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Metal Oxide (TiO_2, MoO_3, WO_3) Substituted Silicate Xerogels as Catalysts for the Oxidation of Hydrocarbons with Hydrogen Peroxide

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TiO_2, MoO_3, and WO_3 have been dispersed in amorphous silica using the low temperature sol–gel procedure for xerogel preparation. These simply prepared amorphous compounds are proposed as possible alternatives to metal-substituted crystalline molecular sieves in H_2O_2 oxidations. The metallosilicate compounds are catalytically active in the 30% aqueous H_2O_2 oxidation of alkenes and alcohols provided the metal oxide precursor in the xerogel synthesis is a metal–dichlorodialkoxy compound yielding $MO_x(Cl)–SiO_2$, and not the tetraalkoxy derivative yielding $MO_x–SiO_2$. Catalyst efficiency is increased by using low loading of metal oxide in the silica framework. Excess H_2O_2 reduces yield due to the detrimental effect of water, so more hydrophobic silicates with phenyl-silicon units increases catalyst efficiency. IR studies show that in the xerogels, the absorption at ∼950 cm^{-1} is mainly due to the Si–OH vibrations in $(SiO)_3Si–OH$ units and not $(SiO)_3Si–OM$ as has often been reported in studies of titanium-substituted zeolites. ^{29}Si MAS NMR spectra, sensitive to second neighbor atoms, of catalytically active $MO_x(Cl)–SiO_2$ *versus* inactive $MO_x–SiO_2$ reveals that the former have larger Q_3 peaks and therefore more $(SiO)_3Si–OM$ units, indicating higher molecular dispersion of the metal oxide in the xerogels. Diffuse reflectance UV-vis measurements indicate, however, that this molecular dispersion is not complete as absorptions attributable to polymeric forms of metal oxide are observable. ESR spectra of the metal oxide substituted silicates in the presence of hydrogen peroxide or in the reduced form are not useful in differentiating between active and inactive xerogel compounds. Atomic force microscopy imaging of the xerogels at ∼10 nm resolution shows that the xerogel has a basically smooth surface. Large cylindrical pits of 500–700 nm diameter and depth of 15–40 nm are also observable as imperfections in the xerogel. There is also formation of small silicate droplets on the surface with dimensions similar to that of the pits. The catalytic xerogels are microporous with an average pore diameter of 15 Å and a surface area of 750 m^2/g.

INTRODUCTION

Historically, epoxidation of alkenes has been carried out using peracids. The strong recent concern over the detrimental effects of wastes produced in such processes has led to a search for new "clean" catalytic procedures. Of the most environmentally benign oxidants, dioxygen, ozone, and hydrogen peroxide, the latter is the most attractive for the organic laboratory and small-scale procedures due to the simplicity inherent in performing reactions with liquid rather than gaseous reactants. Therefore, many investigations has been carried out designed to optimize the use of hydrogen peroxide for epoxidation of alkenes (1). Since catalyst stability is a key factor in the development of a usable process, the use of inorganic compounds which are *a priori* stable to oxidation has been recently emphasized. One approach has been to use dissolved homogenous oxo- or peroxometalate catalysts (2, 3). Another alternative is to use metal-substituted molecular sieves, zeolites, and aluminophosphates as catalysts in a heterogeneous reaction mode.

The research with these heterogeneous catalysts was originally carried out at Enichem in Italy and was based on the use of the titanium-substituted silicalite-1, TS-1 (4). The incorporation of a titanium atom at a silicon site within the MFI structure and high dispersion of the titanium within the zeolite are believed to be the major reasons for the unique behavior of TS-1, which includes fairly high activity and selectivity, minimal nonproductive hydrogen peroxide decomposition, and high catalyst stability (5). Early research was difficult to reproduce so an important and recent development is the standardization of the TS-1 catalyst such that differently prepared catalysts can now be compared (6). TS-1 catalyzed oxygen transfer processes with 30% hydrogen peroxide (7) include the selective oxidation of organic substrates such as alcohols (8), phenol (9), alkenes (10), and alkanes (11), and ammonoxidation of cyclohexanone (12). Despite the obvious attraction of TS-1 and the similar TS-2 (13) (MEL structure) as catalysts for hydrogen peroxide activation, the small pore size, ∼0.5–0.6 nm, of these zeolites will limit their use as a general tool for oxidation in organic chemistry. In order to overcome this limitation, research has also been carried out into the substitution of titanium into different and also larger pore zeolites such as ZSM-48 (14), β-zeolite (15), ETS-10 (16), MCM-41 (17),

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and HMS (18), although the structure and catalytic activity (generally poorer than TS-1) of these compounds is still relatively poorly defined. Although the majority of the published reports deal with titanium-substituted zeolites, the use of other metals and frameworks has also been reported. Examples include vanadium (19), chromium (20), and zirconium (21) substituted silicalites, and chromium (22) and cobalt (23) substituted aluminophosphates.

As stated above, small pore size, in addition to involved and/or difficult preparations of metal substituted molecular sieves, may hinder the wide acceptance of such materials for catalysts in organic synthesis. An alternative approach is to use amorphous titanium silicates. Originally, amorphous catalysts were prepared by treating silica gel with titanium tetrachloride. These TiO_2–SiO_2 catalysts, which have been known since the 1960s, were effective in epoxidation with organic hydroperoxides derived from *i*-butane and ethylbenzene and are used in the heterogeneous version of propene oxide manufacture (24). These catalysts, however, do not activate hydrogen peroxide. Thus, others as well as our research group have investigated amorphous metallosilicate glasses prepared by the use of the sol–gel method where pore size is thought to be in the 1–10-nm range (25). Using the sol–gel technique amorphous mesoporous silicates containing titanium oxide (26–28), vanadium oxide, molybdenum oxide, and tungsten oxide (26) have been prepared. These MO_x–SiO_2 ($M = Ti^{IV}, Mo^{VI}, W^{VI}, V^{V}$) metallosilicates were tested for catalytic liquid phase heterogeneous oxygen transfer with hydrogen peroxide as oxygen donor (26–28). "Molecularly mixed" metallosilicates (metal oxide substituted silicates), both xerogels and aerogels, may be synthesized easily by using a modified low temperature sol–gel method using metal alkoxides as precursors (29). However, analysis of the literature clearly indicates that the exact preparation procedure has a critical effect on the eventual activity of the metallosilicate. For example, we found that a xerogel based on titanium (IV) tetraisopropoxide, TTIP, was a poor catalyst (26). On the other hand, Keshavaraja *et al.* (28) found that similar xerogels prepared using titanium (IV), tetrabutoxide, TTB, were active catalysts for aromatic hydroxylation. Hutter *et al.* demonstrated the use of acetylacetone modified TTIP and aerogel formation as the key to high epoxidation activity (27). For the vanadium oxide containing compounds the importance of the preparatory procedure was also very obvious (26).

In this paper we present our results on the use of titanium, molybdenum, and tungsten oxide-substituted silicate xerogels as catalysts in the oxidation of various organic substrates with 30% aqueous hydrogen peroxide as the oxygen donor. The catalytic results, the various spectroscopic studies (IR, ^{29}Si MAS NMR, diffuse reflectance UV-vis, and ESR), the microscopic investigation by AFM and the physical characterization by BET adsorption measurements lead to the conclusion that high molecular dispersion of the metal oxide in the silicate glass appears to be the key factor in realizing catalytic activity.

EXPERIMENTAL PART

Metal Alkoxide Precursors

Silicon tetraethoxide (TEOS; Fluka > 98%) and titanium tetra-isopropoxide (TTIP; Aldrich > 98%) were used without further treatment. Other alkoxides were prepared in the laboratory. MoO(O*i*-Pr)$_4$ and WO(O*i*-Pr)$_4$ were prepared by adapting the method described in the literature (30). In an ice-cooled magnetically stirred flask containing 14 ml dry benzene and 13 ml dry 2-propanol one dissolves 2.5 mmol $MoOCl_4$ or $WOCl_4$. Dry ammonia, ∼20 ml/min is bubbled through the solution for 30 min, during which a white solid, NH_4Cl precipitates. The solution turns progressively from blue to green and finally to light brown for the molybdenum precursor and from yellow to white for the tungsten analogue. The solution is purged with argon to remove excess ammonia and the mixture filtered. The MoO(O*i*-Pr)$_4$ or WO(O*i*-Pr)$_4$ compounds were not isolated. The resulting solution was used for the xerogel preparation. $TiCl_2$(O*i*-Pr)$_2$ was prepared by adding 2 mmol of $TiCl_4$ to 10 ml dry 2-propanol, whereby a yellow–green solution was obtained and used without further treatment (31). $MoOCl_2$ (O*i*-Pr)$_2$ and $WOCl_2$(O*i*-Pr)$_2$ were similarly prepared by dissolving 2.5 mmol $MoOCl_4$ or $WOCl_4$ in 14 ml dry benzene and 13 ml. Dry ammonia was bubbled through the solution at a rate of ∼20 ml/min for 5 min, during which deeply blue–green colored solutions of $MoOCl_2$(O*i*-Pr)$_2$ and yellow solutions of $WOCl_2$(O*i*-Pr)$_2$ were obtained (32). The solutions were immediately and vigorously purged with argon, the NH_4Cl was filtered and the solutions were used for xerogel preparation without further purification.

Preparation of $MO_x(Cl)$–SiO_2 and MO_x–SiO_2 Xerogels

The required MO_x(Cl)–SiO_2 and MO_x–SiO_2 xerogels were prepared using the following procedure. TEOS, 40 mmol, was dissolved in 12 ml ethanol followed by addition of 80 mmol of water as a 0.15 *M* HCl solution. The solution was heated for 2 h at 60°C and then cooled to room temperature. To the partially hydrolyzed TEOS now was added a solution containing 2 mmol of the metal alkoxide precursor as described above and another portion of 80 mmol of distilled water or alternatively 80 mmol of water as a 30% H_2O_2 solution. The solution was allowed to stand between 18 to 24 h in the hood until all the volatile solvent had evaporated, leaving a homogenous transparent xerogel. Colors of the resulting xerogels varied and ranged from colorless for TiO_2–SiO_2 and WO_3–SiO_2, very light brown for MoO_3–SiO_2, light yellow for WO_3(Cl)–SiO_2, orange for TiO_2(Cl)–SiO_2 and blue–green for MoO_3(Cl)–SiO_2. The xerogels were then dried under air at 120°C for 16 h to remove excess solvent and water. Heating at this temperature is known to cause minimal changes in the xerogel. At this point the titanium and tungsten gels are all practically colorless, the MoO_3–SiO_2 is slightly brownish and the $MoO_3(Cl)$–SiO_2 is light green.

The residual chloride remaining in the $MO_x(Cl)$–SiO_2 xerogels was first evaluated by treating 500 mg of the silicate with 25 ml water for 12 h at room temperature. Chloride titration using the Mohr method revealed that only 6–8 mol% of the original chloride remained in the xerogel. A comparative treatment with 0.1 *M* NaOH for 12 h at reflux showed the same amount of chloride in the xerogel. The $MO_x(Cl)$–SiO_2 xerogels were also treated with methylene chloride in order to extract remaining alcohol. None could be determined by GC. The amount of water remaining was determined by Karl-Fischer titration. Less than 0.5 wt% water was found.

Catalytic Oxidation Procedure

The catalytic oxidation reactions were carried out in 5 ml sealed vials. In the general case, 5 mg of the metallosilicate xerogel, 1 mmol substrate, for most studies cyclooctene, and 0.5 ml methanol or *t*-butanol as solvent were magnetically stirred. The vials were placed in a temperature equilibrated oil bath and 30% hydrogen peroxide was added to initiate the reaction. Aliquots from the reaction mixture were analyzed using gas chromatography. Analysis was on a 30-m long 0.25 mm ID capillary silica column bonded with a 0.25 μm coating of methyl silicone, RTX-100 (Restex). Where standards were available and all peaks identified, analyses were performed on a HP 5980 (Hewlett Packard) instrument equipped with a flame ionization detector. In other cases, the identity of products was deduced from mass spectra obtained on a HP 5790A chromatograph (Hewlett Packard) equipped with a mass selective detector. Hydrogen peroxide was determined iodometrically, whereby an aliquot of the reaction mixture was dissolved in 95% ethanolic NaI containing 10% of acetic acid. From the optical density ($\varepsilon = 3.4 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) of I_3^- at 360 nm the amount of peroxide was calculated after calibration. The result was crosschecked by titration with a factored thiosulfate solution, two equivalents/mol H_2O_2.

Spectroscopic Investigations

Atomic absorption measurements were carried out using a single beam GBC 903 spectrometer using a nitrous oxide–acetylene flame. Infrared spectra of the metal oxide substituted silicate xerogels were taken as KBr pellets on a Nicolet 510M FTIR spectrometer. The effect of hydrogen peroxide on the IR spectra was measured by mixing the xerogel in a large excess of 30% H_2O_2 for 30 min, filtering, and drying under vacuum at room temperature for 2 h, then preparing pellets as usual. UV-vis spectra were taken in reflectance mode with a Hitachi U-2000 spectrophotometer equipped with an integrating sphere. ESR spectra were taken on a Varian E-12 instrument at the required temperatures. Spectra were taken at a frequency of 9.089 GHz, microwave power 10 mW, modulation frequency 100 KHz, modulation amplitude 0.5 G, and time constant 0.1 s. Spectra of hydrogen peroxide treated samples were taken after the relevant xerogel was mixed with 30% H_2O_2 and dried under vacuum for 2 h at room temperature as described above for the IR samples. Reduced Ti(III) xerogels were prepared by adding ammonia to the TiO_2 containing silicates mixed with a very small piece of sodium metal at −78°C. Reduction could be followed by the formation of the purple reduced xerogel. The ammonia was then removed by placing the ESR tube under vacuum which was then sealed. ^{29}Si MAS NMR spectra were taken on a home built 200 MHz spectrometer in the laboratory of Professor Shimon Vega at the Weizmann Institute of Science, Rechovot, Israel at a frequency of 39.7 MHz with magic angle spinning at 3 KHz at room temperature. Typically between 2000 and 4000 scans were taken with a repetition time of 20 and a dwell time of 10–40 μs. Atomic force microscope measurements were made on a Nanoscope 3A from Digital Instruments. Resolution was approximately 10 nm. Samples for adsorption measurements were prepared by heating the xerogel for 48 h at 120°C. Adsorption isotherms were measured on a Micromeritics ASAP 2000 Surface Analyzer using the generic operating and data analysis software, with N_2 as adsorbed gas.

RESULTS AND DISCUSSION

Preparation of Catalytically Active Metal Oxide (TiO_2, MoO_3, WO_3) Substituted Silicate Xerogels

The sol–gel method for preparation of amorphous silicate glasses from alkoxide precursors, e.g., silicon tetraethoxide, is very well documented; however, numerous variant procedures are available. In the presence of water as reagent and alcohol as solvent the alkoxide is hydrolyzed and condensed to eventually form a polymerized hydroxylated silicate sol, Eq. [1]:

$$\begin{gathered}\mathrm{Si(OR)_4} + n\mathrm{H_2O} \rightarrow \mathrm{Si(OH)}_n\mathrm{(OR)}_{4-n} + \mathrm{nROH}\\ 2\mathrm{Si(OH)}_n\mathrm{(OR)}_{4-n} \rightarrow\\ \mathrm{(OH)}_{n-1}\mathrm{(OR)}_{4-n}\mathrm{SiO{-}Si(OH)}_n\mathrm{(OR)}_{3-n} + \mathrm{ROH}.\end{gathered} \qquad [1]$$

Procedures may be coarsely divided into those carried out under acidic or basic conditions. Under acidic conditions hydrolysis is faster than condensation, whereas at basic pH the reverse is true. These differences lead to silicate xerogels with different pore structures after solvent evaporation. In trying to make “molecularly dispersed” metallosilicates, the relative rate of reaction of the metal alkoxide precursor such as $Ti(i\text{-}OPr)_4$ *versus* the $Si(OEt)_4$ also must be taken into account. As a rule the metal alkoxides are hydrolyzed and condensed at much higher rates than the silicon alkoxide and in addition also strongly catalyze the polymerization of the latter. The best reported method for obtaining highly dispersed metal oxide silicates (33, 34) is thus based on prehydrolyzation of silicon alkoxides with substoichiometric addition of water at acidic pH, followed by addition of the metal alkoxide and the remaining quantity of required water.

In such a typical procedure, $Si(OEt)_4$ was first partially hydrolyzed with two equivalents of acidic water for 2 h. After cooling, 0.05 equivalents of metal alkoxide, $Ti(Oi\text{-}Pr)_4$, $MoO(Oi\text{-}Pr)_4$, or $WO(Oi\text{-}Pr)_4$ were added along with two additional equivalents of water. After solvent evaporation, xerogels termed 5% TiO_2–SiO_2, 5% MoO_3–SiO_2, 5% WO_3–SiO_2, respectively, are obtained and dried at 120°C for 16 h. This temperature was chosen since it is accepted that under these conditions there is little structural change by aging (25). In order to test the catalytic activity of these compounds, 5% MO_x–SiO_2, the epoxidation of cyclooctene to cyclooctene oxide with 30% H_2O_2 was used as a model reaction. From the results in Fig. 1, one can observe that catalysts prepared in such a way have little or no catalytic activity. Likewise, prehydrolysis under basic conditions or addition of hydrogen peroxide during formation of the sol and gel yielded catalytically inactive xerogels. Catalytically active xerogels were formed; however, with the same reaction protocol described above using the metal dichlorodialkoxides, $TiCl_2(Oi\text{-}Pr)_2$, $MoOCl_2(Oi\text{-}Pr)_2$, and $WOCl_2(Oi\text{-}Pr)_2$, as precursors instead of the tetraalkoxides. The xerogels, noted here as 5% $TiO_2(Cl)$–SiO_2, 5% $MoO_3(Cl)$–SiO_2, 5% $WO_3(Cl)$–SiO_2, respectively, all have very significant catalytic activity (Fig. 1). Catalysts of similar catalytic activity are also obtained when adding hydrogen peroxide to the sol. It is important to note that in our preliminary paper, (26a), we noted that the TiO_2-based gel had very little catalytic activity. This result is fully repeated in this account (TiO_2–SiO_2). On the other hand, it was reported that MoO_3–SiO_2 and WO_3–SiO_2 had some catalytic activity. These then so-named catalysts were in fact mixtures of the now and newly represented MoO_3–SiO_2 and $MoO_3(Cl)$–SiO_2, and WO_3–SiO_2 and $WO_3(Cl)$–SiO_2 silicates. This is because at that time, the tetraalkoxy precursors of molybdenum and tungsten contained some impurities of the dialkoxy-dichloro precursors which were responsible for the catalytic activity. The results in this paper supersede those previously reported and are based on a considerable refinement of the experimental techniques in the xerogel preparation.

Catalytic Activity of $TiO_2(Cl)$–SiO_2, $MoO_3(Cl)$–SiO_2, $WO_3(Cl)$–SiO_2

From the results described in the previous section, it is clear that the $MO_x(Cl)$–SiO_2 xerogels have appreciable catalytic activity. We, therefore, sought to further describe the effect of various reaction parameters on the effectiveness of the metal oxide catalysts. For the $TiO_2(Cl)$–SiO_2 compound, methanol was the only solvent in which significant catalytic activity could be observed. In all other solvents tested (*t*-butanol, *i*-propanol, acetonitrile, 1,2-dichloroethane, toluene, tetrahydrofuran, and dimethyformamide) yields were always less than 2% for the oxidation of cyclooctene under the conditions in Fig. 1. For the $MoO_3(Cl)$–SiO_2 and $WO_3(Cl)$–SiO_2 analogs, methanol was about 20–40% more effective than *t*-butanol. In the other solvents there was only slight reaction, <2%, except in the case of acetonitrile (see below).

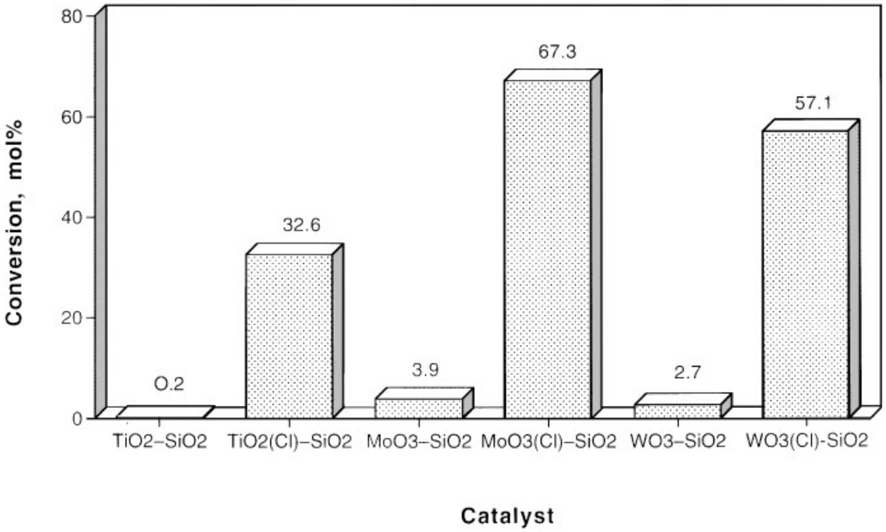

FIG. 1. Catalytic activity for cyclooctene epoxidation as a function of the metal alkoxide precursor. Reaction conditions: 1 mmol cyclooctene, 2 mmol of 30% H_2O_2, 5 mg of xerogel in 0.5 ml methanol at 65 ± 3°C for 24 h. Cyclooctene oxide was the sole product.

In order to verify that the oxidation reaction is truly heterogeneous and not the result of dissolution of metal oxides into the liquid solvent phase, leaching of all metal oxides was quantified by atomic absorption spectrometry. Thus, 50 mg MO_x(Cl)–SiO_2 catalyst was mixed with 2.5 ml solvent (methanol, *t*-butanol, and acetonitrile) and 10 mmol 30% H_2O_2 at 70°C for 24 h. The organic phase was then diluted with water and analyzed. No measurably significant amount of metal was observed in the use of methanol or *t*-butanol by atomic absorption. For acetonitrile, a known coordinating solvent, there was considerable leeching of the molybdenum and tungsten oxide into the solvent. Acetonitrile was, therefore, not considered in the following studies. Furthermore, liquid phases derived from such treatments of the xerogels showed no catalytic activity, as was shown from the following experiment. The xerogels were treated as stated with hydrogen peroxide at 70°C for 8 h, the solid was removed by filtration, and the appropriate amount of cyclooctene and hydrogen peroxide was added to the filtrate. The mixture was heated to 70°C and after 24 h no conversion of cyclooctene was observed.

Reaction profiles for cyclooctene epoxidation using the MO_x(Cl)–SiO_2 catalysts at various temperatures (Fig. 2) show improved reaction yields as a function of temperature with the following relative catalytic activities: MoO_3(Cl)–SiO_2 ~ WO_3(Cl)–SiO_2 > TiO_2(Cl)–SiO_2. The activation energy of the reactions varied in a similar order, with values of 15.1, 15.6, and 19.1 kcal mol^{-1} being calculated for the molybdenum, tungsten, and titanium catalysts, respectively. It is quite conceivable that at high temperatures of 100 to 120°C (superatmospheric pressure) higher conversions could be obtained. This was not tested, due to safety considerations in our laboratory (peroxides at high temperature). A further examination of reaction selectivities in terms of hydrogen peroxide efficiency is presented in Fig. 3. One may notice that the decomposition of hydrogen peroxide paralleled the epoxidation reactions with final efficiencies of 26.6, 37.4, and 39.5 mol% for TiO_2(Cl)–SiO_2, WO_3(Cl)–SiO_2, and MoO_3(Cl)–SiO_2, respectively, for reactions at 80°C.

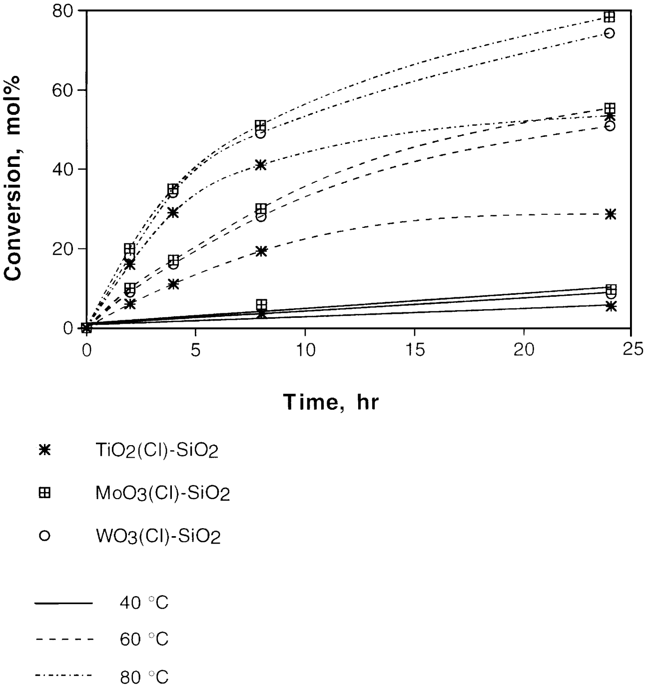

FIG. 2. Reaction profiles for cyclooctene epoxidation for MO_x(Cl)–SiO_2 catalysts at various reaction temperatures. Reaction conditions: 1 mmol cyclooctene, 2 mmol of 30% H_2O_2, 5 mg of MO_x(Cl)–SiO_2 in 0.5 ml methanol. Cyclooctene oxide was the sole product.

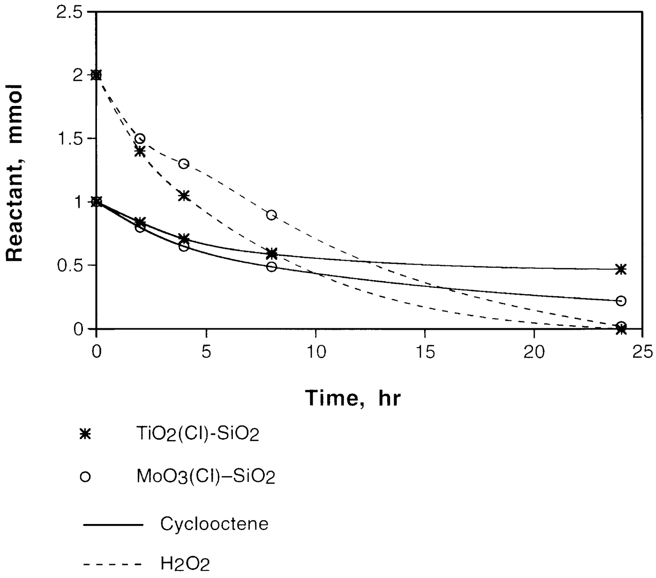

FIG. 3. Reaction profiles for cyclooctene epoxidation with 30% H_2O_2 at 80°C. Reaction conditions: 1 mmol cyclooctene, 2 mmol of 30% H_2O_5, 5 mg of MO_x(Cl)–SiO_2 in 0.5 ml methanol. Cyclooctene oxide was the sole product.

The effect of the amount of catalyst on the conversion was the next reaction parameter investigated. At 5% catalyst loading of MO_x(Cl)–SiO_2 (Fig. 4) it is clear that increased amounts of catalyst leads to higher conversions; however, due to the fact that the decomposition (dismutation) of hydrogen peroxide to oxygen and water is a competing reaction, quantitative yields were not obtained. In the insert of Fig. 4, one may observe that at lower TiO_2(Cl)–SiO_2 loading of 2 and 0.5% TiO_2 conversions are somewhat increased. The increase of ~25% in conversion is, however, much more on a molar basis (turnovers), considering the tenfold decrease in the absolute amount of TiO_2 when going from 5 to 0.5% loading. This result is probably most easily explained by an increase in the molar efficiency of the xerogel catalysts at lower loadings, due to the better "molecular dispersion" of metal oxide (see below).

The effect of addition of increased amounts of 30% aqueous hydrogen peroxide on the reaction yield was also

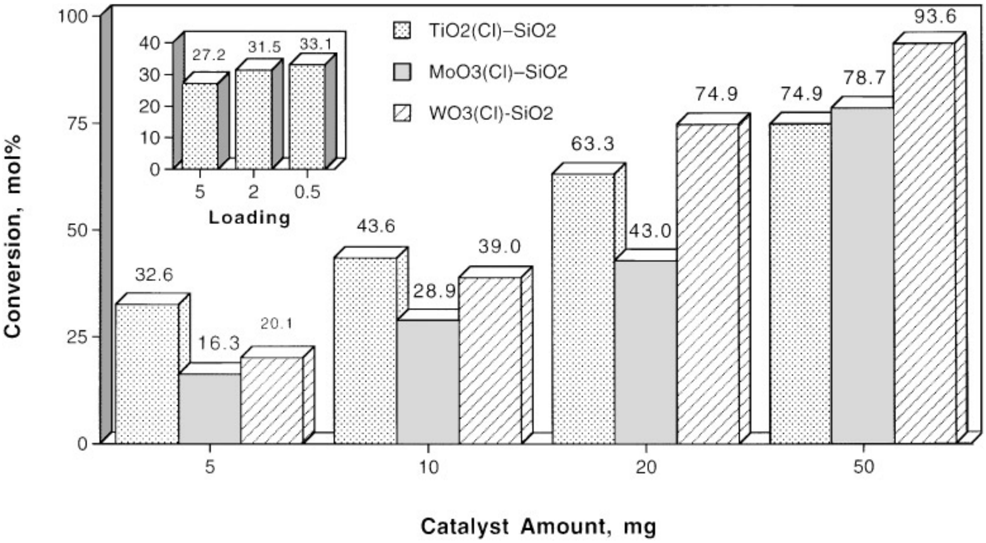

FIG. 4. Catalytic activity as a function of the amount of catalyst and catalyst loading. Reaction conditions: 1 mmol cyclooctene, 2 mmol of 30% H_2O_2, 5–50 mg of xerogel in 0.5 ml methanol ($TiO_2(Cl)$–SiO_2) or *t*-butanol ($MoO_3(Cl)$–SiO_2 $WO_3(Cl)$–SiO_2) at 65°C for 24 h. For the insert: 1 mmol cyclooctene, 2 mmol of 30% H_2O_2, 5 mg of 0.5–5.0% ($TiO_2(Cl)$–SiO_2) in 0.5 ml methanol at 60°C for 24 h. Cyclooctene oxide was the sole product.

studied (see Fig. 5). Surprisingly, increased amounts of hydrogen peroxide had a detrimental effect on the reaction effectivity, instead reducing final conversions. Our explanation for this result is that since the silicate can be viewed as having a hydroxylated hydrophilic surface (see also IR results below) increased addition of hydrogen peroxide and the adjutant water causes their preferential adsorption and/or coordination to the solid catalyst, reducing the accessibility to the more hydrophobic organic substrate and thus reducing oxidation yields. A verification of this hypothesis (Fig. 5) could be carried out by preparing a more hydrophobic metal oxide xerogel. Thus, in a manner analogous to the preparation of $TiO_2(Cl)$–SiO_2 we prepared a xerogel using phenyltriethoxysilane, $PhSi(OEt)_3$, and $TiCl_2(Oi\text{-}Pr)_2$ as precursors for the xerogel formation, where the phenyl group causes the xerogel to be of a more hydrophobic nature. The resulting hydrophobic $TiO_2(Cl)$–$Si(Ph)O_2$ amorphous glass had significantly higher catalytic activity than the analogous $TiO_2(Cl)$–SiO_2 compound, although also here the larger amounts of aqueous hydrogen peroxide led to lower conversions, suggesting strong coordination of water (also a reaction product) to the titanium metal center as being detrimental to catalytic activity. This negative effect of water is well documented in the literature. On a technical

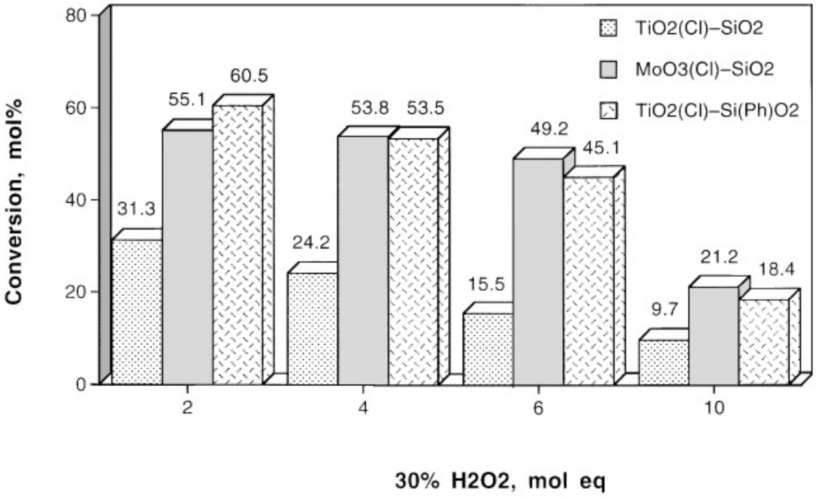

FIG. 5. Catalytic activity as a function of the amount of 30% H_2O_2. Reaction conditions: 1 mmol cyclooctene, 2–10 mmol of 30% H_2O_2, 5 mg of $MO_x(Cl)$–SiO_2 in 0.5 ml methanol at 60°C for 24 h. Cyclooctene oxide was the sole product.

TABLE 1

Oxidation of Various Substrates with TiO_2(Cl)–SiO_2 and 30% H_2O_2

Substrate	Conversion (mol%)	Product (% selectivity)
1-phenyethanol	86.5	Acetophenone (100)
Benzyl alcohol	10.7	Benzaldehyde (100)
Cyclohexanol	13.4	Cyclohexanone (100)
1-heptanol	0	None
2-heptanol	0	None
Styrene	87.9	Benzaldehyde (46) Benzoic acid (20) Phenylacetaldehyde (19) 1-phenyl-1,2-ethanediol (12) Unknown (3)
Cyclooctene	70.1	Cyclooctene oxide (100)
Cyclododecene	11.0	Cyclododecane oxide (100)
Cyclohexene	42.5	Cyclohexene oxide (7) Cyclohexen-2-ol (10) Cyclohexen-2-one (83)
2,3-dimethyl-2-butene	84.5	2,3-dimethyl-2-butene oxide (90) 2,3-dimethyl-2,3-butanediol (10)
1-octene	0	None
2-octene	0	None
2-methyl-1-heptene	6.2	2-methyl-1-heptene oxide (20) 2-methyl-1,2-heptanediol (35) Hexanoic acid (45)
2-methyl-2-heptene	30.6	2-methyl-2-heptene oxide (14) 2-methyl-2,3-heptanediol (71) 2-methyl-2-hepten-4-one (15)

Note. Reaction conditions: 1 mmol substrate, 2 mmol of 30% H_2O_2, 10 mg of TiO_2(Cl)–SiO_2 in 0.5 ml methanol at 80°C for 24 h. The conversion to all products is given as mol% of substrate reacted. Selectivity is given in terms of specific product as percentage of total product.

level this can be corrected by the use of more concentrated hydrogen peroxide, although higher concentrations of peroxide in organic phases do represent a significant safety risk.

A further evaluation of the catalytic activity was carried out by testing the activity of the TiO_2(Cl)–SiO_2 xerogel with a variety of substrates, both alkenes and alcohols (see Table 1). For the oxidation of alcohols, acyclic primary and secondary alcohols, 1-heptanol and 2-heptanol were found to be inert as was the solvent methanol. Cyclic alcohols, cyclohexanol, and benzylic alcohols, 1-phenylethanol, and benzyl alcohol, were oxidized to the corresponding ketones or aldehydes at low yields. In the case of alkenes, there was some reactivity for most alkenes tested with the reactivity being proportional to the nucleophilicity of the double bond in the following order: styrene and 2,3-dimethyl-2-butene > cyclooctene > 2-methyl-2-heptene > 2-methyl-1-heptene > 2-octene and 1-octene. In general, reactions were not selective to epoxidation except for cyclooctene and cyclododecene. Often epoxides were hydrolyzed to the corresponding diols or reacted further via carbon–carbon bond cleavage to yield acids or aldehydes. In addition, in some cases oxidation at the allylic position was a competing reaction, especially with cyclohexene, where 2-cyclohexenol and 2-cyclohexen-one were the major products. Alkylaromatic compounds such as toluene or ethylbenzene were unreactive, although in the oxidation of tetrahydronaphthalene some 1-tetralol and 1-tetralone were observed.

The activity of the amorphous TiO_2(Cl)–SiO_2 was compared to the activity of the crystalline TS-1 (Fig. 2). For alkenes TS-1 was slightly more active and selective to the epoxide product. In alcohol oxidation the TiO_2(Cl)–SiO_2 xerogel was more active. It might be useful, however, to note that for TiO_2(Cl)–SiO_2 the excess hydrogen peroxide added is decomposed, whereas for TS-1 there was little nonproductive decomposition.

Spectroscopic and Microscopic Investigation and Evaluation of the Metal Oxide (TiO_2, MoO_3, WO_3) Substituted Silicate Xerogels

Spectroscopic and microscopic studies on the MO_x(Cl)–SiO_2 xerogel catalyst were carried out (a) to better characterize these compounds, (b) to gain an appreciation of the differences or similarities between TiO_2(Cl)–SiO_2 and TS-1, and (c) to try to understand the large difference found in the catalytic activity of MO_x(Cl)–SiO_2 *versus* MO_x–SiO_2. One hypothesis to explain the difference between MO_x(Cl)–SiO_2 and MO_x–SiO_2 centers around the fact that the dichloro-dialkoxy precursors hydrolyze and condense more slowly than the tetraalkoxy precursors (25, 35); this would bring about a more highly dispersed metal oxide in the silicate bulk, as is known from control experiments and the literature that the amorphous polymeric oxides TiO_2, MoO_3, and WO_3 have little or no catalytic activity. Another explanation centers around the coordination environment of the MO_x(Cl)–SiO_2 *versus* MO_x–SiO_2 xerogels. In the latter case it is possible that the chloride groups remain attached to the metal center, leading to sites more accessible to hydrogen peroxide or organic substrate or less coordinatively saturated in the xerogel, thus enabling improved catalytic activity.

TABLE 2

Comparison of the Catalytic Activity of TiO_2(Cl)–SiO_2 and TS-1

Substrate	Conversion (selectivity), mol% TiO_2(Cl)–SiO_2	Conversion (selectivity), mol% TS-1
1-phenyethanol	56.5	40.4
Styrene	36.9 (10)	15.8 (55)
Cyclooctene	32.6 (100)	46.7 (100)
2,3-dimethyl-2-butene	74.1 (93)	62 (100)
1-octen-3-ol[a]	31.3	10.7

Note. Reaction conditions: 1 mmol substrate, 2 mmol of 30% H_2O_2, 10 mg catalyst in 0.5 ml methanol at 65°C for 24 h. The conversion to all products is given as mol% of substrate reacted. Selectivity is for epoxide.

[a] 1-octen-3-one was the major product.

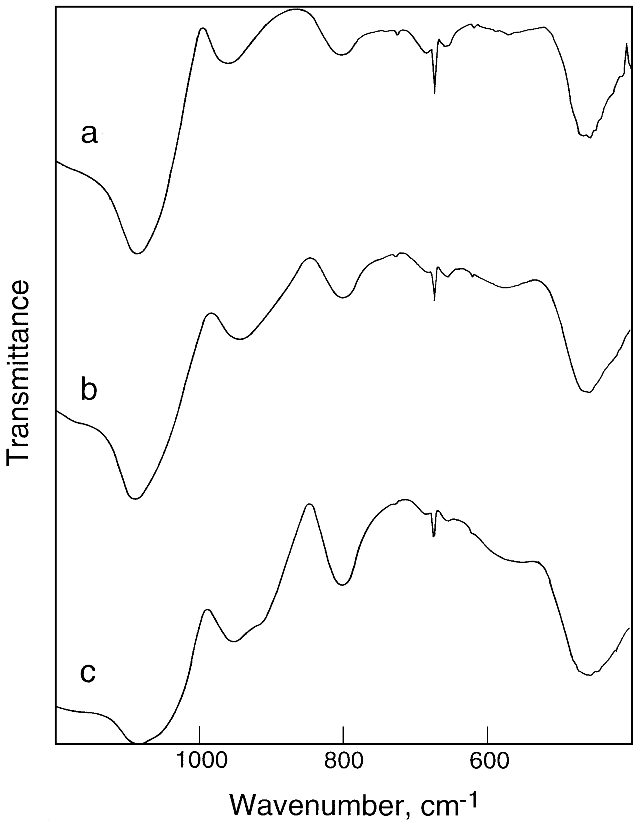

FIG. 6. IR spectra of various xerogels: (a) SiO_2, (b) $MoO_3(Cl)$–SiO_2, (c) $MoO_3(Cl)$–SiO_2, treated with hydrogen peroxide.

Initial spectroscopic characterization was performed by measurement of the IR spectra of the various silicates as prepared and also in the presence of hydrogen peroxide (Fig. 6). From the spectra (the molybdenum oxide substituted xerogels are given as an example) one observes the peaks common for all silicate structures at ~1100, ~800, and ~450 cm^{-1} due to stretching and bending vibrations of Si–O. Of special interest is the peak at ~940–950 cm^{-1}. In the past this peak has been attributed to one of three vibrations: (a) $(SiO)_3Si$–OH units in the xerogel and the associated Si–OH vibrations due to the hydroxylated surface (36), (b) the Si–O stretching in the polarized Si–O–M bond, and (c) $(SiO)_2M{=}O$ vibrations. In the case of TS-1 and other titanium substituted zeolites this peak is associated with the Si–O stretching in the polarized Si–O–Ti(IV) bond and disappears upon addition of hydrogen peroxide (37, 38). It is considered a signature for potential catalytic activity. In our case of the molecularly dispersed metallosilicates, this peak is also present in silicate xerogels in the absence of transition metals and, also, does not disappear upon addition of hydrogen peroxide. These spectra indicate that the peak at ~950 cm^{-1} is at least for the most part due to the hydroxylated surface, $(SiO)_3Si$–OH, in the xerogel. This is not surprising since it is known that the silicates prepared by this sol–gel method have highly hydroxylated surfaces (25). It is, however, likely that there is at least some partial contribution of $(SiO)_3Si$–OM and/or $(SiO)_2M{=}O$ vibrations to this band in the spectrum, for there is some difference in the peak location and intensity when the silica is substituted by different metal oxides, and in the molybdenum case even a small shoulder may be observed. The IR spectra are not influenced by the identity of the metal alkoxide precursor (dichloro-dialkoxy or tetraalkoxy).

Further characterization of the $MO_x(Cl)$–SiO_2 and MO_x–SiO_2 xerogels was carried out using ^{29}Si MAS NMR. Since the ^{29}Si chemical shifts are sensitive to the second neighbor environment (39), ^{29}Si MAS NMR might be an appropriate probe to study the difference between the catalytically active and inactive xerogels. Comparison of ^{29}Si MAS NMR spectra of catalytically active $MO_x(Cl)$–SiO_2 and the inactive MO_x–SiO_2 xerogels (Fig. 7) shows that there is a definite difference in the ^{29}Si MAS NMR spectra for the two types of xerogel for all three metal oxides. In all three cases, TiO_2, MoO_3, and WO_3, the Q_3 signal at

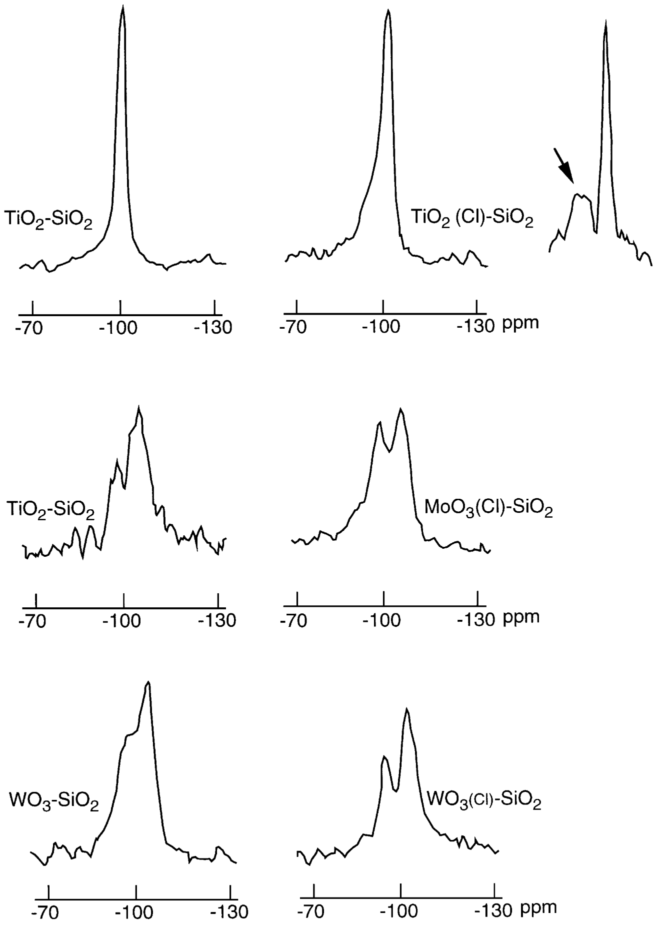

FIG. 7. ^{29}Si MAS NMR spectra of the $MO_x(Cl)$–SiO_2 and MO_x–SiO_2 xerogels. Insert—difference spectra of $TiO_2(Cl)$–SiO_2–TiO_2–SiO_2. The difference peak, Q_3, is pointed out by the arrow. The difference spectrum is not ideal (intensity of Q_3 *versus* Q_4 peak is not exact) since the original spectra were taken for samples with slightly different weights and volume.

97–98 ppm is stronger for the MO_x(Cl)–SiO_2 xerogels than for the MO_x–SiO_2 xerogels even though the metal oxide is only 5 mol% of the xerogel. In the case of TiO_2, the difference is less obvious, but from the difference spectrum (see insert to Fig. 7 and note in the caption) definitely significant.

SiO_2 gels are known to exhibit signals corresponding to the well-known resonances of Q_n ($n = 0$–4) species, where Q represents four-coordinated silicon species and the subscript n represents the number of bridging oxygens in the coordination tetrahedron. Thus, the abbreviation, Q_n, denotes sites of the type Si(−O−Si)$_n$(−O−X)$_{4-n}$, where X is an ionically bound ligand other than silicon, most frequently a proton (40). Recently, in TiO_2–SiO_2 xerogels, Q_3 lines have been attributed to contributions from both Si(−O−Si)$_3$(−O−H) and Si(−O−Si)$_3$(−O−Ti) structural units (41) as O−H and O−Ti(IV) groups have a similar influence on the central ^{29}Si nucleus. Since procedures for preparing the xerogels were identical except for the identity of the metal oxide precursor, the proportion of hydroxylated Si(−O−Si)$_3$(−O−H) groups to Si(−O−Si)$_4$ (Q_4 peak) should be similar for each metal oxide xerogel. The increased intensity of the Q_3 peak is therefore attributable to increased abundance of Si(−O−Si)$_3$(−O−M) species. The ^{29}Si MAS NMR spectra support the hypothesis that the catalytically active xerogel was formed through improved molecular dispersion because the dichloro-dialkoxy precursors hydrolyze and condense more slowly than the tetraalkoxy precursors.

The UV-vis diffuse reflectance spectra of both TiO_2(Cl)–SiO_2 and TiO_2–SiO_2 are shown in Fig. 8. For TiO_2(Cl)–SiO_2 the absorption edge is at 350 nm, whereas for TiO_2–SiO_2 the absorption edge is red-shifted to 400 nm. These near UV absorptions have been attributed to ligand-to-metal charge transfer, indicative of the presence of polymeric oxides (42). Isolated TiO_2 sites in octahedral or tetrahedral configurations absorb only at higher energies, ∼220 nm. The fact that the absorption for TiO_2(Cl)– SiO_2 is blue-shifted *versus* that of TiO_2–SiO_2 indicates higher but not complete metal oxide dispersion in the former.

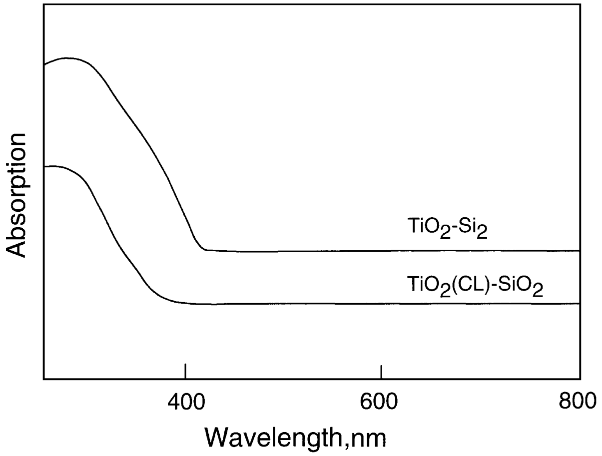

FIG. 8. Diffuse reflectance UV-vis spectra of TiO_2(Cl)–SiO_2 and TiO_2–SiO_2.

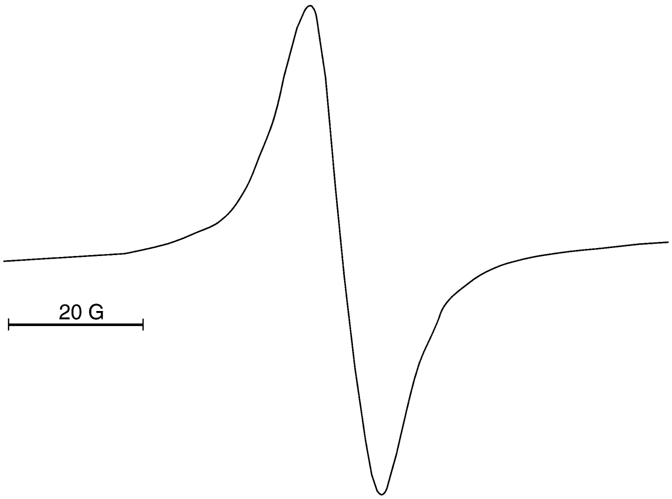

FIG. 9. ESR spectrum of partially reduced TiO_2–SiO_2.

Additional spectroscopic investigations of the xerogel compounds were carried out by use of ESR spectroscopy. The TiO_2(Cl)–SiO_2 and TiO_2–SiO_2 compounds are both ESR-silent as all titanium centers are in the +4 oxidation state. Therefore, in order to study the coordination environment of the titanium center, reduction of Ti(IV) to ESR-active Ti(III) (d^1) was carried out under very mild conditions using dilute sodium in liquid ammonia at −78°C as reductant, followed by removal of the NH_3 under vacuum (43). The ESR spectrum of the resulting purple–blue xerogel is given in Fig. 9. The spectrum is identical for both the TiO_2(Cl)–SiO_2 and TiO_2–SiO_2 xerogels, consisting of a single isotropic absorption at $g = 1.99$. This corresponds to a Ti(III) atom in a tetrahedral or octahedral coordination sphere with little tetragonal distortion. This result can be interpreted by concluding that the titanium is isomorphously substituted at silicon positions within in the silica framework (44). It is significant that there is no difference in the ESR spectra as a function of the titanium precursor. Probably, the chloride, originally at the titanium center during formation of the sol, is weakly bound and is completely hydrolyzed and or condensed in the gel formation and the subsequent drying of the xerogel at 120°C.

The more intense Q_3 peak in the ^{29}Si NMR spectra and the blue-shifted UV-vis spectrum for TiO_2(Cl)–SiO_2, coupled with the absence of a chloride effect in the Ti(III) ESR spectrum, lead us to suggest that the difference between the catalytically active MO_x(Cl)–SiO_2 and inactive MO_x–SiO_2 is that in the former the metal oxides are more dispersed. The presence of chloride as an explanation for catalytic activity could be eliminated by using an aqueous NaOH treated xerogel in the catalytic reaction. Indeed, for cyclooctene oxidation at 80°C no appreciable difference was observed for untreated and treated xerogel. The remaining chloride (6–8%) present in nonwashed xerogels is apparently present as free chloride.

Further use of ESR spectroscopy was made by the addition of hydrogen peroxide to the various (nonreduced) xerogels. In the case of molybdenum and tungsten, no spectra were observable at room temperature or at 150 K indicating that reduced and/or radical species are not extensively formed during the catalytic cycle. In the case of the titanium-based xerogels a different picture is obtained. When hydrogen peroxide is added to $TiO_2(Cl)–SiO_2$ or $TiO_2–SiO_2$ a yellow xerogel may be isolated (see the UV-vis spectrum insert in Fig. 10), typical for the formation of titanium-peroxo intermediates. Similar, red-shifted UV-vis spectra are also observed for both molybdenum and tungsten containing silicates. The ESR spectra both at ambient and subambient temperatures derived from both xerogels are identical (Fig. 10). The spectra are anisotropic with peaks between $g = 2.023$ and 2.045 and may be attributed to intermediates (not necessarily catalytically active) related to electron transfer of a peroxo ligand to the titanium center or *vice versa*. To describe the mechanistics of the interaction of hydrogen peroxide with the titanium center would be highly speculative on the basis of the ESR, UV-vis, and IR spectra and many intermediates could be formulated. However, it is clear that none of these methods reveal any distinguishing parameters between active and inactive xerogels. This situation is not unique to the xerogels discussed in this paper. Similar spectroscopic comparisons of different samples of TS-1 zeolites have also been inadequate in distinguishing between inactive and active samples, where it has been shown that the particle size is a crucial factor (45), given even that titanium is present in isolated framework positions.

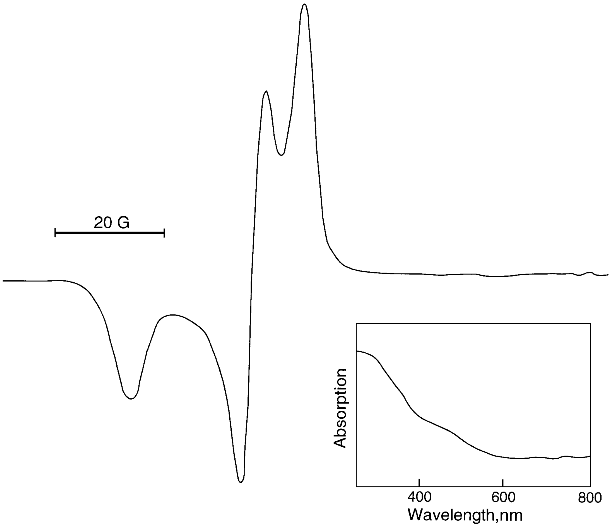

FIG. 10. ESR and UV-vis (insert) spectra of $TiO_2(Cl)–SiO_2$ treated with H_2O_2.

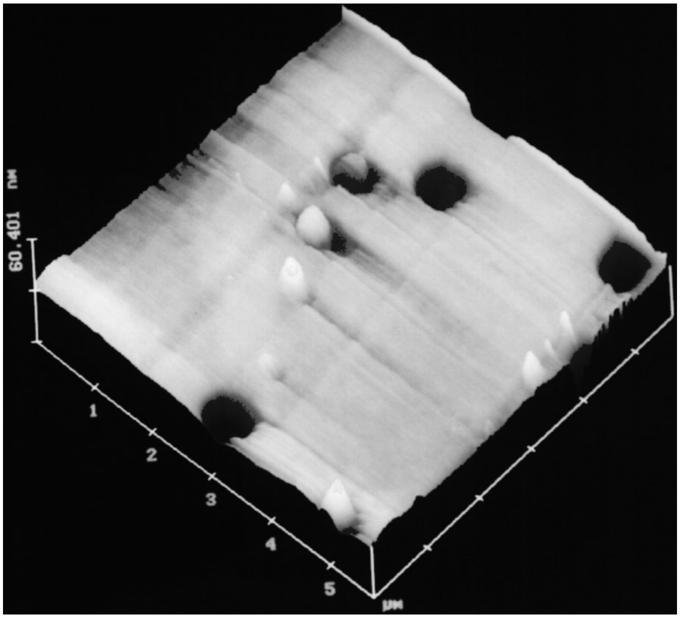

FIG. 11. Atomic Force Microscope image of a $TiO_2(Cl)–SiO_2$ xerogel.

Up to this point we have presented spectroscopic results aimed at revealing structure at the molecular level. From the literature and earlier TEM measurements (46), silica-based xerogels such as we have described that are produced under acidic conditions have generally been viewed as porous compounds with pore diameters in the range of 1–10 nm. In order to better define the macrostructure of the metal oxide substituted silicates described above, we have used atomic force microscopy, AFM, to produce images of the xerogels. From such micrographs (Fig. 11), one may easily observe a basically flat surface scattered with occasional pits or “craters.” These pits have dimensions of 600–700 nm across and depths of up to 30–40 nm. It is also important to note that in some areas, silicate islands having a diameter 200–500 nm and height of 10–30 nm tend to be deposited on the surface. The pits and islands observed are clearly “imperfections” in the formation of the xerogel as no “pores” were observed in the 10–50 nm region. Pores in the xerogel are, therefore, clearly smaller than 10 nm, the maximum resolution obtained in our measurement. Indirect information on the pore size and surface area of the xerogel was obtained by measurement of the adsorption isotherm using nitrogen as the adsorbed gas (Fig. 12). The adsorption isotherm is clearly of the Langmuir type (virtual plateau at $P/P_0 = 0.5$) indicating fairly small pores and narrow pore-size distribution. Using the Langmuir method a surface area of 750 m^2/g and an average pore diameter of 1.47 nm were computed. Clearly these values show that diffusion of fairly large organic substrates in the xerogel is feasible. This result is in contradiction to a recent paper where a bimodal pore distribution was observed in a titanium substituted silicate (28).

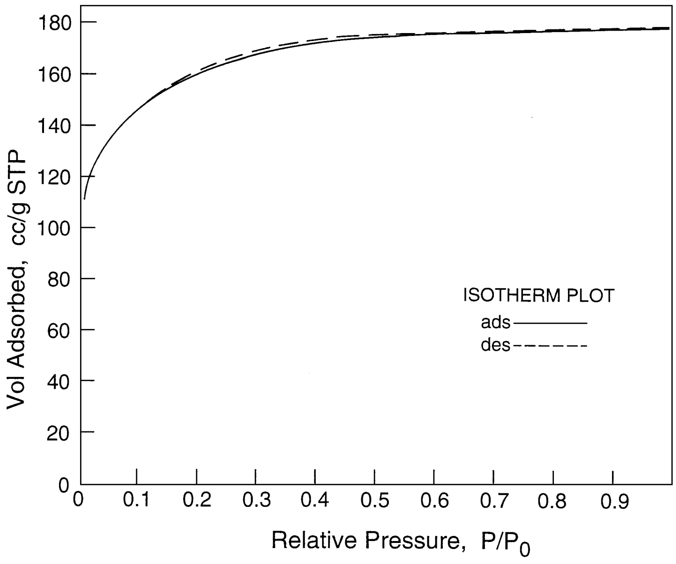

FIG. 12. Adsorption isotherm of N_2 at 77 K on $TiO_2(Cl)–SiO_2$ xerogel.

CONCLUSIONS

Catalytically active metal oxide substituted silicate xerogels for the oxidation of alkenes and alcohols with hydrogen peroxide can be prepared by molecularly mixing metal-dichlorodialkoxy and silicon tetraalkoxy compounds in the sol–gel procedure. In certain cases, high catalytic yields and selectivities may be obtained. The reported xerogel compounds were prepared in order to test them as possible alternatives to the better known, but less chemically accessible, metal substituted molecular sieves. It seems clear from our research that such easily prepared xerogels having a porous structure with sufficiently large pores for fairly large organic substrates have the important potential as active oxidation catalysts valuable for the development of environmentally friendly processes, provided the important parameter of molecular dispersion of the metal oxide is maximized.

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