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Photochemical and FT-IR Probing of the Active Site of Hydrogen Peroxide in Ti Silicalite Sieve

Wenyong Lin and Heinz Frei*

Contribution from the Physical Biosciences Division, Mailstop Calvin Laboratory, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

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Abstract: Upon loading of aqueous hydrogen peroxide into Ti silicalite sieve and removal of the solvent by evacuation, a thermally stable hydroperoxo species was detected by infrared spectroscopy with an OO stretch absorption at 837 cm^{-1} (^{18}O, 793 cm^{-1}) and a broad OH band at 3400 cm^{-1}. The species, assigned to TiOOH (η^2), is photolabile and is very efficiently converted to a titanol group upon excitation of its UV−vis ligand-to-metal charge-transfer (LMCT) absorption. Growth of H_2O (^{16}O, 1629 cm^{-1}; ^{18}O, 1625 cm^{-1}) and of the 960 cm^{-1} framework mode indicate that a substantial fraction of the titanol groups recondense with adjacent Si−OH to Ti−O−Si. The TiOOH moiety was shown by in situ FT-IR monitoring to oxidize small olefins at room temperature in the dark (propylene) or under photoexcitation of the LMCT chromophore (ethylene). This is the first direct detection of the active oxidation site in H_2O_2-loaded Ti silicalite sieve.

Introduction

Ti silicalite molecular sieve (TS-1) is an efficient and stable catalyst for the partial hydrocarbon oxidation by H_2O_2 under mild conditions.[1−7] Selectivities are remarkably high, especially in olefin epoxidation.[8] Accordingly, considerable effort has been invested into attempts to detect and identify the active oxidation site. Early studies of hydrocarbon oxidation in H_2O_2-containing TS-1 revealed a blue and UV light-absorbing chromophore attributed to a ligand-to-metal charge-transfer transition (LMCT) of a peroxo moiety interacting with a framework Ti center.[9,10] The yellow color of the H_2O_2-loaded TS-1 persisted at room temperature when keeping the sieve under vacuum but decreased upon hydrocarbon oxidation.[6] Hence, the UV−visible light-absorbing species must be involved in the oxidation reaction. However, characterization of the active site by a structure-specific method such as vibrational spectroscopy has eluded these earlier studies. Infrared absorptions of unstable (hydro)peroxo species have been reported by Zecchina and co-workers at low temperature (230 K) when maintaining the H_2O_2-loaded sieve in a hydrated state.[11] A feature at 886 cm^{-1}, strongly overlapping with physisorbed H_2O_2, was attributed to unstable TiOOH (η^1), while a band at 837 cm^{-1} was assigned to anionic triangular Ti(O_2^-). However, both absorptions were reported to disappear upon removal of H_2O or upon warmup to room temperature.[11] Hence, possible reactivity under exposure to hydrocarbons could not be explored.

XAFS measurements of the active site of *tert* butyl hydroperoxide on Ti-grafted MCM-41 sieve were recently reported for the first time by Sankar et al.[12] Combined with DFT calculations on a $(H_3SiO)_3TiOOH$ model cluster, the best fit of the data indicates a bidentate (side-on) peroxo structure.[12] Earlier ab initio and density functional calculations on model compounds by several groups also indicate a bidentate TiOOH (η^2) group as the most stable species formed upon interaction of H_2O_2 with TS-1 sieve.[13−15] However, some DFT calculations suggest an undissociated H_2O_2 molecule weakly interacting with Ti centers as the active species,[16] and others suggest an active role by Ti−O−O−Si peroxo moieties.[17] Clearly, direct spectroscopic observation of H_2O_2 interacting with the metal centers is needed to determine the precise nature of the active site in Ti silicalite sieve.

In this paper, we present direct infrared spectroscopic evidence for the TiOOH moiety in TS-1 sieve. The species is found to photodissociate efficiently under irradiation with visible or near UV light. In situ FT-IR monitoring of the phototriggered or thermally induced oxidation of small olefins in the absence of solvent led to the direct observation of the reaction of the peroxidic species.

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* Address correspondence to this author. E-mail: hmfrei@lbl.gov.

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II. Experimental Section

TS-1 sieve was prepared according to the literature procedure[8] with a typical molar composition 1.0 SiO_2 : 0.01 TiO_2: 0.46 TPAOH: 35 H_2O. Chemicals used for the synthesis were tetraethyl orthosilicate (Aldrich, 98%), tetrabutylorthotitanate (Fluka, 99%), and tetrapropylammonium hydroxide (TPAOH, Aldrich, 1 M). Crystallization of the gel was conducted in an autoclave at 448 K for two days. The sample was calcined under O_2 flow at 773 K for 10 h. Silicalite-1 sieve was prepared using the same procedure except for addition of the Ti source.

Powder XRD measurements were performed with a Siemens model D5000 diffractometer using Cu K_α ($\alpha = 1.5406$ Å) radiation. Data collection was conducted in the range $4° < 2\Theta < 40°$ at steps of 0.02° and a sampling rate of 1 min per degree. The measured patterns matched those of published MFI data.[18] No extra peak or phase was detected. UV−vis diffuse reflectance spectra were recorded on a Shimadzu model UV-2100 spectrometer equipped with an integrating sphere Model ISR-260. $BaSO_4$ was used as reference. The sieve crystallites were pressed into a self-sustaining pellet (5 mg, 2×10^5 kPa) and mounted in a home-built DRS vacuum cell.[19]The spectrum agreed with those of TS-1 materials reported in the literature.[9,10,20,21] It shows the ligand-to-metal charge-transfer absorption (LMCT) attributed to tetrahedrally coordinated Ti.[22,23] There is no absorption at wavelengths longer than 330 nm, consistent with the absence of extraframework Ti oxide species.[10,20] Emission and luminescence excitation spectra were in full agreement with those reported in the literature.[23] Thermal and photochemical experiments were also conducted with a TS-1 sample that was previously characterized by XANES,[24]leading to the same results.

In situ FT-IR measurements were performed by mounting the self-sustaining TS-1 pellet in a miniature stainless steel cell equipped with KCl windows. Hydrogen peroxide was loaded by placing a drop (0.05 mL) of aqueous H_2O_2 solution onto the mounted pellet and evacuating the cell at 10^{-5} Torr for 8−12 h. The intensity of the H_2O bending mode at 1629 cm^{-1} indicated a residual water content in the sieve of approximately one molecule per unit cell. For experiments at temperatures other than 295 K, the infrared cell was mounted in a temperature-programmable Oxford Cryostat model Optistat. Photolysis at 355 nm was conducted with emission of a pulsed Coherent Nd:YAG laser model Infinity. The beam intensity was either 2.6 mJ cm^{-2} or 7.8 mJ cm^{-2} at a repetition rate of 10 Hz. For photolysis with visible light, a conventional W−X lamp equipped with a UV-blocking filter (Corning No. 3-73) was used. Oxidation reactions were conducted by loading olefin gas into the infrared cell through a vacuum manifold. The same procedures were used for loading the DRS vacuum cell. Infrared spectra were recorded at 1 cm^{-1} resolution using an IBM-Bruker FT-IR model IR-97 or a Bruker FT-IR model Vector 33.

Aqueous H_2O_2 solution (Aldrich, 30% or 50%), aqueous $H_2{}^{18}O_2$ (ICON, 2.7%, ^{18}O 90%), propylene (Matheson, 99.5%), ethylene (Matheson, 99.98%), O_2 (Air Products, 99.997%), and ethylene oxide (Aldrich, 99.5%) were used as received. Propylene oxide (Aldrich, 99%), propionaldehyde (Aldrich, 97%), acrolein (Aldrich, 90%), and acetaldehyde (Aldrich, 99.5%) were degassed by several freeze−pump−thaw cycles before loading the gas into the IR cell.

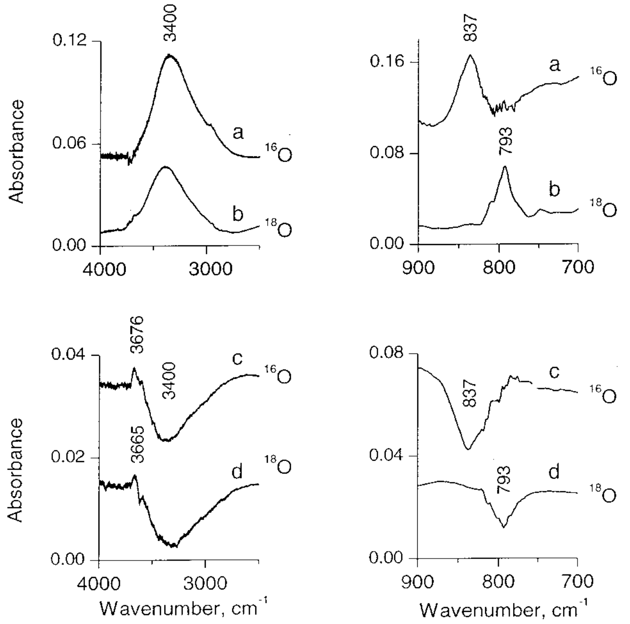

Figure 1. Infrared difference spectra before and after loading of aqueous $H_2{}^{16}O_2$ (trace a) and $H_2{}^{18}O_2$ (trace b) into TS-1 sieve followed by 12 h evacuation (10^{-5} Torr). Traces c and d are infrared difference spectra recorded upon 20 min irradiation of samples a and b at 355 nm (45 mW cm^{-2}).

III. Results

1. Identification and Photodissociation of TiOOH. Upon adsorption of 0.05 mL aqueous H_2O_2 solution (30 or 50%) onto a dehydrated TS-1 pellet at room temperature (RT), an infrared band is observed at 877 cm^{-1}. The absorption, which coincides with the OO stretching frequency of free H_2O_2,[25] disappears after a few minutes evacuation of the sieve at RT and is attributed to hydrogen peroxide physisorbed on the pore walls.[11] By contrast, an infrared absorption observed at 837 cm^{-1} and a very broad band centered at 3400 cm^{-1} do not undergo intensity changes upon removal of water by continued evacuation for days (Figure 1a). No bands were observed at 837 or 3400 cm^{-1} when the same loading and evacuation experiment was conducted with parent silicalite-1. Hence, the two infrared absorptions originate from a peroxo species interacting with framework Ti. Trace b of Figure 1 shows the corresponding bands of $H_2{}^{18}O_2$ loaded TS-sieve at 793 and around 3400 cm^{-1}. Frequency and ^{18}O shift of the 837 cm^{-1} absorption are characteristic of a peroxidic OO stretching mode.[26] The broad 3400 cm^{-1} band signals the presence of a H-bonded OH group.[27] The large red shift of the OO mode relative to physisorbed H_2O_2 indicates a peroxo group covalently bound to the Ti center. According to recent ab initio and DFT cluster calculations by several groups, TiOOH is predicted as the most stable Ti peroxo species.[12−15] While the 3400 cm^{-1} frequency as such may not be characteristic of a hydroperoxy OH stretch, the computational results combined with the fact that the OO and OH stretch absorptions show concerted behavior make assignment to TiOOH most probable. Hence, these observations indicate that loading of H_2O_2 solution into TS-1 sieve and subsequent removal of the solvent and of physisorbed H_2O_2 results in the formation of a Ti−OOH species that is indefinitely stable at RT. The UV−vis diffuse reflectance spectrum of a TS-1 pellet

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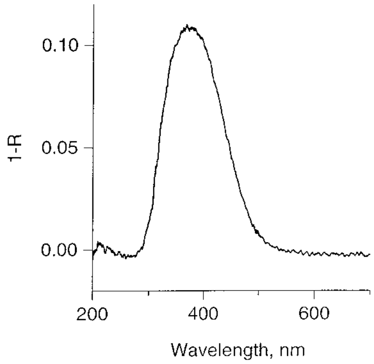

Figure 2. Diffuse reflectance difference spectrum of the LMCT absorption upon 355 nm photolysis of TS-1/TiOOH sieve (20 min at 45 mW cm^{-2}).

treated according to the same H_2O_2 loading procedure revealed upon prolonged evacuation an accompanying LMCT absorption with a maximum around 360 nm and a tail extending to 550 nm. The stability of the LMCT band of the active site under these conditions was already reported by Davis.[6]

When irradiating the H_2O_2 loaded sieve with 355 nm light of a Nd:YAG laser, or the visible emission of a conventional tungsten source, the UV−vis absorption decreased under concurrent absorbance loss of the infrared bands at 837 cm^{-1} (^{18}O, 793 cm^{-1}) and 3400 cm^{-1}. At the same time, an absorption grew in at 3676 cm^{-1} (3665 cm^{-1} for the ^{18}O labeled sample). Figure 1c shows the infrared difference spectrum following 20 min irradiation at 355 nm (45 mW cm^{-2}) of $H_2{}^{16}O_2$ loaded TS-1, and trace d shows the result with $H_2{}^{18}O_2$ loaded sieve. The 11 cm^{-1} ^{18}O shift of the 3676 cm^{-1} product band is typical for an OH absorption and indicates that the oxygen originates from H_2O_2.[28] The frequency coincides with that of titanol groups of Ti-grafted MCM-48[29] and is therefore assigned to the hitherto unobserved Ti−OH group in TS-1 sieve. The quantum efficiency of the photodissociation was estimated to be unity within error bars. Depletion by mere laser-induced thermal heating is ruled out because the TiOOH group was stable upon warmup of the sieve to 60 °C under vacuum. The temperature rise due to irradiation with laser light at the low intensity used is a few degrees at the most.[30] The photolysis result confirms that the 837 cm^{-1} ν(OO) and the 3400 cm^{-1} ν(OH) bands originate from the functionality that gives rise to the UV−vis LMCT absorption, shown in Figure 2. We conclude that the LMCT chromophore in solvent-free TS-1 sieve is due to the Ti−OOH hydroperoxo moiety. The net result of the photodissociation is disproportionation of the Ti−OOH moiety to Ti−OH and oxygen.

As shown in Figure 3, the photodissociation of TiOOH is accompanied by growth of two additional bands, namely, at 1629 cm^{-1} (1625 when using $H_2{}^{18}O_2$) and at 960 cm^{-1} (no ^{18}O shift in the $H_2{}^{18}O_2$ experiment). The 1629 cm^{-1} band and its ^{18}O isotopic shift are characteristic for the bending mode of H_2O[28] (Figure 3 insert). While the growth of 3676 and 1629 cm^{-1} bands shows the same trend, the relative intensities vary substantially from experiment to experiment. This indicates that the two bands do not belong to the same species, consistent with the assignment to titanol groups and H_2O, respectively. The OH stretching absorption of H_2O product is expected to be very broad and to overlap with the decreasing ν(OH) band of TiOOH. It is likely that, in addition, H_2O also contributes intensity to the absorption in the 3600−3700 cm^{-1} regions. The ^{18}O frequency shifts indicate that the oxygen of H_2O and Ti−OH originates from hydrogen peroxide. The 960 cm^{-1} band appears as an intense feature in dehydrated TS-1 sieve and is assigned to the well-known Si−O stretching mode of SiO_4 units perturbed by adjacent Ti framework centers.[23,31−35] After loading of H_2O_2 and prolonged evacuation, its intensity decreases by approximately 20%, presumably because of the change of the coordination around Ti upon formation of TiOOH moieties. The growth of the band upon photolysis of TiOOH, shown in Figure 3, points to at least partial restoration of the original coordination environment of the metal center.

2. Thermal and Photoinduced Reaction of Propylene. Loading of TS-1/H_2O_2 sieve, after evacuation at 10^{-5} Torr for 10 h, with 5 Torr propylene resulted in infrared absorptions at 912, 1373, 1415, 1443, 1646, 2724, 2856, 2888, 2920, 2980, and 3081 cm^{-1}, shown in Figure 4. As can be seen from the infrared difference spectrum of Figure 5, spontaneous loss of propylene and TiOOH at 837 cm^{-1} (Ti^{18}O^{18}OH, 788 cm^{-1}, apparent peak shift from 793 cm^{-1} because of overlap with 830 cm^{-1} epoxide product band) and 3400 cm^{-1} is observed on the minute-to-hour time scale while several product bands grow in. No reaction of propylene occurred in the absence of TiOOH. After 80 min (trace a), the product spectrum consists of bands at 830 (810), 895 (890), 1372, 1409 (1406), 1452, 1460, and 1493 (1490) cm^{-1} (numbers in parentheses are ^{18}O labeled product). The rate of decay of the 837 cm^{-1} absorption mirrors within uncertainties the growth rate of the product (0.020 ± 0.005 min^{-1}). The rate constants refer to a fit over the first 40 min after propylene loading; kinetic fits over longer periods yield successively lower rate constants. The origin of this heterogeneity may reflect the different local environment of Ti in the nonrandom framework position.[36−38] All absorptions originate from propylene oxide (methyloxirane) as indicated by a comparison with the spectrum of an authentic CH_3CH-CH_2-O sample loaded into the sieve. We conclude that the TiOOH group is the active site of olefin epoxidation in TS-1. Upon prolonged reaction (trace b), a very small product band grows in at 1721 cm^{-1}. This additional product was readily identified as propionaldehyde by spectroscopy of authentic samples in TS-1.

In a separate series of experiments with an authentic sample of propylene oxide, we have found that, in the presence of TiOOH groups, loading of the gaseous epoxide into TS-1 sieve results in the conversion of small amounts of propylene oxide

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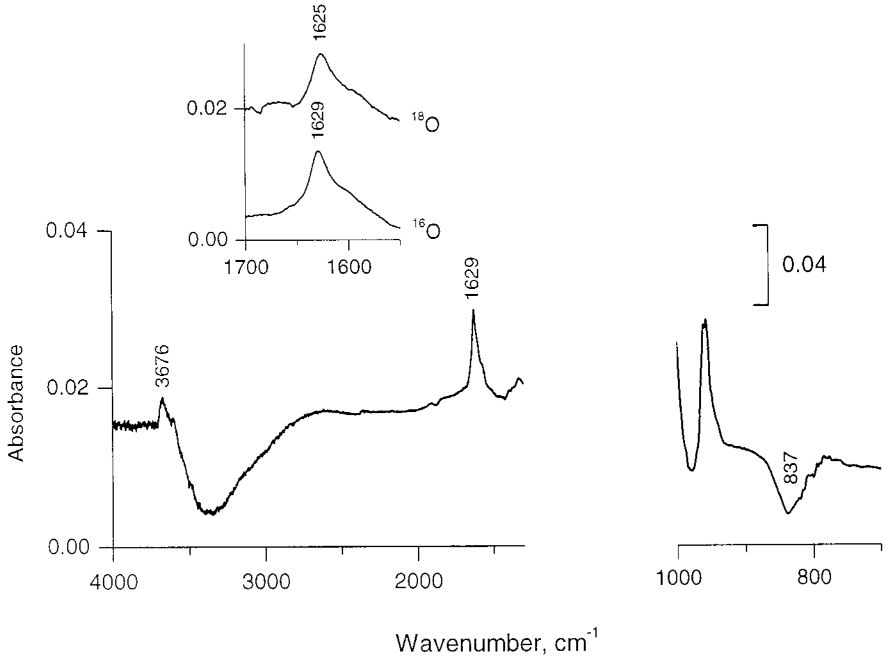

Figure 3. FT-IR difference spectrum recorded upon 20 min irradiation of TS-1 sieve containing TiOOH at 355 nm (45 mW cm^{-2}). The insert shows the ^{18}O isotope shift of the 1629 cm^{-1} product attributed to H_2O.

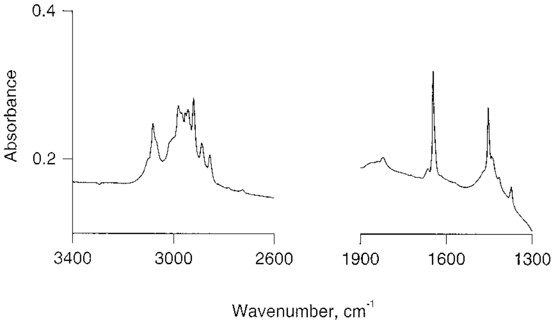

Figure 4. Infrared difference spectrum recorded immediately after loading of 5 Torr propylene gas into TS-1 sieve containing TiOOH. The TS-1/TiOOH sieve was prepared as described in the text. While the main peaks originate from adsorbed C_3H_6, the small shoulders of the bands at 1443, 1646, 2980, and 3081 cm^{-1} are due to gas-phase propylene.

to propionaldehyde, presumably by spontaneous 1,2 H shift[39] (no rearrangement of the epoxide is observed in TS-1 sieve free of H_2O_2). This strongly suggests that the slow growth of aldehyde upon spontaneous reaction of propylene in H_2O_2 treated TS-1 sieve is due to thermal rearrangement of the accumulating propylene oxide. We conclude that the spontaneous epoxidation of propylene by TiOOH in solvent-free TS-1 sieve is completely selective. Upon irradiation of the LMCT absorption with 355 nm light, the oxidation of propylene is accelerated and a more significant yield of propionaldehyde is observed. As in TiOOH photolysis (Section 1), the 960 cm^{-1} framework absorption regains intensity as the active site is depleted by reaction with the olefin.

The decrease of the TiOOH infrared bands upon reaction with propylene is accompanied, as expected, by depletion of its UV−vis LMCT absorption shown in Figure 6. The asymptotic propylene oxide yield upon prolonged reaction is 0.6 per Ti framework center present in the sieve. This was determined by measuring the propylene oxide extinction coefficients of the well-isolated bands at 1409 and 1493 cm^{-1} using manometric techniques described previously.[40]The implication is that at least 60% of all framework Ti (or 80% of the surface-exposed Ti) is derivatized by H_2O_2. The observation of a single O−O stretch band (837 cm^{-1}) of TiOOH suggests the formation of just one peroxo ligand per Ti center.

3. Photoinduced Reaction of Ethylene. In contrast to propylene, admission of 100−200 Torr ethylene to a TS-1/H_2O_2 pellet prepared as described in the preceding sections was not followed by spontaneous dark reaction even for hours at room temperature. On the other hand, excitation of the UV−vis LMCT absorption of the TiOOH group resulted in efficient reaction with ethylene as indicated by absorbance loss at 837 (793) cm^{-1} and 3400 cm^{-1} and by growth of ethylene oxide at 871 (846) cm^{-1} and acetaldehyde at 1353, 1724 (1692) cm^{-1}. These observations constitute again direct evidence that TiOOH is the active oxidation site. The ratio of the peak intensities of the epoxide band at 871 cm^{-1} and the aldehyde absorption at 1721 cm^{-1} of 1 remained constant as function of photolysis time. Concurrent formation of TiOH groups was signaled by growth at 3676 (3665) cm^{-1} and of H_2O at 1629 cm^{-1}. Frequencies in parentheses refer to experiments with $H_2{}^{18}O_2$. Product assignments were established by comparison with authentic samples of $\overline{CH_2\text{-}CH_2\text{-}O}$ and $CH_3\text{-}CH{=}O$ loaded into TS-1 sieve. Figure 7 shows infrared difference spectra following 355 nm photolysis for 30 min. Direct proof for O transfer involving the TiOOH moiety is furnished by the ^{18}O isotope frequency shifts of the photoproducts when preparing TS-1 featuring a $Ti^{18}O^{18}OH$ moiety. While the $\overline{CH_2\text{-}CH_2\text{-}{}^{18}O}$ product was isotopically pure, two acetaldehyde isotopomers appeared as indicated by a CO stretch absorption at 1721 cm^{-1} ($CH_3CH{=}^{16}O$) and 1693 cm^{-1} ($CH_3CH{=}^{18}O$) (Figure 8a). We noticed a spontaneous interconversion of the ^{18}O labeled product to the parent compound, as illustrated in trace b of Figure 8.

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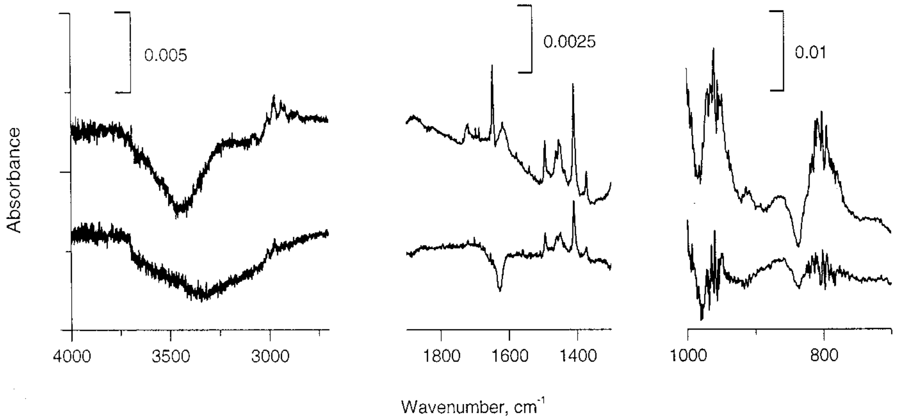

Figure 5. FT-infrared difference spectrum recorded 80 min (trace a) and 320 min (trace b) after loading of TS-1/TiOOH sieve with 5 Torr propylene at room temperature.

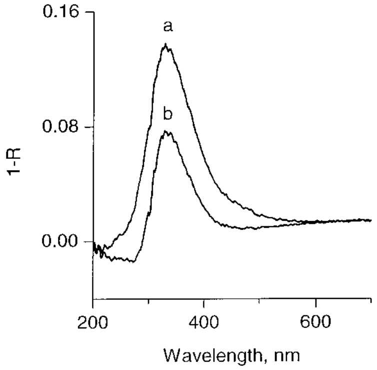

Figure 6. Diffuse reflectance spectra recorded (a) before and (b) after 20 min thermal reaction of propylene in TS-1/TiOOH sieve at room temperature.

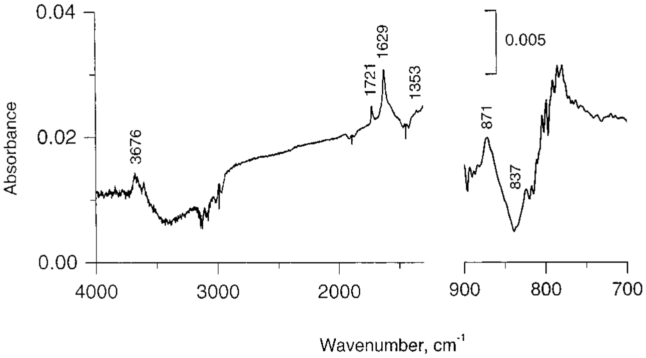

Figure 7. FT-infrared difference spectrum before and after 355 nm photolysis for 30 min (45 mW cm^{-2}) of TS-1/TiOOH sieve loaded with 200 Torr ethylene.

This suggests that the origin of the unlabeled product is exchange of the initially produced CH_3–$CH=^{18}O$ with residual $H_2{}^{16}O$ in the sieve, a phenomenon already observed in the formaldehyde in TS-1.[24]

To establish the branching ratio between ethylene oxide and acetaldehyde photoproducts, a 1:1 gas mixture of $\overline{CH_2\text{–}CH_2\text{–}O}$ and $CH_3CH=O$ was loaded into TS-1 sieve. The peak intensity ratio of the ethylene oxide band at 871 cm^{-1} and the aldehyde absorption at 1721 cm^{-1} was 0.12. Hence, the 871/1721 intensity ratio of 1 observed upon photoreaction of ethylene in TS-1/H_2O_2 sieve indicates an epoxide/aldehyde branching ratio of 8.3. In a separate series of experiments with ethylene oxide loaded into TS-1/TiOOH sieve, we found that only a minute amount of epoxide isomerizes to aldehyde on the tens of hour time scale. Even under irradiation of a TS-1/TiOOH/$\overline{CH_2\text{–}CH_2\text{–}O}$ matrix with 355 nm light, epoxide-to-aldehyde conversion was negligible. Therefore, the large aldehyde yield observed upon irradiation of TS-1/TiOOH sieve loaded with ethylene cannot be due to secondary reaction of initially produced ethylene oxide. We conclude that the aldehyde and epoxide originate from a common transient precursor.

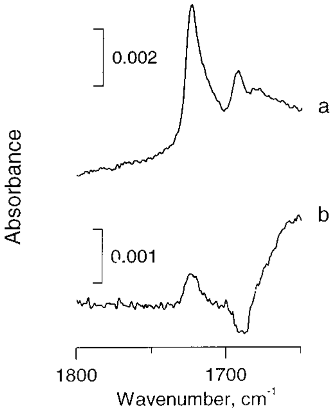

Figure 8. (a) FT-IR difference spectrum upon 355 nm photolysis for 6 min (45 mW cm^{-2}) of TS-1/$Ti^{18}O^{18}OH$ sieve loaded with 200 Torr $CH_2=CH_2$. (b) Difference spectrum after 1 h in dark.

IV. Discussion

1. Photodissociation of TiOOH. According to the most recent structural study of the Ti centers of dehydrated Ti silicalite sieve by EXAFS spectroscopy based on the detection of (second sphere) Si neighbors,[41] the majority of framework Ti centers are tetrahedrally surrounded by four –OSi linkages. Therefore, exposure of dehydrated TS-1 sieve to H_2O_2 is expected to involve mainly the conversion of tetrapodal framework Ti to $(Si-O)_3TiOOH$, as shown in Scheme 1. The very large bandwidth and red shift of ν(OH) of the hydroperoxo group is most likely due to H-bonding to the oxygen of the SiOH moiety formed by cleavage of the Ti–O–Si linkage. To the extent that tripodal framework $(Si-O_3)TiOH$ centers are present in the

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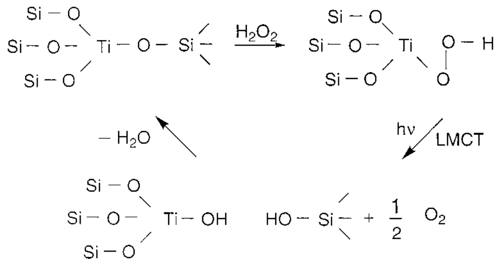
[41] Gleeson, D.; Sankar, G.; Catlow, C. R. A.; Thomas, J. M.; Spano, G.; Bordiga, S.; Zecchina, A.; Lamberti, C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4812–4817.

Scheme 1



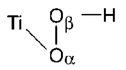
dehydrated TS-1 sieve,[23,42,43] substitution of OH by OOH rather than opening of Si−O−Ti bridges is expected to occur.[9,43] Hence, independent of whether H_2O_2 reacts with tetrapodal or tripodal framework Ti, the result is the same, namely, the formation of a TiOOH moiety adjacent to a Si−OH group. The decrease of the 960 cm^{-1} framework absorption characteristic for tetrahedrally coordinated Ti[23,31−34] indicates the expansion of the Ti coordination sphere. This is consistent with the formation of a side-on coordination of the hydroperoxo group as predicted by most ab initio and DFT calculations[13−15] and is in agreement with the configuration of *tert* butyl hydroperoxide interacting with Ti centers derived from XAFS measurements.[12]

In the η^2 configuration, the oxygen of the OH group of the TiOOH is very close to the Ti center[12−15] thus facilitating the formation of a Ti−OH group upon photoinduced expulsion of an O atom. The concurrent growth at 960 cm^{-1} is consistent with reconstitution of the tetrahedral coordination of the Ti center. Similarly, the production of H_2O indicated by the growth of 1629 cm^{-1} signals subsequent closure of a substantial fraction of the Ti−O−Si linkages.

$$\mathrm{Ti-OH+HO-Si \rightarrow Ti-O-Si+H_2O}$$

The fact that the oxygen of H_2O originates from H_2O_2, as indicated by the ^{18}O isotope shift, implies that the titanol (not the silanol) group is displaced. Efficient closure of such hydrolyzed linkages is known to occur even in the neat (Ti-free) silicate frameworks[44] and has been demonstrated in TS-1 by $H_2{}^{18}O$ and $H_2{}^{17}O$ exchange studies.[35] Recondensation of Ti−O−Si linkages is presumably a main reason for the lack of Ti leaching upon catalytic oxidation by H_2O_2.

Absorption of a photon by the LMCT band results in the excitation of an electron from a π^*(OO) orbital (HOMO) of TiOOH to a vacant d_e orbital of Ti,[45] thus creating a transient electron distribution approximately described by Ti^{+III} and a superoxo moiety. With the lone electron pair of O_β already



interacting with a d(Ti) orbital before excitation,[13,14,45] likely the absorption of a photon is followed by disproportionation, that is, elimination of O_α under concurrent formation of a Ti−O_βH bond. According to the recent DFT results on $Ti(OH)_3OOH$ models,[13,45] d_e (Ti) is energetically close to the antibonding σ^*-(OO) orbital, and there may be significant coupling between them. Such coupling would further facilitate expulsion of oxygen by weakening of the OO bond.

2. Photoreactivity toward Ethylene. The photoreactivity of TiOOH toward ethylene can readily be rationalized on the basis of frontier orbital considerations.[46] The $\pi^*(OO) \rightarrow d_e(Ti)$ excitation converts the HOMO of TiOOH into a singly occupied molecular orbital (SOMO), rendering the OO group highly electrophilic. Interaction of the SOMO with the doubly occupied π orbital (HOMO) of $CH_2{=}CH_2$ results in a substantial stabilization of the reactants as the orbitals split into a fully occupied, stabilized component and a singly occupied, destabilized level. The C=C group is expected to interact with the more electrophilic O_α.[14,15,47] The orientation of the olefin for maximum overlap with the SOMO of TiOOH is close to the orientation required for maximum HOMO−LUMO overlap in the thermal reaction (see below).[45] The energy minimum of the LMCT state of TiOOH is not known accurately, but the onset of the absorption tail at 550 nm suggests no more than 50 kcal mol^{-1} above the ground state. This implies that the energy available to the photoexcited reactants lies well above the theoretical estimate of 13−23 kcal mol^{-1} for oxygen transfer between TiOOH and ethylene.[13,14,16,45]

The concurrent formation of about 10% acetaldehyde in addition to ethylene oxide points to the intermediacy of an oxirane biradical as common precursor. We have previously observed simultaneous production of ethylene oxide and acetaldehyde upon mild O transfer from NO_2 to ethylene in a rare gas matrix cage.[48,49] The product branching was explained by the formation of a short-lived oxirane biradical intermediate. In light of the NO_2 + ethylene results, we propose that O transfer from TiOOH to the C=C bond yields a (singlet) oxirane biradical whose fate, ring closure versus 1,2 H-shift, determines the branching ratio of epoxide and aldehyde.[48,49]

3. Thermal Reaction with Propylene. The reactivity of ground-state TiOOH toward olefins has been discussed by several authors. It is dictated by the interaction of the π^*(OO) orbital of the Ti hydroperoxo group (HOMO) and the π^*(CC) LUMO of the CC bond.[13,14,45] This, and the fact that propylene reacts spontaneously with ground-state TiOOH while ethylene with its less electron-rich CC bond does not, is consistent with the electrophilic nature of the O transfer.

Clerici et al. were the first to propose the TiOOH group as the active site of hydrocarbon oxidation by H_2O_2 in TS-1 sieve.[3,4,35,50] On the basis of the observed solvent and acid/base effects on the kinetics and yield of olefin epoxidation in various alcohols, an end-on TiOOH (η^1) group with a simultaneously coordinated alcohol group was envisioned. It is conceivable that, in the presence of a solvent, interaction of an alcohol OH group with the Ti center of end-on TiOOH results in an energetically preferred situation compared to side-on TiOOH, especially if the alcohol and hydroperoxo groups would engage in H bonding.[3,4,35,50] On the other hand, other earlier proposals for the active site, in particular a triangular $Ti(O_2)$ group[1,5,50−53] or

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the formation of the Ti−O−O−Si moieties,[17] are inconsistent with our infrared results since they would not explain the observation of the 3400 cm^{-1} OH band.

V. Conclusions

In situ FT-infrared spectroscopy has allowed the first direct observation of the active peroxide species formed upon interaction of H_2O_2 with solvent-free Ti silicalite sieve. Most compelling evidence for the identification of the TiOOH moiety is furnished by the photodissociation difference spectrum observed upon irradiation of the LMCT absorption of the hydroperoxide. Growth of H_2O and of the 960 cm^{-1} TS-1 framework absorption indicate that a large fraction of the Ti−OH groups formed after photodissociation of TiOOH recondense with adjacent Si−OH to form a Ti−O−Si bridge. The TiOOH group is shown by in situ FT-IR monitoring to be the active oxidation site upon exposure of the sieve to small olefins under light irradiation (ethylene) or in the dark at room temperature (propylene). These observations open up a new level of mechanistic studies of hydrocarbon oxidation by hydrogen peroxide in Ti silicate sieves.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

JA012477W

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