active species is a five-membered cyclic structure which is formed by a titanium hydroperoxo (Ti–OOH) and a protic molecule ROH (Scheme 1a). The proposed mechanism for the alkene epoxidation is depicted in Scheme 4. On the basis of steric arguments, Clerici and Ingallina argue that the oxygen atom closer to the hydrogen atom (Scheme 4a) is transferred directly from the titanium hydroperoxo complex into the epoxide. However, there is really no strong evidence to rule out oxygen transfer from the oxygen atom closer to the titanium (Scheme 4b). Thus, the question of which oxygen atom is transferred to the olefin remains unresolved at this time. As reported earlier, the presence of solvents (ROH, $R_1R_2C{=}O$) have a significant effect on the catalytic activity of TS-1 for alkene epoxidation (43). However in the absence of solvents, TS-1 still shows activity for alkene epoxidation (~5% conversion versus 7% conversion of 1-hexene in MEK), indicating that organic solvent is not necessary for activity (it only enhances the catalytic activity).



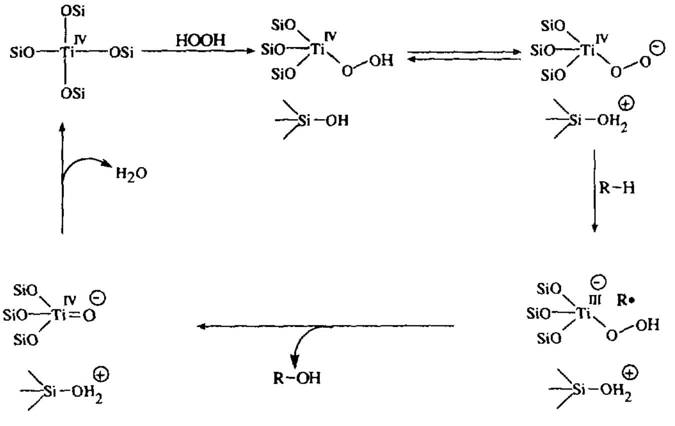
SCHEME 4. Possible mechanism for alkene epoxidation on TS-1 (adapted from Ref. 43).



SCHEME 5a. Possible mechanism for alkane activation on TS-1.

The mechanism for alkane oxidation remains far less clear. Assuming the same titanium hydroperoxo complex is involved, two possible mechanisms are illustrated in Schemes 5a and 5b. The first (Scheme 5a) involves an alkyl(hydroperoxo)titanium(IV) intermediate, which rearranges to an (alkoxo)(hydroxo)titanium(IV) species. Such a route has precedence in the organometallic literature (although the properties of the metal centers involved there are probably quite different from that here). Activation of C–H bonds at high-valent, early transition metals such as Sc(III) are well known (44); also, the hafnium(IV) complexes $(h^5\text{-}C_5Me_5)_2Hf(R)(OOCMe_3)$ readily rearrange to $(h^5\text{-}C_5Me_5)_2Hf(OR)(OCMe_3))$ for a variety of alkyl groups *R* (45). On the other hand, such a route would not explain either the stereochemical scrambling or the regioselectivity: retention of configuration and preference for terminal activation would be expected.

The second mechanism (Scheme 5b) proceeds via homolytic H· abstraction by a coordinated peroxo group, which may have some superoxo-like character (36). (Such a species is not accessible from ROOH, consistent with the lack of alkane activation by that reagent.) This step generates an alkyl radical, accompanied by reduction to Ti(III). Ti(III) centers have been generated in TS-1, by reduction with CO, under fairly mild conditions (46). The subsequent O–O bond cleavage to form the C–O bond would be facilitated by formation of a relatively stable Ti═O bond. The alkyl radical must either have a very short lifetime or somehow be restricted within the zeolite to account for the fact that stereoscrambling but not radical clock rearrangement is observed.



SCHEME 5b. Possible mechanism for alkane activation on TS-1.

This radical mechanism would also be consistent with low reactivity at terminal positions, but it does not fully account for the *complete* absence of terminal activation, especially at benzylic C–H bonds as in toluene; the explanation remains uncertain at this time.

SUMMARY

We have shown that the absence of water is crucial for the catalytic activity of silica supported titanium as has been known for quite some time (29). Since TS-1 is hydrophobic, the concentration of water surrounding the titanium is maintained at a low value. Thus, TS-1 can be used as an oxidation catalyst with aqueous H_2O_2 as the oxidant. The titanium atoms of TS-1 are incorporated in the zeolite framework and hence they are all isolated. Isolated titanium minimizes H_2O_2 decomposition at low temperatures and enables all the titanium to be exposed to the reaction environment. Our results show that if there is a low concentration of titanium in an amorphous TiO_2–SiO_2 coprecipitate, the state of the titanium is not much different than in TS-1. Recently, EXAFS data suggest this is true as well (47). However, if the concentration of titanium is increased, phase separated TiO_2 is formed (47) and these types of titanium centers are not active for partial oxidation. Consequently, TS-1 is much more reactive than the TiO_2–SiO_2 coprecipitate for partial oxidation reactions even when nonaqueous H_2O_2 is used as the oxidant.

The lack of both epoxidation and oxidation activities on TS-1 when alkyl hydroperoxides are used as the oxidants is attributed to the bulkiness of the alkyl group on the Ti-alkylperoxo complex that blocks the reactants from approaching the active titanium. On the TiO_2–SiO_2 coprecipitate, no activity is observed for alkane oxidation when alkyl hydroperoxide is used as the oxidant. This may be due to the lack of hydrogen abstraction for the titanium alkylperoxo complex. Since no hydrogen abstraction occurs in epoxidation, nonaqueous alkyl hydroperoxide is active as an oxidant for alkene epoxidation on the TiO_2–SiO_2 coprecipitate.

The stereoselectivity differences between alkane oxidation and alkene epoxidation on TS-1 suggests that these reactions proceed through different mechanisms. The presence of stereoscrambling without any "radical clock" rearrangement during alkane oxidation indicates that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur.

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