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Reactions of Titanium Silicalite with Protic Molecules and Hydrogen Peroxide

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The properties of titanium silicalite (TS-1) in reactions with water, hydrogen peroxide, and alcohol molecules have been studied by means of IR and NMR spectroscopy, and acid activity tests. An IR absorption is shown by TS-1 in the region 900–975 cm^{-1}. Its exact position depends on the amount of adsorbed water, on exchange reactions with ^{17}O- and ^{18}O-labeled water, and on the average size of the crystallites. In ^{17}O MAS NMR spectra a peak is shown at δ 360 ppm from $H_2{}^{17}O$ ($\delta = 0$). IR and NMR spectra are discussed and interpreted in terms of Ti sites as constituted by tetrahedral $[TiO_4]$ units. Ti—O—Si bonds react with water at near room temperature, producing Ti—OH and Si—OH species. Reactions with hydrogen peroxide produce acidic derivatives, which catalyze the hydrolysis of *cis* and *trans* 2,3-epoxybutane in methanol, ethanol, and aqueous media. A five-membered ring hydrogen bonded structure, in which a titanium hydroperoxo moiety, Ti—OOH, and a protic molecule, ROH (R = H, CH_3, C_2H_5), are involved, is proposed for these species. Their possible role in selective oxidations of hydrocarbons is discussed. © 1992 Academic Press, Inc.

INTRODUCTION

The structure and chemical properties of active sites are essential concerns in explaining the catalytic behaviour of titanium silicalite (TS-1). Research on these issues has been hampered in part by the difficulties in the synthesis of TS-1 and mostly by the lack of direct techniques to study Ti sites. No such effective tool as ^{27}Al MAS NMR spectroscopy, which gave important contributions to the knowledge of acid sites in zeolites, is as yet available for titanium silicalite. The characterisation of the latter can rely on indirect procedures, based on the evaluation of the effects of selected reagents.

Active species and reaction mechanisms have occasionally been proposed in the past, by analogy with Group IV–VI transition metal peroxo compounds and oxidation catalysts (*1*, *2*). However such an argument can be misleading because TS-1 shows unique properties which are not shared by other catalysts. These are a zeolitic type structure, an unusually high activity with hydrogen peroxide, and no inhibition effects by protic solvents.

First insight into the structure of Ti sites was provided by Boccuti *et al.*, mostly on the basis of UV-Vis spectra (*3*). According to their results, Ti sites are constituted by tetrahedral $[TiO_4]$ units, while a previously proposed titanyl structure [Ti═O] (*1*) was shown to be unlikely. The 960 cm^{-1} IR band was assigned to a stretching vibration mode of $[SiO_4]$ tetrahedra bound to lattice Ti. They also suggested that one or two Ti—O—Si bonds were reversibly hydrolyzed by water. More recently Tuel *et al.* provided further support for tetrahedral coordination, on the basis of EPR spectra (*4*).

One of us proposed that hydroperoxo species are formed at Ti sites in methanol solution of hydrogen peroxide (*5*). This assump-

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tion was consistent with the results of the oxidation of n-hexane in the presence of acids and bases. We have further investigated the reactions of titanium silicalite with hydrogen peroxide and with other protic molecules. In this paper we present the results of this study.

EXPERIMENTAL

General

X-ray powder diffraction analyses (XRD) were performed on a Philips diffractometer equipped with a pulse height analyzer, using Cu$K\alpha$ radiation (λ = 0.154178 nm). Morphology of TS-1 samples was observed by a Philips PSEM-5000 scanning electron microscope (SEM). FT–IR spectra were collected on a Perkin–Elmer 1730 instrument, using the KBr wafer technique. XPS analyses were made with a VG Escalab MKII spectrometer, using Mg$K\alpha$ radiation at 1253.6 eV, as previously described (*6*). Gas chromatographic–mass spectrometric (GC–MS) analyses were performed on a Finnigan model 4500 mass spectrometer.

Materials

Oxygen-17 (51.5 at.%) and oxygen-18 (97 at.%) enriched water were obtained from MSD Isotopes and from Aldrich, respectively. Deuterium oxide was purchased from Merck (99.8 at.%). Methanol and ethanol were pure reagent grade from Carlo Erba. They were repurified by fractional distillation and stored under nitrogen on 3 A molecular sieves. Hydrogen peroxide (35% wt/vol), formic acid, and benzene were Carlo Erba (RPE grade) and were used as received. *t*-Butyl methyl ether (MTBE) was 99.5% pure. *Cis*- and *trans*-2,3-epoxybutane (Aldrich), 1,2-dimethoxyethane (Fluka, purum), tetraethylorthotitanate (Merck, 98%), tetraethylsilicate (Dynasil A, by Dynamit Nobel), tetrapropylammonium hydroxide (Enichem Synthesis, aqueous solution), and tetraethylammonium hydroxide (Merck, purum) were used without further purification. Titanium silicalite samples were obtained by different procedures (*7*, *8*). Extra framework titanium dioxide was undetectable by XPS and XRD analyses. Phenol oxidation tests with hydrogen peroxide were also used to check purity of titanium silicalite (*6*). Small crystal TS-1 (0.1–0.3 μm) was used for catalytic reactions.

Analytical Procedures

Gas chromatographic analyses (GLC) of *trans*-2,3-epoxybutane and its hydrolysis products were performed on a Hewlett-Packard HP 5890 instrument, with flame ionization detection (FID), a 60 m × 0.23 mm SPB-1 (dimethylpolysiloxane phase) fused silica capillary column, and helium as carrier gas. All other analyses used a HP 5880 gas chromatograph with FID and a 2.4 m × 2 mm glass column packed with Porapak PS. The identities of the products were verified by GC/MS analyses. The yields were determined by using the internal standard method. The stabilities of MTBE, benzene, and 1,2-dimethoxyethane GLC standards were checked at the reaction conditions.

Infrared spectra of TS-1 samples were recorded in the transmission mode. Samples were 1% dispersions in KBr pellets, dried 4 h at 400°C and 5.3-Pa pressure. After exposure for 0.5 h to 13.2-kPa water vapor, IR spectra were taken again.

^{17}O MAS NMR spectra were collected, after drying the samples 2 h at 60°C under 0.1-kPa pressure, on a Bruker CXP-300, using a solid echo pulse sequence, to overcome dead time effects ($90°_x$–20 μs–$90°_y$–24 μs–ACQ). A 90° pulse duration of 8.5 μs and a spectral window of 100 KHz were used.

Synthesis of small crystal titanium silicalite (*7*). Small crystal TS-1 was prepared in the previously described manner (crystallite size 0.1–0.3 μm, TiO_2 2.8 wt%).

Synthesis of large crystal titanium silicalite (*8*). A solution of 1.9 g tetraethyltitanate in 34.7 g of tetraethylsilicate was added to a mixture consisting of 3.1 g of a 50 wt% aqueous solution of tetraethylammonium hydroxide (TEAOH) and 13.4 g of a 31.5 wt% aqueous solution of tetrapropylammonium hydroxide (TPAOH), under vigorous stirring. The resulting solution was kept at 40–50°C, with stirring, for 4 h. Occasionally distilled water was added to compensate for evaporation. Molar ratios in the final solution were: $SiO_2/TiO_2 = 20$, $(TPAOH + TEAOH)/SiO_2 = 0.18$, $(TPAOH)/(TEAOH) = 2$, $H_2O/SiO_2 = 35$. The mixture was transferred to a 260-ml stainless-steel autoclave and heated in an oven at 165°C, under autogenous pressure, with stirring, for 4 days. After cooling to room temperature, the crystalline product was separated from the liquid by filtration, washed several times with water, dried for 4 h at 120°C, and finally calcined for 5 h at 550°C in air (TiO_2 = 2.3 wt%, SiO_2/TiO_2 molar ratio 57, crystallite size 2–3 μm).

The sample having 10 μm crystallite size was prepared by a similar procedure, without stirring in the crystallization step (TiO_2 = 2.2 wt%, SiO_2/TiO_2 molar ratio 59).

Preparation of silicalite-1. Products of different crystal size were obtained by the methods described for TS-1. Tetraethyltitanate was omitted.

Preparation of ^{2}H-labeled TS-1. Titanium silicalite (0.1 g, 0.1- to 0.3-μm crystallite size) was dried for 2 h at 600°C, cooled under nitrogen, and then treated with 0.1 g of deuterium oxide. The mixture was kept for 7 days at room temperature (*9*). Infrared spectra were collected as previously described.

Preparation of oxygen-17-labeled TS-1. To 0.42 g of titanium silicalite, previously dried for 2 h at 600°C and cooled to room temperature under nitrogen, 0.10 g of oxygen-17-enriched water (51.5 at.%) was added. The mixture was heated for 40 h at 60°C and then left several days at room temperature.

Preparation of oxygen-18-labeled TS-1. To 0.11 g of titanium silicalite, dried for 3 h at 600°C and cooled to room temperature under nitrogen, 0.070 g of oxygen-18-enriched water (97 at.%) was added. The mixture was kept for 7 days at room temperature and then excess water was removed by heating for 7 h at 120°C and 0.1 kPa pressure. Labeled water (0.10 g) was added again, the mixture left for 4 more days at room temperature, and infrared spectra recorded as described.

Preparation of labeled S-1. Silicalite-1 was treated with oxygen-17- or oxygen-18-enriched water as described for titanium silicalite.

Hydrolysis of trans-2,3-epoxybutane. A typical procedure for the catalytic hydrolysis of *trans*-2,3-epoxybutane was carried out with 0.212 g of TS-1 suspended in a solution consisting of 0.659 g of epoxide, 0.263 g of MTBE (GLC internal standard), 38 ml of methanol, and 0.311 g of 35% aqueous hydrogen peroxide. The hydrogen peroxide concentration was determined by iodometric titration (0.081 *M*). The slurry was heated at 60°C, under vigorous stirring, in a 50-ml round bottom flask fitted with a septum, a thermometer, and a condenser. Aliquots were withdrawn periodically from the reaction mixture, with the aid of a hypodermic syringe, for gas chromatographic analyses. Hydrogen peroxide titration was repeated at the end of the reaction (0.061 *M*). The reaction is stereospecific. The same isomer is formed as by perchloric acid catalyzed solvolysis.

Reactions with either titanium silicalite or silicalite-1 and hydrogen peroxide catalysts were carried out similarly.

Hydrolysis of trans-2,3-epoxybutane, catalyzed by TS-1 and hydrogen peroxide in the presence of sodium hydroxide. Titanium silicalite (0.216 g) was added to a solution of 0.662 g of epoxide, 0.226 g of MTBE, 2.0 ml of sodium hydroxide (0.0051 *M* in methanol), and 38 ml of hydrogen peroxide (0.085 *M* in methanol). The reaction was carried out at 60°C, as previously described.

Hydrolysis of trans-2,3-epoxybutane, catalyzed by formic acid. A solution of 0.179 g of formic acid, 0.670 g of epoxide, and 0.275 g of MTBE in 40 ml of a 0.083 *M* solution of hydrogen peroxide in methanol was heated at 60°C. The products were determined as already described.

Hydrolysis of cis-2,3-epoxybutane in methanol. A typical procedure for the catalytic hydrolysis of *cis*-2,3-epoxybutane in methanol was carried out with 0.202 g of titanium silicalite suspended in a solution consisting of 0.660 g of *cis*-2,3-epoxybutane, 0.413 g of benzene (GLC internal standard), and 40 ml of a solution of hydrogen peroxide in methanol. Hydrogen peroxide concentration was shown to be 0.081 *M* by iodometric titration. The suspension was heated at 30°C, with magnetic stirring, as previously described. Aliquots, for gas chromatographic analysis, were withdrawn at time intervals from the reaction mixture. Hydrogen peroxide concentration was 0.0801 *M* at the end of the run. The solvolysis reaction is stereospecific.

The reactions catalyzed by titanium silicalite in methanol and by titanium silicalite and hydrogen peroxide in aqueous methanol were carried out in a similar manner.

Hydrolysis of cis-2,3-epoxybutane, catalyzed by titanium silicalite and hydrogen peroxide in ethanol. Titanium silicalite (0.178 g) was added to a solution of 0.575 g of epoxide, 0.351 g of benzene, in 35 ml of a solution of hydrogen peroxide in ethanol. The reaction mixture was titrated for hydrogen peroxide (0.090 *M*). The suspension was heated at 30°C, with stirring. Aliquots were withdrawn as previously described. The reaction was stopped after 1 h and the solid was removed by centrifugation. Hydrogen peroxide was determined on a 5 ml aliquot of the clear solution (0.071 *M*). Total H^+ concentration was determined by basic titration of the remaining solution (0.011 *M*).

Hydrolysis of cis-2,3-epoxybutane in aqueous solutions. A solution 0.026 g of titanium silicalite, 5 ml of a 0.083 *M* solution of hydrogen peroxide in water, 0.085 g of *cis*-2,3-epoxybutane, and 0.087 g of 1,2-dimethoxyethane (GLC internal standard) were added to a 7-ml total volume conical flask, tightly capped with a rubber septum. The suspension was heated at 30°C, with magnetic stirring. Samples were withdrawn periodically with a GLC syringe and injected.

The reactions with titanium silicalite and 0.50 *M* hydrogen peroxide, with silicalite-1 and 0.081 *M* hydrogen peroxide, and with titanium silicalite as catalysts, were carried out similarly.

RESULTS

IR and NMR Spectra of TS-1 exchanged with Labeled Water

A weak band, which is regarded as the fingerprint of titanium silicalite, is shown in the frequency range of 950–975 cm^{-1} of the infrared spectrum. Its relative intensity is directly proportional to the content of titanium (*10*), while its exact position is determined by the degree of hydration and the average size of the crystallites (Table 1 and Fig. 1). In large crystal titanium silicalite (10 μm) the IR absorption occurs at 952 cm^{-1}, while in smaller ones (0.1–0.3 μm) it occurs at 960 cm^{-1}. Adsorbed water shifts these values upward to 962 and 973 cm^{-1}, respectively. At the same time the peaks become slightly broader and weaker.

The strong absorptions at 1000–1200 cm^{-1} are dependent on the size of the crystallites as well (Fig. 1). An extra peak grows in intensity and decreases in frequency, from 1050 to 1033 cm^{-1}, for average crystal size larger than 2 μm. Powdering the particles to less than 1 μm leads to the disappearance of the extra peak and to an increase of the intensity of the absorption at 1100 cm^{-1}. Why crystal size affects the IR spectrum of titanium silicalite is not well understood. Similar results were observed by Le Fêbre *et al.* (*11*) on ZSM-5 samples and were attributed to heterogeneity in the particles.

The band absorption at 950–975 cm^{-1} is in the frequency range where Si—OH, Ti=O, and Ti—O—Si IR absorptions are expected to occur (*3*). It was assigned by Boccuti *et al.* (*3*), in a simplified model, to a stretching vibration mode of Ti—O—Si bonds. We have further studied this issue by means of isotopically labeled TS-1 samples.

TABLE 1

Infrared Spectra of Titanium Silicalite in the 900–1000 cm^{-1} Region

SiO_2/TiO_2 (molar ratio)	Crystallite size (μm)	TS-1[a]	TS-1(^{2}H)[a]	TS-1(^{17}O)	TS-1(^{18}O)
46	0.1–0.3	962–973	962–973	952	937
52	2–3	957–964[b]	—	—	937
57	10	952–962[b]	—	—	—
69	0.1–0.3	961	—	—	—
94	0.1–0.3	964	—	—	—
325	0.1–0.3	962	—	—	—

[a] First value refers to dried TS-1 samples. See Experimental.

[b] The absorption was shifted to 962 cm^{-1} after powdering to particle size <1 μm (dried material).

The IR absorption of Si—OH groups on silica occurs at about 985 cm^{-1} and is deuterium-exchange sensitive (9). We similarly exchanged titanium silicalite with deuterium oxide and verified that the 962 cm^{-1} band was not affected (Table 1). This makes unlikely any attribution of the latter to Si—OH groups. The IR spectrum in the region of 950–975 cm^{-1}, however, was clearly modified by oxygen exchange with either ^{17}O- or ^{18}O-labeled water (Table 1). The absorption initially at 962 cm^{-1} was shifted to 952 and 937 cm^{-1}, respectively. The exchange was reversible. The original band at 962 cm^{-1} was restored after exposure of isotopically labeled TS-1 samples to $H_2{}^{16}O$.

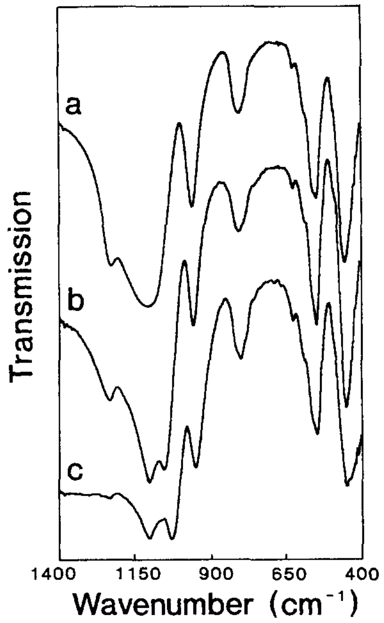


FIG. 1. Infrared spectra of titanium silicalite. Average particle size 0.1–0.3 μm (a), 2–3 μm (b), 10 μm (c).

Further information on exchange reactions was given by ^{17}O MAS NMR spectra of enriched silicalite-1 and titanium silicalite. Only one peak, due to the presence of residual $H_2{}^{17}O$, was shown in the spectrum of large crystal S-1 (Fig. 2b), while several more peaks were observed in the spectrum of small crystal S-1 (Fig. 2a). These are most likely due to oxygen-17 incorporated at nonbridging Si—OH groups, at nonequivalent sites of the crystals. In the spectra of titanium silicalite, besides the peaks already shown by silicalite-1, an extra peak was observed at δ 360 ppm from oxygen-17 water taken as reference (Fig. 2c and 2d).

Interaction between TS-1 and H_2O_2

We have already briefly reported that TS-1 catalyses the hydrolysis of propylene oxide in aqueous methanol solutions (7). The results were typical of a very weak acid, as shown by the low value of hydrolysis constants. Thus, high yields of propylene oxide were obtained in the epoxidation of propylene, despite the fact that the reaction was carried out in a protic medium. How-

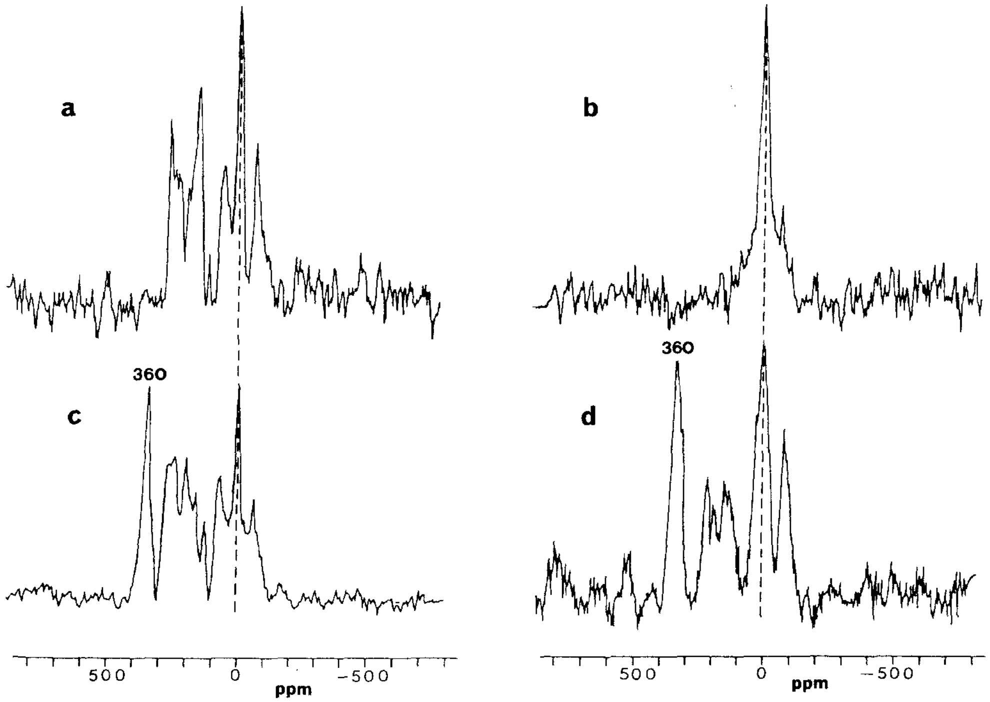


FIG. 2. ^{17}O MAS NMR spectra of titanium silicalite and silicalite-1 exchanged with $H_2{}^{17}O$. $H_2{}^{17}O$ is also present in the spectra as an impurity ($\delta = 0$). Chemical shifts are reported in ppm from an external standard of tap water. (a) 0.1–0.3 μm S-1, (b) 2–3 μm S-1, (c) 0.1–0.3 μm TS-1, (d) 2–3 μm TS-1.

ever, a careful inspection of product distribution made apparent that the extent of the hydrolysis reaction was somewhat higher than expected on the grounds of rate constant values, as determined in the absence of hydrogen peroxide (*7*). Also, the hydrolysis was not consistent with the total acidity of the liquid phase, which was negligible. We have further extended this investigation to include the effect of various chemical reagents on acid properties of titanium silicalite in a protic medium.

Acid strength of solid acids is normally evaluated by establishing the Hammett H_0 function or by studying the reaction sequence of a proper model reaction (*12*). The first method, although more convenient, is unreliable in our case, because organic indicators that are used for this purpose cannot diffuse inside the TS-1 pore system. Hence we used a test reaction, i.e., the hydrolysis of 2-butene oxides. These are particularly suitable compounds. They are low-molecular-weight molecules, which can diffuse unhindered inside titanium silicalite. Ring opening of oxiranes by protic molecules is a well-known reaction and occurs under mild conditions (*13*). Solvolysis of 2-butene oxides gives rise to glycol derivatives at secondary sites on the alkyl chain. These are slowly oxidized to carbonyl compounds by TS-1/H_2O_2 reagent, but do not form acid by-products that might further catalyze the hydrolysis reaction.

In methanol solution, the hydrolysis of *trans*-2,3-epoxybutane in the absence of hydrogen peroxide is very slow (Fig. 3). In agreement with previous results on propylene oxide (*7*), less than 4% epoxide was hydrolyzed after 3 h at 60°C. The reaction catalyzed by titanium silicalite was only slightly faster than that with silicalite-1. Thus titanols and silanols at Ti sites of TS-1 are just stronger acids than silanols on S-1.

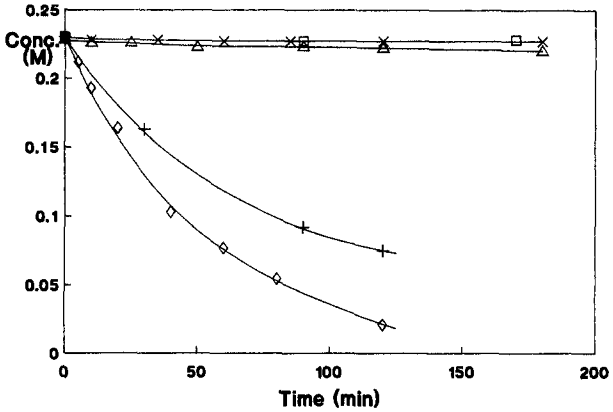


FIG. 3. Solvolysis of *trans*-2,3-epoxybutane in methanol. The concentration of the epoxide is plotted against time. Reaction conditions: Temp., 60°C; TS-1, 5.4 g/liter; *trans*-2,3-epoxybutane 0.23 *M*. Catalysts: (◇) TS-1 and H_2O_2 0.081 *M*, (+) Formic acid 0.1 *M*, (△) TS-1, (×) S-1 and H_2O_2 0.081 *M*, (□) TS-1 and H_2O_2 0.081 *M* and NaOH 0.005 *M*.

The effectiveness of titanium silicalite was greatly improved by hydrogen peroxide. The initial rate of hydrolysis was enhanced by two orders of magnitude when both TS-1 and hydrogen peroxide were employed as catalysts. Conversely the catalytic activity of silicalite-1 was unaffected by hydrogen peroxide. The experiment with sodium hydroxide (Fig. 3) showed that an acid species was produced by titanium silicalite and hydrogen peroxide and that the hydrolysis of *trans*-2,3-epoxybutane was mainly due to this species. As far as its nature is concerned, we found that during hydrolysis a minor but significant amount of hydrogen peroxide (24%) was consumed by side reactions. It is unlikely that formic acid is produced by the oxidation of methanol, under our reaction conditions (*14*). Nevertheless, we checked that the hydrolysis of *trans*-2,3-epoxybutane, catalyzed by 0.1 *M* formic acid (an exceedingly high concentration), occurred at a rate significantly lower than that with TS-1/H_2O_2 reagent (Fig. 3). Any major involvement of organic acid by-products to acid catalysis seems most unlikely.

Cis-2,3-epoxybutane provided further support for this conclusion. The hydrolysis of *cis*-epoxide was considerably faster than that of *trans*-isomer and could be studied at a lower temperature. At 30°C in methanol solution, the amount of H_2O_2 consumed by side reactions, and hence the formation of organic acid by-products, could be neglected. Under these conditions, the initial hydrolysis rate was again increased by two orders of magnitude by hydrogen peroxide cocatalyst (Fig. 4).

Acid activity of titanium silicalite and hydrogen peroxide was solvent dependent. The rate of hydrolysis decreased in the order: $CH_3OH > C_2H_5OH > H_2O$ (Figs. 4 and 5). In ethanol, the reaction was stopped after 1 h to prevent alcohol oxidation to acetic acid to any significant extent (0.011 *M*).

Although the reactions exhibited analogous features in water and in alcohol media, aqueous solutions of hydrogen peroxide had a lower effect on the catalytic activity of titanium silicalite (Fig. 5). No further improvement of the rate of hydrolysis was shown by a 10-fold increase of hydrogen peroxide concentration. However, adding methanol to the aqueous solution greatly enhances the reaction kinetics (Fig. 5).

DISCUSSION

Oxygen-17 MAS NMR spectra show that the hydrolysis of lattice Si—O—Si bonds on silicalite-1 is undetectable at near room

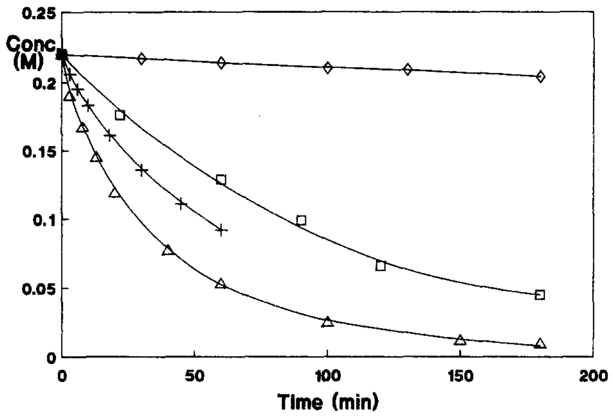


FIG. 4. Solvolysis of *cis*-2,3-epoxybutane in alcohol solvents. The concentration of the epoxide is plotted against time. Reaction conditions: Temp., 30°C; TS-1, 4.9 g/liter; *cis*-2,3-epoxybutane 0.22 *M*. Catalysts: (△) TS-1 and H_2O_2 0.081 *M* in methanol, (+) TS-1 and H_2O_2 0.090 *M* in ethanol, (□) TS-1 and H_2O_2 0.081 *M* in aqueous methanol (37 vol%), (◇) TS-1 in methanol.

temperature and under neutral conditions. Reactions with water proceed faster and reversibly at nonbridging Si—OH units, in agreement with higher ^{17}O incorporation on small crystal samples. Silanol Si—OH species are expected to increase as the average size of crystallites decreases.

An extra absorption is shown in the spectrum of titanium silicalite, at δ 360 ppm, irrespective of crystal size. Its attribution to ^{17}O of Si—O—Si bonds is unlikely on the grounds that no such peak is shown in the spectrum of silicalite-1, in spite of strong similarities between S-1 and TS-1 structures. This correlates better with titanium content of TS-1, whether it is lattice titanium or TiO_2 impurities. The latter hypothesis is unlikely on the basis of both XPS analyses and reactivity tests, which show that extra framework titanium is negligible.

Infrared spectra of ^{17}O- and ^{18}O-labeled titanium silicalite strengthen the conclusion

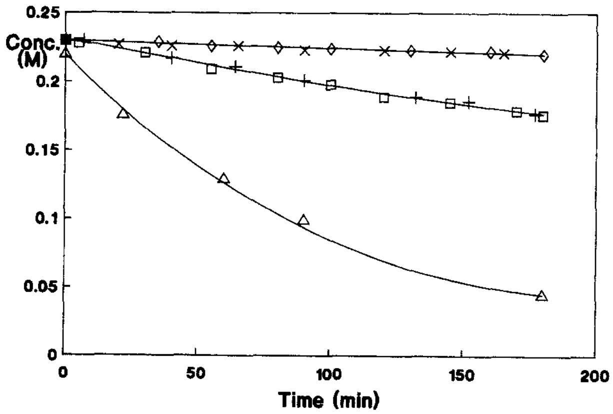
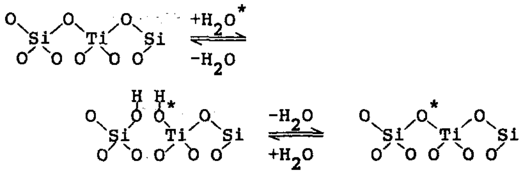


FIG. 5. Solvolysis of *cis*-2,3-epoxybutane in aqueous solutions. The concentration of the epoxide is plotted against time. Reaction conditions: Temp., 30°C; TS-1, 4.9 g/liter; *cis*-2,3-epoxybutane 0.23 *M*. Catalysts: (□) TS-1 and H_2O_2 0.081 *M*, (+) TS-1 and H_2O_2 0.5 *M*, (◇) TS-1, (×) S-1 and H_2O_2 0.081 *M*, (△) TS-1 and H_2O_2 0.081 *M* in aqueous methanol (37 vol%).

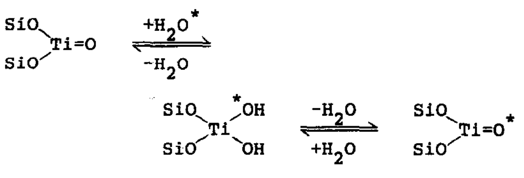
reached on the basis of NMR data; i.e., oxygen exchange occurs at Ti sites. The absorption at 962 cm^{-1}, characteristic of lattice titanium (*10*), is shifted to lower frequencies by reactions with labeled water.

Both spectroscopic and chemical properties of TS-1 are best explained by assuming, like Boccuti *et al.* (*3*), that Ti sites are constituted by tetrahedral $[TiO_4]$ units. A strain in the crystal lattice results, owing to larger ionic radius of the Ti^{4+} ion as compared to that of the Si^{4+} ion. Because of this and because of bond polarization, which assists water coordination on titanium atoms (*3*), Ti—O—Si bonds are cleaved by water, and possibly by other protic molecules, faster than Si—O—Si bonds. In agreement with NMR and IR results, titanol Ti—OH and silanol Si—OH species are reversibly formed at Ti sites (Scheme 1). The frequency decrease of the IR absorption at 962 cm^{-1} is consistent with the expected shift, based on the change in the reduced mass of the harmonic oscillator Ti—O—Si, as substitution of heavier oxygen isotopes for ^{16}O occurs.



SCHEME 1

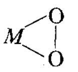
Both IR and NMR spectra might be as well accounted for by assuming that titanium sites have titanyl Ti═O structure (Scheme 2). However, the presence of Ti═O species on titanium silicalite was shown to be unlikely, on the basis of UV-Vis spectra (*3*).



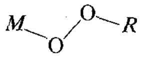
SCHEME 2

Figures 3 and 5 show that the acid strength of Ti—OH and Si—OH species on TS-1 is barely higher than that of Si—OH species present on silicalite-1. Hence, the increase of acid activity effected by hydrogen peroxide cannot be ascribed to Ti—OH and Si—OH forming at titanium sites. Experimental results are best explained by assuming that acid properties, and oxidant properties as well, are the results of species having peroxidic nature. These catalyze the hydrolysis of epoxide compounds and form stable salts with inorganic bases (*15*).

According to literature data (*16*), Group IV–VI transition metal peroxo-compounds have structure (I). They are produced by the reaction of metal oxides or metal complexes with either organic hydroperoxides or hydrogen peroxide.



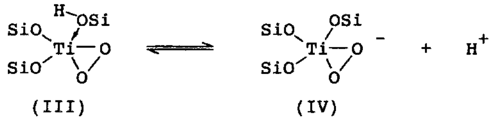
(I)



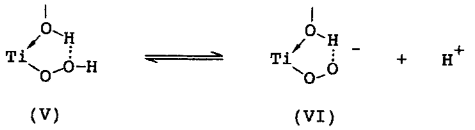
(II)

Species (II) have been proposed as intermediates or as active species in several oxidation reactions with hydroperoxides (R = alkyl, aryl) or hydrogen peroxide (R = H) as the oxidant, catalyzed by transition metal complexes (*17–22*). Their isolation and characterization have proven unsuccessful because an alcohol or a water molecule respectively is eliminated, to form derivatives of type (I) (*16*). In a brief report, the preparation of $MoO_2(OH)(OOH)$ has been claimed (*23*). No titanium hydroperoxo-compounds appear to have been prepared so far.

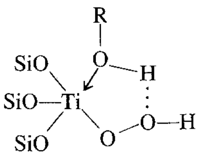
In principle, either peroxo- (I) or hydroperoxo-species (II) (R = H), might be formed by TS-1 and excess hydrogen peroxide, irrespective of whether titanium sites have a tetrahedral $[TiO_4]$ or a titanyl Ti═O structure. Reactions with hydrogen peroxide can proceed likewise with water (Schemes 1 and 2). A $Ti(O_2)$ species of type (I) has no acid activity, unless a vicinal Si—OH group is coordinated by titanium (Scheme 3). The pK_a values of hydroperoxo-species (II) (R = H) are not known, but are likely to be lower than those of Ti—OH counterparts. Similarly, alkyl hydroperoxides are stronger acids by about 3 pK_a units as compared to the corresponding alcohols (*24*). Moreover, a Ti—OOH species is able to form a stable five-membered cyclic structure (V), with a donor hydroxyl moiety coordinated on titanium. This further enhances acid dissociation as a result of greater hydrogen bond strength in anionic species (VI) (Scheme 4). Several examples known in organic chemistry show that pK_a values of acid molecules are significantly affected by forming stable cyclic structures (*25*). As far as the origin of the hydroxyl group in (V) is concerned, it might be provided by a solvent molecule, by neighboring Si—OH species or by a Ti—OH group. Structures are all consistent with this argument.



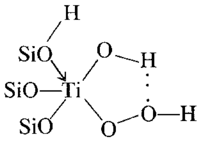
SCHEME 3



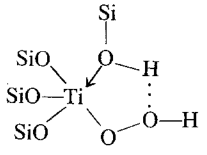
SCHEME 4



(VII)



(VIII)



(IX)

The behavior of the TS-1/H_2O_2 system is in better agreement with Scheme 4. Scheme 3 does not account for positive effects of protic solvents on reactions catalyzed by TS-1. Furthermore, it is unlikely that the acid strength of silanol species, which we have shown to be negligible on TS-1, could be significantly enhanced in (III) by the coordination of a peroxide anion on titanium centres.

Species (VIII) and (IX) suffer from two major shortcomings. Like (III), they fail to account for solvent effects. With (IX) the strain in the lattice of titanium silicalite, previously released by the hydrolysis of one Ti—O—Si bond, is reestablished. Water elimination in (VIII), to form stable peroxo-species (I), is favored (*16*).

The presence of (VII) is most likely in methanol, ethanol, and aqueous media. Coordination of a protic ligand at Ti sites to give a five-coordinated species is in agreement with the fact that tetrahedral configuration is unusual, while higher coordination numbers are common on titanium complexes (*26*). More importantly, species (VII) are consistent with the main features of either hydrolysis and oxidation reactions (*5, 7*):

(a) The relevant role played by the protic molecule on the stability of the five-membered ring hydrogen bonded structure explains why protic media do not inhibit titanium silicalite, as it occurs with soluble metal catalysts, but favor its reactions with hydrogen peroxide (*5, 7*). It also accounts, at least in part, for the synergism between hydrogen peroxide and methanol, ethanol, or water, respectively, on the acid strength of titanium silicalite (Scheme 4).

(b) Exchange reactions between (VII) and alkali metal salts produce anionic derivatives with reduced electrophilic power. Maximum and minimum concentrations of (VII) are achieved in acid and basic solutions, respectively. Accordingly the rate of oxidation of *n*-hexane is improved by acids, lowered by salts, and inhibited by bases (*5*). Similar results are shown by epoxidation reactions.

(c) Steric crowding inside pores of 0.55 nm average diameter is strongly dependent on the nature of ROH and increases rapidly in the order: $CH_3 < C_2H_5 < t\text{-}C_4H_9$. Hence, species (VII) are expected to be most stable, and therefore most easily formed with methanol ligand, as a result of small size and donor properties of the latter. Accordingly, methanol is among the best solvents as far as reaction kinetics are concerned. Particularly, it is the solvent of choice for the epoxidation of propylene and other olefins (*7*). As the size of the alcohol ROH increases, the hydrolysis of *cis*-2,3-epoxybutane and the epoxidation of propylene become increasingly slower.

Species (VII) are formed by an equilibrium reaction. All attempts to prepare and fully characterize, as pure products, hydroperoxo-derivatives of TS-1 ended in failure. These are unstable and slowly release hydrogen peroxide in the solvent, during the work-up (*15*). Whether peroxo-species of type (I) are involved or not in this equilibrium reaction (Scheme 5) is a question which is left unanswered by our results.

$$\mathrm{Ti} + H_2O_2 + \mathrm{ROH} \rightleftharpoons \mathrm{Ti(H_2O_2)(ROH)} \rightleftharpoons \mathrm{Ti(O_2)} + \mathrm{ROH}$$

SCHEME 5

Peroxo-species (I) have no acid properties and cannot be revealed on the basis of hydrolysis experiments of butene oxides. Further research is required to fully clarify all species formed by TS-1 and hydrogen peroxide in different chemical environments.

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