JOURNAL OF CATALYSIS **171,** 420–430 (1997)
ARTICLE NO. CA971820

Synthesis of Hydrophobic TiO_2–SiO_2 Mixed Oxides for the Epoxidation of Cyclohexene

Hafedh Kochkar and François Figueras

Institut de Recherches sur la Catalyse du CNRS, 2 Avenue A, Einstein 69626, Villeurbanne, Cedex, France

Received November 28, 1996; revised May 26, 1997; accepted July 7, 1997

A series of Ti-silica mixed oxides were prepared using sol-gel polycondensation of Ti and Si alkoxydes. The polarity of the surface was changed by substituting partly tetraethoxysilane by phenyl or methyl triethoxysilane. This type of solid adsorbs much less water but more *n*-hexane than the mixed oxide obtained by the normal procedure; thus it shows hydrophobic character. From UV-vis and IR spectra, titanium is incorporated in the lattice of silica. Drying with supercritical carbon dioxide at low temperature produces a mesoporous solid which was used as catalyst for the reaction of cyclohexene with hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP). The selectivity of epoxidation with TBHP is very high and reaches >95% in acetonitrile as solvent. In acetonitrile as solvent, the rate of epoxidation of cyclohexene with TBHP decreases when the polarity of the surface decreases, but the reverse effect is observed when *tert*-butanol is the solvent. The reaction with hydrogen peroxide (30% in water) produces both cyclohex-2-en-1-ol and epoxide by two parallel paths. In presence of an aprotic solvent the oxygen balance overpasses 100%, which means that radical reactions involving atmospheric oxygen are involved. The selectivity of the allylic attack leading to cyclohex-2-en-1-ol is sensitive to the nature of the solvent and is minimized in *tert*-butanol. The epoxide is partly hydrolyzed to glycol, whatever the solvent and polarity of the surface. These catalysts epoxidize norbornene with high selectivity using hydrogen peroxide as oxidant.

INTRODUCTION

The development of redox zeolites in which a fraction of Si atoms is replaced by transition metal cations has demonstrated the potential of these materials as catalysts for oxidation and epoxidation in liquid phase (1). The main inconvenience of these solids for many applications is the presence of microporosity which limits the accessibility to substrates of small kinetic diameter. For instance, cyclohexene cannot be epoxidised with titanosilicalite-1, which has the MFI structure (2).

One of the hypotheses in this field is that site isolation could yield an active solid, the porosity of which could be engineered more easily. The first attempt in this direction was the Shell catalyst obtained by the surface reaction of titanium tetrachloride with silica (3). Active catalysts have also been obtained by the reaction of silica (4) with $Ti(OPr^i)_4$ or MCM-41 with a titanocene (5). These solids are not real substitutes of TS-1, since they are active in epoxidation using hydroperoxides but not diluted hydrogen peroxide. TiF_4 anchored on silica has also been proposed and is indeed active with concentrated hydrogen peroxide (6). It is commonly agreed that this behaviour could be related to the hydrophilicity attributed to the hydroxyl groups of silica: water is strongly adsorbed and the organic substrate has a limited access to the surface (7). Silanols are present at the surface as defects, the number of which depends on the conditions of crystallization. Blasco *et al.* (8) recently reported the synthesis of an Al free Ti-BEA (F) zeolite, grown in a fluoride medium, showing a high crystallinity and adsorbing small amounts of water (only 2 H_2O/Ti). This hydrophobic solid is much more active and selective than a conventional Ti-BEA (OH) when using hydrogen peroxide as oxidant.

Hydrophobic solids can also be obtained by sol-gel chemistry. Indeed sol-gel is very attractive since it permits us to prepare homogeneous mixed oxides of high specific area (9). Moreover, it is long known (10) that it is possible to cocondensate chlorosilanes with alkylchlorosilanes with incorporation of phenyl groups at the surface. The C–Si bond is chemically stable in acid media and it has been shown that these phenyl groups are stable up to 623 K in air (11, 12). The polycondensation of Ti alkoxide and alkyl or arylalkoxides of silicium results in the substitution of hydroxyl by phenyl or methyl groups and then in a hydrophobic solid. This type of modification opens then a route to a control of the polarity of the surface. Klein and Maier (13) recently reported the synthesis of microporous amorphous Ti–Si mixed oxides made from the polycondensation of titanium tetraisopropoxide, tetramethylethoxysilane, and methyltriethoxysilane. These solids show pores of about 0.7 nm, but relatively low activities in epoxidation with hydrogen peroxide.

Dutoit *et al.* (14) performed a systematic investigation of the different parameters of preparation of titania–silica gels on their activity. These solids were found active for epoxidation with organic peroxides only. With H_2O_2 as oxidant

0021-9517/97 $25.00

the samples were inactive, owing either to severe inhibition of the catalyst by water or to leaching of Ti from the solid. The method used for drying was a most critical point. Drying at room temperature yielded microporous xerogels of low activity. Drying in supercritical conditions with alcohols led to a macroporous solid, in which titania segregated due to hydrolysis of Si–O–Ti bonds. The application to these titania–silica catalysts of the techniques of supercritical drying using CO_2 produced a mesoporous solid in which Ti was incorporated to the lattice and more selective than Ti on silica for many epoxidations.

The effective concentration of water at the surface of the catalyst can also be controlled by the use of a proper solvent for the reaction. Indeed the comparison of TS-1 and Ti-BETA for the oxidation of *n*-hexene and cyclohexanol by hydrogen peroxide has shown that the solvent must be chosen according to the polarity of the surface (15); for the epoxidation of *n*-hexene, the best solvent is methanol (protic) for TS-1 and acetonitrile (aprotic) for Ti-beta.

This paper is devoted to the preparation and characterization of hydrophobic mixed oxides obtained by substitution of surface OH groups by phenyl groups using sol-gel synthesis with mixtures of tetraethoxysilane, phenyltriethoxysilane, and titanium tetraisoproxide. The reaction used to investigate the catalytic properties was the epoxidation of cyclohexene since it has been used very commonly as a model reaction. Both hydrogen peroxide and alkyl hydroperoxides were used as oxidizing agents.

EXPERIMENTAL METHODS

(1) Synthesis of the Titania–Silica Gels

The method is the sol-gel technique, i.e., polycondensation of Ti and Si alkoxides, catalyzed by acids. In order to change the polarity of the surface a mixture of tetraethoxysilane (TEOS, Aldrich, 98%) and phenyltriethoxysilane (Aldrich, 98%) was used. A typical preparation consists in a prehydrolysis at 343 K for 2 h of 0.166 mol of tetraethoxysilane (or mixture of TEOS and phenyltriethoxysilane) in a mixture of isopropanol (50 ml), water (6.25 ml), and HCl (0.3 ml of aqueous solution at 37%). The solution is then heated at 363 K and a solution (0.01 mol in 11.4 ml) of titanium tetraisopropoxide (TiOP; Aldrich) in isopropanol (Rhône Poulenc, Normapur) is added. Finally water (6.25 ml) is added dropwise (time of addition: 30 min), and a transparent gel is obtained, which is dried in different conditions.

The ratio P of phenyltriethoxysilane to tetraethoxysilane was changed from 0 to 0.6 in order to control the surface properties. Phenyltriethoxysilane was also substituted in a few cases by methyltriethoxysilane in order to study the influence of the size of the surface organic moiety. In that case the ratio methyltriethoxysilane/tetraethoxysilane is defined as Q.

Drying was done according to three different procedures previously described by Dutoit *et al.* (14): (a) conventional drying in air at 393 K for 24 h; (b) high temperature supercritical drying using isopropanol at 533 K; and (c) low temperature extraction using supercritical CO_2 at 313 K and 24 MPa.

(2) Physico Chemical Characterization

The composition of the samples was determined by atomic absorption spectroscopy after dissolution of the solids. The specific BET surface area and average pore radius were obtained from the isotherms of nitrogen adsorption at 77 K, using a homemade automatic volumeter. The samples were first evacuated at 473 K for 16 H.

The FTIR spectroscopic study of the lattice was performed on a Bruker lFS-48 instrument. Sample wafers consisted of 99 mg of dry KBr and 1 mg sample. The sample cell was purged with a flow of dry nitrogen during the measurements, 100 scans were accumulated for each spectrum in transmission at a spectral resolution of 4 cm^{-1}. The spectrum of dry KBr was taken for background substraction. UV-visible spectra were recorded on a Perkin Elmer Lambda 9 spectrometer using a homemade cell equipped with quartz windows.

The amount of water adsorbed by the different solids was determined by microgravimetry, using Sartorius equipment on samples previously dried at 473 K under a flow of nitrogen and then evacuated at the same temperature for 1 h. Water adsorption was measured at 293 K. The isotherms of adsorption show no saturation, and therefore, the different samples were characterized by the amount adsorbed at a relative partial pressure $p/p_0 = 0.5$.

Adsorption of hydrogen peroxide: this adsorption was investigated by infrared spectroscopy, UV-vis spectroscopy, and by EPR. The sample in powder form was treated with hydrogen peroxide (30% aqueous solution) and then dried at room temperature in a vacuum. The resulting solid was analyzed by the different techniques, using a wafer in KBr for infrared spectroscopy, or a powder for UV-vis and EPR.

(3) Catalytic Experiments

The oxidation reactions have been carried out at 348 K, in a 20-ml round-bottom flask immersed in a thermostatted bath and equipped with a condenser, a thermometer, and a magnetic stirrer. In a typical experiment 63 mmol of alkene, 5 g of solvent, and 250 mg of catalyst were mixed in the flask and heated at the desired reaction temperature under stirring (1000 rpm). Then 3.125 mmol of diluted hydrogen peroxide (30% aqueous solution) were instantaneously added to the mixture (time zero) in order to permit a kinetic study of the reaction. Small samples were taken (1 μl) with a syringe at different reaction times through a septum fitted with the flask, diluted in the solvent, to which *n*-decane was added as the internal standard for quantitative analysis.

The products were analyzed by gas chromatography (SHIMADZU GC 14 B) equipped with a capillary column SUPELCOWAX 10 TM, 30-m length, 0.25 mm ID, and 0.25 μm film thickness), and a flame ionization detector (FID). The consumption of hydrogen peroxide was measured by iodometric titration, using a potentiometric detector equipped with two similar platinum electrodes.

RESULTS

(1) Characterization of the Mixed Oxides

The chemical analysis of the samples was performed before and after the chemical test in order to check the possible dissolution of titanium in the reaction medium. The results reported in Table 1 show that no Ti was lost when the catalytic test was performed with hydrogen peroxide. By contrast, traces amounts of Fe, Ni, and Cr were observed on the aerogels, but not on the xerogels. These metals are characteristic of stainless steel, and introduced by the corrosion of the autoclave by the acid contained in the original gel. Fe is well known to promote Fenton activation of hydrogen peroxide. Its possible catalytic effect was checked on Fe/SiO_2 model catalysts obtained by the surface reaction of $Fe(acac)_3$ with Aerosil Degussa 200, followed by a calcination of the sample.

All these gels are X-ray amorphous. The surface areas and porosities of the gels are reported in Table 2. As generally reported the gels dried in air (xerogels) are microporous solids of high surface area. The surface areas of these materials are high in all cases and supercritical drying shows the main advantage to increase the size of the pores, but not the surface area. As expected from the method of preparation the texture of the gels is not very dependent on the amount of Ti. The substitution of surface OH groups by phenyl or methyl groups does not dramatically affect the surface area or porosity.

TABLE 1

Chemical Composition of the Aerogels

Sample	%Ti	%C	Fe (ppm)	Ni (ppm)	Cr (ppm)
Ti-free silica	0		147	25	63
P_0	0.74	8.8	102	18	27
P_0	0.77		After reaction using TBHP		
P_0	0.86		After reaction using H_2O_2		
P_{10}	0.99	13.59	75	11	21
P_{20}	0.86				
Q_{10}	0.76				
Q_{20}	0.86				
SiO_2 Degussa			<5	<10	20
Fe/SiO_2-1			375	<10	<10
Fe/SiO_2-2			933	<10	<10
Ti-HMS	0.87	<0.3			
TS-1	0.8				

TABLE 2

Surface Areas and Porosities of Titania–Silica Mixed Oxides Prepared Using Different Amounts of Alkyl or Aryltriethoxysilane (ATEOS) in the Reaction with Tetraethoxysilane and Titanium Tetraisopropoxide

Sample	%ATEOS (mol%)	%Ti	Surface area (m^2/g)	Pore radius (nm)
Xerogel	0	0.74	553	<1
Aerogel P_0	0	0.74	730	3.4
Aerogel P_{10}	10% phenyltriethoxysilane	0.99	489	3.5
Aerogel P_{20}	10% methyltriethoxysilane	0.76	624	3.7
Xerogel	0	3.68	595	<1
Xerogel	20% phenyltriethoxysilane	3.86	411	<1

The UV-vis spectra are reported in Figs. 1a–3a. They show a band at 220–230 nm, which is found in TS-1 at 210–215 nm (16) and is considered as characteristic of the incorporation of titanium in the lattice of silica. A further argument for this incorporation is the shift of this band to 260 nm when pyridine is adsorbed on the sample (Fig. 4). In this case the coordination of Ti is increased, which accounts for the shift of the band. This change proves that Ti atoms are coordinatively unsaturated and therefore can have a coordination of 4 or 5.

The samples obtained by supercritical drying using isopropanol show by contrast a UV band at 260 nm resulting from the formation of titanium oxide by hydrolysis of Ti–O–Si bonds by the residual water present in the system, as reported previously by Dutoit *et al.* (14).

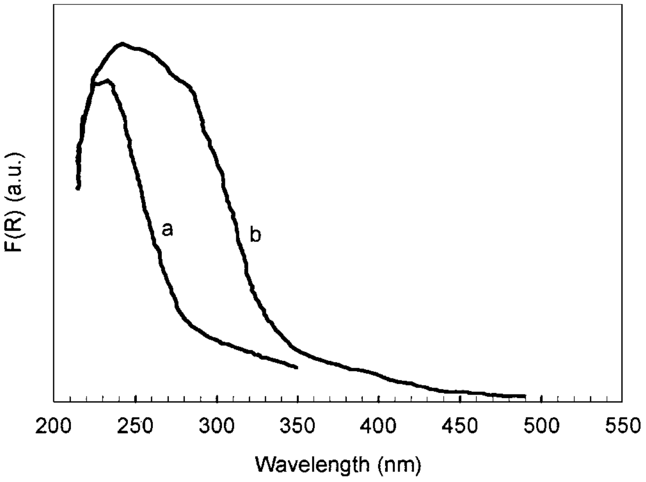


FIG. 1. UV-visible spectra of an hydrophilic TiO_2–SiO_2 xerogel (0.74% Ti): (a) original sample; (b) after treatment by H_2O_2 and drying in vacuum.

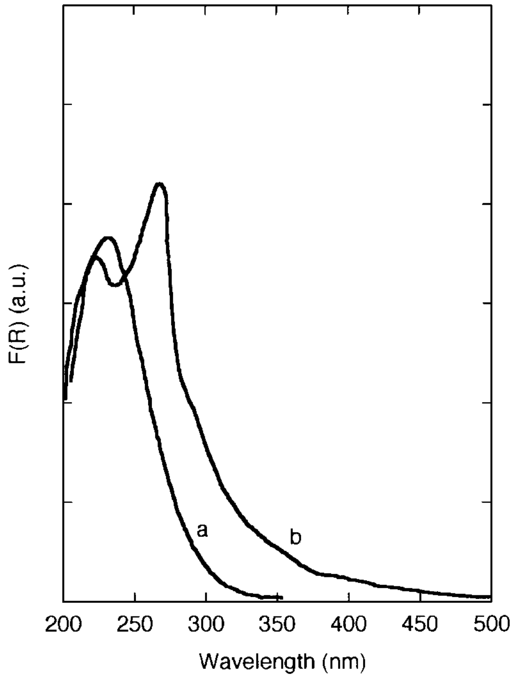


FIG. 2. UV-visible spectra of an hydrophobic TiO_2–SiO_2 xerogel obtained with 10% phenyltriethoxysilane in the gel containing 0.83% Ti: (a) in vacuum; (b) after treatment by H_2O_2 and drying in vacuum.

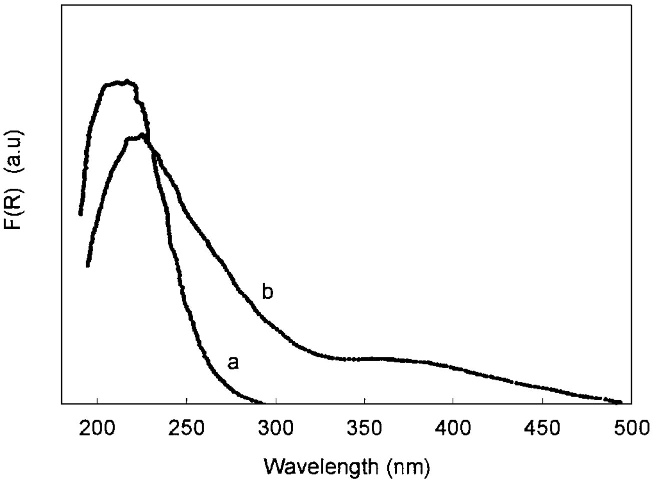


FIG. 3. UV-visible spectra of TS-1 (0.8% Ti): (a) in vacuum; (b) after treatment by H_2O_2 and drying in vacuum.

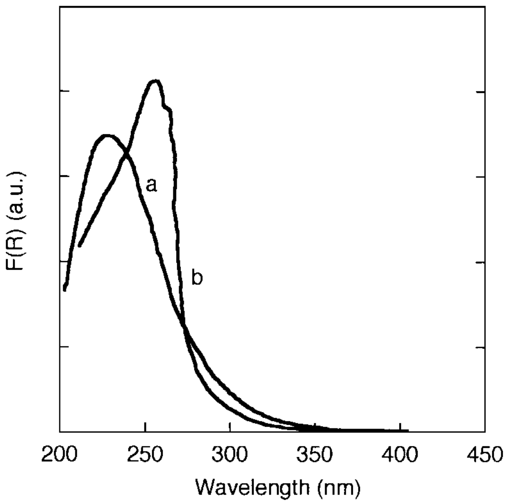


FIG. 4. UV-visible spectra of TiO_2–SiO_2 aerogel (P_0, 0.74% Ti), (a) in vacuum and (b) after adsorption of pyridine.

The FTIR spectra in the range of lattice vibrations of two characteristic xerogels are given in Figs. 5–7. They show the presence of a band at 930–940 cm^{-1}, attributed by many authors to the deformation of SiO_4 tetrahedra by the formation of Si–O–Ti bonds (14, 17–23). Two recent arguments support this assignment: the absence of this band in Ti-free Si gels (13) and its shift upon isotopic exchange with ^{18}O in the case of Ti-MOR (23). This band appears in TS-1 (Fig. 5a) and in the mixed oxides (Figs. 6a and 7a). Then both UV-vis and IR spectra suggest that Ti is effectively incorporated in the lattice of silica in these gels and, thus, that site isolation has been reached.

The adsorption of water was performed in order to investigate the possible hydrophobicity of the surface. The results obtained for a series of samples are reported in Table 3. In both cases of xerogel and aerogel the introduction of

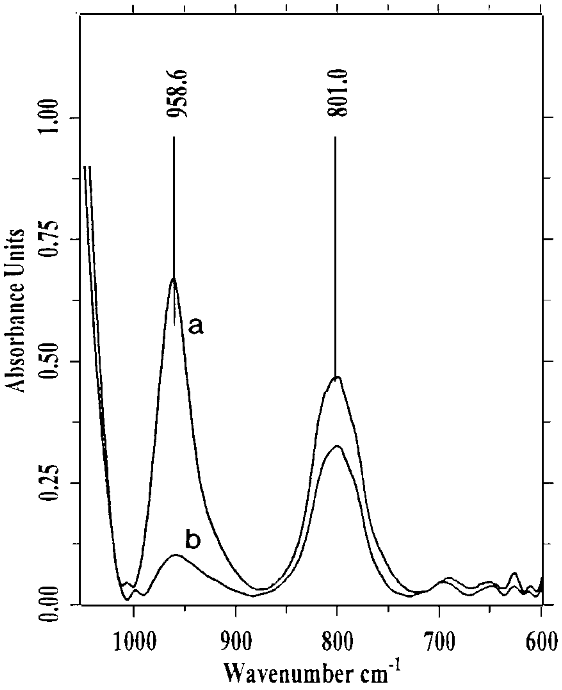


FIG. 5. FTIR spectra of TS-1 in the range of lattice vibrations: (a) before and (b) after treatment with hydrogen peroxide.

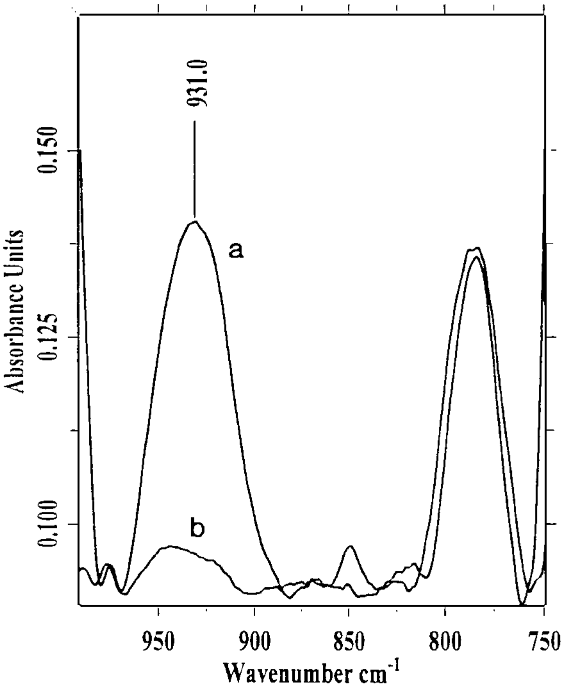


FIG. 6. FTIR spectra in the range of lattice vibrations of an hydrophobic TiO_2–SiO_2 xerogel obtained with 10% phenyltriethoxysilane in the gel, containing 0.83% Ti: (a) before and (b) after treatment with hydrogen peroxide.

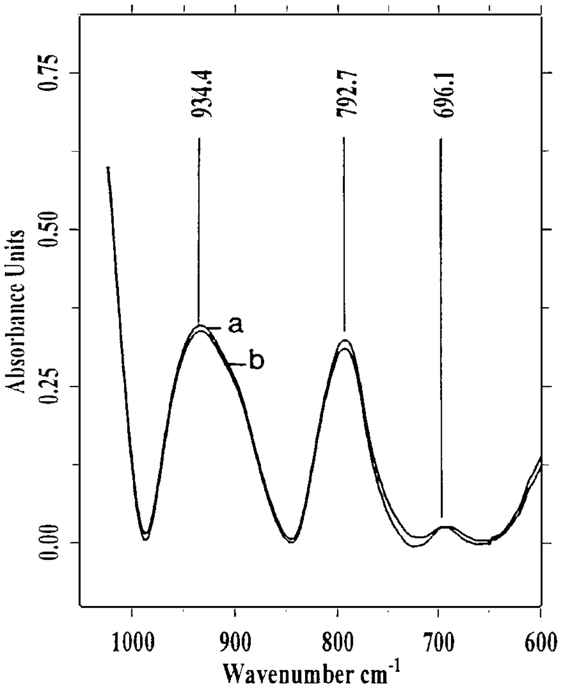


FIG. 7. FTIR spectra in the range of lattice vibrations, of an hydrophilic TiO_2–SiO_2 xerogel (0.7% Ti): (a) before and (b) after treatment with hydrogen peroxide.

TABLE 3

Adsorption Properties of Titania–Silica Mixed Oxides Containing 0.8% Ti

Sample	%ATEOS (mol%)	wt% adsorption of Water	wt% adsorption of Hexane
Xerogel	0	11.6	4.3
Xerogel	20% phenyltriethoxysilane	5	15
Aerogel P_0	0	8	7.6
Aerogel P_{10}	10% phenyltriethoxysilane	6	10
Aerogel P_{20}	20% phenyltriethoxysilane	3	14

alkyl or aryl groups decreases the adsorption of water by the solid. The adsorption of water decreases and that of *n*-hexane increases when the number of phenyl groups increases. This is the behaviour expected for hydrophobic solids. The 3% of water adsorbed by the gel obtained using 20% of phenyltriethoxysilane represents a ratio $H_2O/Ti = 9$, which is intermediate between the values 2.1 for an hydrophobic Ti-BEA (F) and 36.4 for a weakly hydrophilic Ti-BEA (OH) reported by Blasco *et al.* (8).

(2) Adsorption of Hydrogen Peroxide

Former work has evidenced the formation of peroxo species on TS-1, and it was therefore of interest to check their formation in the present case. TS-1 was taken as reference since it has been investigated in detail. By the interaction of hydrogen peroxide with the solid, the band at 960 cm^{-1} in infrared decreases in intensity on TS-1 (Fig. 5b) and on the hydrophobic xerogel (Fig. 6b), but it is less affected in the case of the hydrophilic xerogel (Fig. 7b).

This interaction also changes the UV-vis spectra; with TS-1, the band at 220–230 nm decreases in intensity and is shifted to 250 nm, while a new band appears at about 380 nm. This behavior has been attributed to the formation of a peroxo species by substitution of a OH species by OOH from hydrogen peroxide (16). A weak band is observed at the similar position with the hydrophobic xerogel, which suggests that the same species is formed at the surface, but not with the hydrophilic gel. The interaction of hydrogen peroxide is then weaker in that case.

Upon interaction of the hydrophobic xerogel with hydrogen peroxide a paramagnetic species was observed by ESR as reported in Fig. 8. Both hydrophilic and hydrophobic samples show the same ESR signal observed at room temperature after adsorption of hydrogen peroxide and vacuum drying at room temperature. However, the intensity is much greater in the case of the hydrophobic surface.

(3) Catalytic Experiments

The epoxidation of cyclohexene yields the epoxide, the corresponding glycol, but also cyclohex-2-en-1-ol, the

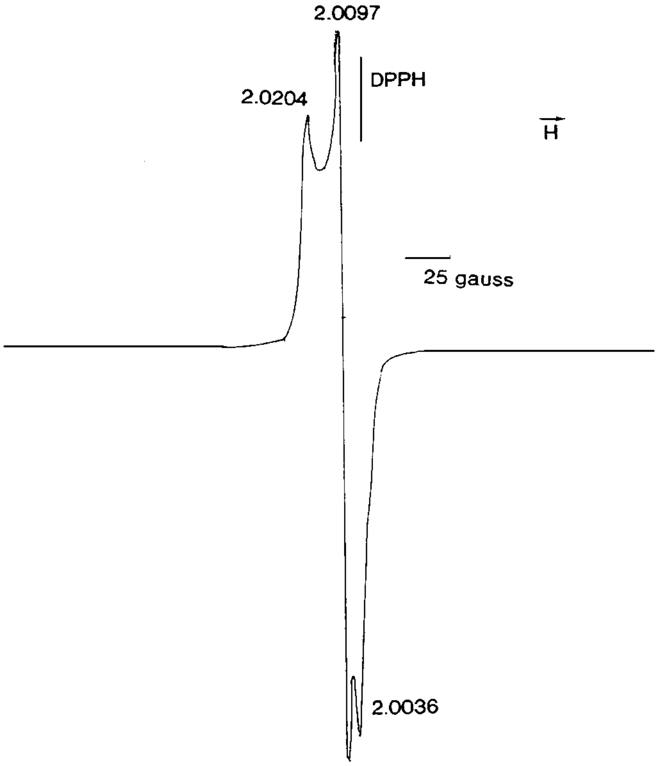


FIG. 8. ESR spectrum at room temperature of a hydrophobic xerogel (0.83% Ti) after contact with hydrogen peroxide and vacuum drying at room temperature.

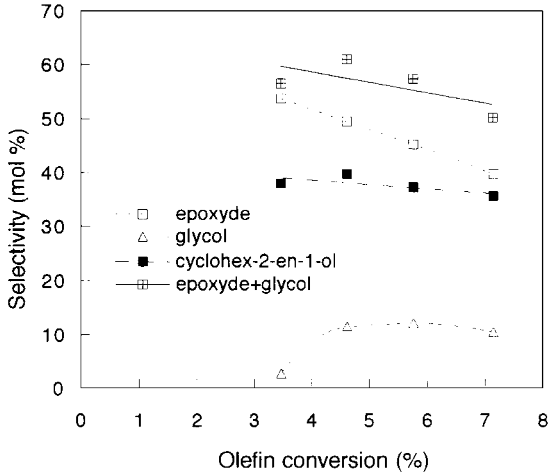


FIG. 10. Selectivities of the hydrophobic P_0 aerogel, containing 0.74% Ti, as a function of conversion, in the same conditions as Fig. 9.

corresponding ketone and epoxide. Allylic alcohols can be formed by different schemes including rearrangement of epoxides (24); therefore the kinetics of their formation was investigated. The curves selectivity/conversion of cyclohexene are reported in Figs. 9 and 10 for two representative catalysts, an aerogel P_0 and a Ti-HMS, prepared according to the method reported by Tanev *et al.* (25), which contains no impurities and has been calcined in air at 773 K. The results show that in both cases the selectivity to cyclohex-2-en-1-ol is high at low conversion and rather constant. The selectivity to the epoxide decreases with time while that for the glycol increases from very low values. It can then be concluded that the epoxide and cyclohex-2-en-1-ol are primary products of the reaction and that glycol is a secondary product. The ratio cyclohex-2-en-1-ol/(epoxide + glycol) varies little; therefore the oxidations follow two parallel pathways: a radical path leading to cyclohex-2-en-1-ol and a presumably ionic path leading to the epoxide, as formerly proposed by Sheldon and van Doorn (26) for the homogeneously catalyzed reaction (Scheme 1).

The catalytic properties can then be expressed by the initial reaction rate and the selectivity of attack at the double bond, which includes the formation of epoxide and glycol versus allylic oxidation, i.e. the sum of cyclohex-2-en-1-ol, the corresponding ketone and epoxide.

The epoxide can be hydrolyzed to the glycol, and the selectivity to the glycol corresponds then to the difference of the selectivity for double bond attack and epoxide formation.

Several parameters can be analyzed including the polarity of the surface, the influence of the oxidizing agent, and

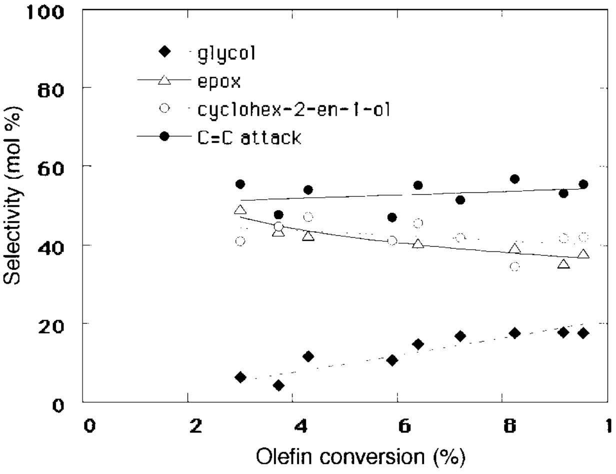
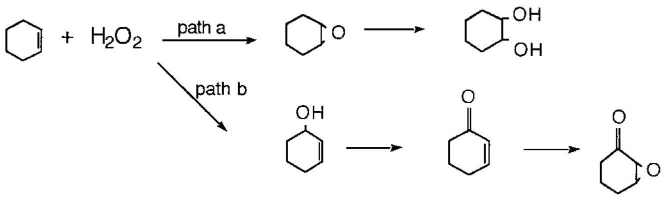


FIG. 9. Selectivities of a Ti-HMS sample (0.87% Ti) as a function of conversion. The reaction conditions are the standard ones, and 1,2-dimethoxyethane is used as solvent.



SCHEME 1

TABLE 4

Activities and Selectivities of Aerogels Obtained Using Hydrogen Peroxide or *tert*-Butyl Hydroperoxide for the Oxidation of Cyclohexene in *tert*-Butanol as Solvent, Using a Reactor Flushed by Nitrogen

	Ti-free silica[a]	P_{10}[a]	Ti-free silica[b]	P_{10}[b]
Rate ($mmol \cdot min^{-1} \cdot g^{-1}$)	0.032	0.15	0.13	0.68
Select for C=C attack	26	79	85	90
Select to epoxyde (mol)	25.6	31	85	90
Conversion of H_2O_2 or TBHP	60	98	51	100
Efficiency of H_2O_2 or TBHP	83	100	69	100
Yield of epoxyde	15.4	30	43	90

[a] H_2O_2 (30%).

[b] TBHP in decane.

the effect of the solvent. In the following, the selectivity for C=C attack represents the relative amount of cyclohexene epoxide and the corresponding glycol to that of cyclohex-2-en-1-ol and the corresponding ketone and epoxide.

3.1. Influence of the oxidizing agent. The results are reported in Table 4 for two aerogels containing Ti (Si/Ti = 100) or not, using *tert*-butanol as solvent. It appears that the hydrophobic aerogel is far more selective to the epoxide when the organic hydroperoxide is used as reactant. The Ti-free aerogel used as reference shows a surprisingly high conversion, with both types of oxidizing agents, which we attribute to the impurities, and a high selectivity for allylic attack with hydrogen peroxide. In that case the hydrolysis of the epoxide is minimized.

3.2. Effect of basic additives. Basic additives are commonly added in order to improve the selectivity to the epoxide. As reported in Table 5, activity decreases in the presence of basic additives such as the selectivity for double bond attack. By contrast the addition of bases blocks the secondary reaction of hydration of the epoxide. The selectivity of C=C attack also decreases in presence of air.

TABLE 5

Effect of the Additives (Ratio Additive/H_2O_2 = 0.01) and of the Atmosphere of Reaction on the Catalytic Properties of Catalyst P_{10} in *tert*-Butanol as Solvent

		Nitrogen atmosphere			
	Air	No additive	Urea	Bu_4NOH[a]	Isoquinoline
Rate ($mmol \cdot min^{-1} \cdot g^{-1}$)	0.15	0.15	0.07	0.04	0.1
Sel. C=C attack (mol%)	72	79	60	62	54
Selectivity to epoxide	27	31	41	46	53
Conversion H_2O_2 (%)	71	98	86	11	45
Epoxide yield	19	30	36	5	24

[a] Tetrabutylammonium hydroxyde (40 wt%).

TABLE 6

Catalytic Properties of Different Aerogels Using H_2O_2 (30%) as Oxidant, *tert*-Butanol as Solvent, Urea as Basic Additive (Urea)/(H_2O_2) = 0.01 (mol/mol), and Reactor Flushed by a N_2 Flow

	P_0	P_{10}	P_{20}
Rate ($mmol \cdot min^{-1} \cdot g^{-1}$)	0.06	0.072	0.12
Selectivity for C=C attack	51	60	54
Selectivity to epoxide (mol%)	45	41	42
Conversion of H_2O_2 (%)	65	86	97
Epoxide yield	29	36	41
Amount of water adsorbed (wt%)	8	6	3

3.3. Influence of the surface polarity. The polarity can be changed by substituting OH groups for phenyl groups, which corresponds as reported above to different amounts of water adsorbed at the surface. The catalytic properties of these aerogels are reported in Table 6. The solid prepared with 20% phenyltriethoxysilane shows a higher activity, but the same selectivity as the hydrophilic Ti-silica sample (P_0).

3.4. Solvent effects. Protic and aprotic solvents of different polarity were used for this reaction in the presence of hydrogen peroxide. The results are reported in Table 7. In methanol (dielectric constant 32.7) no products of reaction were formed. The distribution of products depends significantly on the solvent used when H_2O_2 is the oxidant. The results reported in Tables 7 and 8 illustrate the fact that 1,2 dimethoxyethane is a very particular solvent, since in that case the number of moles of oxygenated products surpasses the amount of hydrogen peroxide engaged in the reaction. Pyridine addition has little effect on this process which is also observed with Ti-HMS. This sample, prepared from the same components as the gels, in the presence of a dodecylamine, is calcined in air at 923 K and contains no impurities. In *tert*-butanol, by contrast, the oxygen balance is respected. The distribution of products with 1,2 dimethoxyethane as solvent is similar to that obtained in the reaction of cyclohexenyl hydroperoxide with cyclohexene.

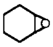
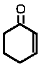
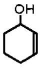
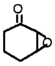
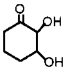
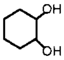
TABLE 7

Influence of the Solvent on the Oxidation of Cyclohexene by Hydrogen Peroxide on a P_{10} Sample

	1,2 Dimethoxy-ethane	Acetonitrile	*tert*-Butanol
Rate ($mmol \cdot min^{-1} \cdot g^{-1}$)	0.29	0.08	0.15
Selectivity for C=C attack (mol%)	68	55	79
Selectivity epoxide	51	36	36
Conversion H_2O_2 (mol%)	81	100	98
Efficiency of H_2O_2 (mol%)	231	98	100
Epoxide yield	41	36	30
Dielectric constant	20	37.5	10.9

TABLE 8

Distribution of the Products for the Reaction of Hydrogen Peroxide with Cyclohexene in a Reactor Open to the Atmosphere in Different Solvents

No.	Sample	Initial rate	Millimoles of product formed						Selectivities (mol%)	
									C=C attack	H_2O_2
1	P_0	0.89	2.4	0.24	1.64	0.04	0.26	0.66	58	163
2	$P_0 + $ pyr	0.2	3.0	0.25	1.99	0.08	0.27	0.18	55	180
3	P_{10}	0.3	3.74	0.44	1.45	0.32	0.19	1.26	67.5	231
4	$P_{10} + $ pyr	0.21	3.8	0.5	1.6	0.24	0.1	1.5	68.5	242
5	Q_{10}	0.16	2.6	0.2	1.1	0.07	—	0.76	70.5	147
6	Ti-HMS (0.87% Ti)	0.23	4.34	—	4.82	0.42	0.94	2	50	269
7	$Q_{10} + $ pyr	0.09	1.9	—	0.97	0.04	—	0.07	67	100
8	P_{10}	0.15	1.08	0.30	0.82	—	—	1.82	72	100
9	Q_{10}		3.18	2.38	—	0.31	0.24	0.18		

Note. Solvent: 1,2 dimethoxyethane in experiments 1–7 and 9, and *tert*-butanol in experiment 8. The oxidant is hydrogen peroxide (30% aq) in experiments 1–8 and cyclohexenyl hydroperoxide in experiment 9.

The interaction between solvent effects and surface polarity was also investigated in the case of *tert*-butylhydroperoxide as oxidant, by comparing the initial rates of reaction on hydrophilic and hydrophobic catalysts. The selectivity to the epoxide and the selectivity for the peroxide are high in all the cases; therefore, the reaction is very specific. The results reported in Table 9 show that acetonitrile is the best solvent for the reaction, but that a decrease of the polarity has a beneficial influence when *tert*-butanol is used and a negative effect when acetonitrile is the solvent. A similar effect has been reported by Corma *et al.* (15) for reactions with hydrogen peroxide on hydrophobic TS-1 and more hydrophilic Ti-BETA.

3.5. Effect of the impurities on the solid. The chemical analysis shows that some Fe, Cr, and Ni impurities are present on the aerogels, and it was then attempted to check the catalytic effect of Fe, with the two types of oxidizing agents. Model catalysts prepared on silica were then used containing a few ppm of Fe. A calcination in air up to 773 K was performed before the catalytic test in order to obtain Fe^{3+} cations. The results are reported in Table 10.

TABLE 9

Effect of the Polarity of the Surface on the Oxidation of Cyclohexene by TBHP in the Presence of Protic or Aprotic Solvents

Sample	Initial rate $(mmol \cdot min^{-1} \cdot g^{-1})$	Final conversion (%)	Selectivities (mol%)	
			TBHP	Epoxide
Solvent tert-butanol				
P_0	0.1	86	91	90
P_{10}	0.69	87	100	82
Q_{10}	0.6	89	100	82
Solvent acetonitrile				
P_0	2.92	91	91	97
P_{10}	1.38	94	100	95
Q_{10}	2.14	97.6	100	95

3.6. Influence of the structure of the substrate. Since the mechanism can change with the availability of allylic hydrogens in the substrate, cyclohexene, norbornene, and α-pinene were compared. The results are reported in Table 11.

DISCUSSION

In agreement with former work (7, 9, 13, 14, 19), Ti can be incorporated into the lattice of silica using sol-gel chemistry. The partial substitution of tetraethoxysilane by phenyl or methyltriethoxysilane permits us to prepare solids with hydrophobic character. The simultaneous control of the retention of the structure and a reasonable porosity can be reached by low temperature supercritical extraction of the solvent using CO_2.

The coordination of titanium in these solids could be tetrahedral from UV-vis spectra; however, ESR suggests a different result. A similar anisotropic signal characterized by $g_{xx} = 2.0030$, $g_{yy} = 2.0099$, and $g_{zz} = 2.0238$ has been reported for TS-1 by Geobaldo *et al.* (16) and attributed to a superoxide radical O_2^- adsorbed on Ti species. Giamello *et al.* (27) recently reported similar results for zirconium dioxide contacted with an aqueous solution of hydrogen peroxide; the spectrum was assigned to the formation of a superoxide radical ion adsorbed on top of a Zr^{4+} cation. This signal was first reported by Shvets and Kazansky (28) on model Ti/SiO_2 catalysts. They proposed that the g_{zz} factor varies with the symmetry of $Ti : g_{zz} = 2.020$ for O_2^- adsorbed on a Ti occupying a square pyramid and $g_{zz} = 2.026$ for O_2^- adsorbed on tetrahedral Ti atoms which exist on

TABLE 10

Catalytic Properties, in *tert*-Butanol as Solvent of Silica and Ti-Free Aerogels of Silica Containing Trace Amounts of Impurities

			Oxidant		Product selectivities	
Sample	Fe content (ppm)	Initial rate (mmol · min^{-1} · g^{-1})	Selectivity (mol%)	Conv. (%)	Epoxide	Allylic attack
With hydrogen peroxide						
No catalyst	0	0.0024	2.2	3.0	44	56
Ti-free SiO_2 aerogel	147	0.032	60	83	26	74
SiO_2 Degussa	<5	0.014	4.6	17.2	51	49
Fe/SiO_2-1	375	0.018	6.5	26	22	70
Fe/SiO_2-2	933	0.025	47	88	22	78
With TBHP						
Ti-free SiO_2 aerogel	147	0.131	69	51	85	15
SiO_2 Degussa	<5	0.021	5.8	30	45	55
Fe/SiO_2-2	933	0.036	6.3	35	46	54

the silica surface at low Ti content. By this criterion, Ti in this gel is closer to square pyramidal coordination than to a tetrahedral coordination as found in TS-1.

The catalytic activities of the gels can be compared to literature data when transformed into turnover frequencies (TOF). These comparisons are only qualitative since the reaction conditions, in particular the solvent, can affect the reactivity. Hutter *et al.* (29) reported a TOF equal to 83 mmol alkene/s/mol Ti for the reaction of cyclohexene with cumene hydroperoxide at 333 K, while at 353 K, Klein *et al.* (7) reported a TOF of 19 s^{-1} for the reaction with TBHP in decane. The higher TOF (200 s^{-1}) found here in acetonitrile at 348 K agrees with the result of Hutter *et al.* and is likely due in large part to the decrease of diffusional limitations, due to the procedure of drying. For the oxidation of cyclohexene by hydrogen peroxide a TOF of about 10 s^{-1} can be calculated at 333 K from the work by Corma *et al.* (30). This result is of the same magnitude as the TOF (3 mmol alkene/mol Ti s) observed here for the same reaction at 348 K. Therefore the catalytic properties of these materials are representative of titanium silicates.

TABLE 11

Effect of the Substrate Structure on the Selectivity for Epoxidation of Aerogels in 1,2 Dimethoxyethane as Solvent Using Hydrogen Peroxide (30%) as Oxidant

		Hydrogen peroxide		Olefin selectivities (%)	
Olefin	Initial rate (mmol · min^{-1} · g^{-1})	Conv. (%)	Select. (%)	C=C attack	Epoxide
Aerogel Q_{10}					
Cyclohexene	0.16	100	147	70.5	55
Norbornene	0.76	97	100	100	95
α-Pinene	0.16	40	97	52	32
Aerogel P_{10}					
Cyclohexene	0.3	100	231	68.5	50.5
Norbornene	1.04	97	100	100	95
α-Pinene	0.14	71	100	26.4	21

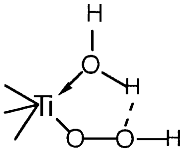
It can be pointed out that the low temperature drying results in the incorporation of trace amounts of Fe, Ni, and Cr ions, which are known to promote the Fenton reaction. The contamination of the sample has little importance if TBHP is used as the oxidizing agent, since yields in the 96% range can be reached. With hydrogen peroxide, poor performances are obtained. However, several observations suggest that the low selectivity is not related to the presence of some impurities:

(1) the residual activity of Fe free silica from Degussa suggests that Fe is not responsible for the decomposition of H_2O_2. Indeed the activity of the Fe-doped silicas is lower by one order of magnitude than that of the TiO_2–SiO_2 mixed oxides. Moreover, the main loss of selectivity is not related to a parallel reaction of hydrogen peroxide decomposition; the selectivity towards H_2O_2 which is 60% in the absence of Ti (Table 10) usually increases up to more than 95% with the mixed oxide, i.e. that 95% of the oxygen is found in the products of reaction.

(2) Ti-HMS prepared from high purity reactants and treated in glass reactors shows the same catalytic behaviour as the mixed oxides.

From the kinetics of the reaction, it appears that two parallel paths exist and that the main cause of selectivity loss is the occurrence of an allylic attack with the formation of cyclohex-2-ene-1-ol, which is much higher in the case of H_2O_2 than with TBHP. This allylic attack is favoured in the presence of air, in an aprotic solvent, or with basic additives, and unfavoured in *tert*-butanol as the solvent. The observation of an oxygen balance above 100% is indicative of a radical mechanism induced by hydrogen peroxide, but using atmospheric oxygen. A similar result has been recently reported by Jorda *et al.* (31) for the oxidation of cyclohexene on Ti/SiO_2 obtained from TiF_4. The comparison of cyclohexene, α-pinene, and norbornene also agrees with the occurrence of an allylic attack. This attack is unfavoured with norbornene, and a very good selectivity is then obtained for epoxidation; α-pinene, which contains more allylic hydrogens, also shows a lower selectivity for C=C attack and epoxidation.

It can be remarked from Table 6 that the selectivity for C=C attack increases on hydrophobic solids (58% on P_0, 67% on P_{10}, and 70% on Q_{10}) using dimethoxyethane as an aprotic solvent. On hydrophilic solids such as Ti-Beta, Corma *et al.* (15) suggested that water competes favourably with nonprotic solvents and proposed the existence of a Ti peroxo species stabilized by water (species 1). By contrast, in *tert*-butanol as solvent the stabilizing ligand would be the alcohol. The lower donor properties of water with respect to alcohols would then account for a higher electrophilic character of the hydrated species 1 and then of a higher reactivity.



Species 1

This intermediate accounts for a *higher conversion* in aprotic solvents, but also for the different *selectivity for the allylic attack*. If we measure the importance of the radical reaction by the balance of oxygen in Table 8, we can conclude that the contribution of this radical process is higher on hydrophobic solids, when dimethoxyethane is used as the solvent. In acetonitrile the H_2O_2 efficiency is 98%, but here also allylic oxidation is observed with a selectivity of 45%. This shows that the surface Ti complex decomposes faster to a radical. An hydrophobic surface should adsorb preferentially ether or acetonitrile (Lewis bases) to water. Then a complex could be formed in which the Lewis base could at least partially neutralize the charge on titanium and then reduce the activity for epoxidation and promote a radical cleavage and allylic oxidation, as indeed observed in Table 8 by the higher importance of radical reactions when pyridine is added to the solid. As reported before by Sheldon (26) and by Fusi (32) this radical oxidation yields hydroperoxides which can be reacted with excess cyclohexene and give epoxy-cyclohexane. The selectivity relative to cyclohexene expected for this process is at most 50%.

In *tert*-butanol as the solvent and using H_2O_2 as the oxidant (Table 7) the selectivity for the attack at the double bond reaches 80%, which indicates that direct epoxidation does occur, but the main product is glycol. By contrast, Fe/SiO_2 gives relatively high selectivities for the attack at the allylic position, which reaches 78% on Fe/SiO_2-2 in *tert*-butanol as the solvent.

The epoxide when formed can be hydrolyzed to glycol by an acid-catalyzed reaction. It can be remarked that on the Ti-free aerogel, the reaction produces some epoxide which is not converted to glycol since the selectivity for the epoxide (25.6%) is close to the selectivity for the attack of the double bond 26% (Table 4). The introduction of Ti in the gel increases the activity, and the selectivity for attack at the double bond reaches 79%, but the selectivity for the epoxide increases only to 30%. This means that most of the epoxide has been converted to glycol. Therefore we can conclude that the acid sites which catalyze the hydration of the epoxide are due to Ti species, as been concluded for TS-1 (33).

As usually observed in the literature (24, 34–36) this reaction can be inhibited by basic additives (Table 5). The selectivity for the epoxide is almost doubled by the addition of isoquinoleine to the reaction mixture. It is interesting to notice that this addition decreases the activity, but it also reduces the selectivity of the attack at the double bond. This is in agreement with the effect of solvents and the proposal that epoxidation catalysts are fairly strong Lewis acids.

With *tert*-butanol as solvent the polarity of the surface has a small influence on the activity (Table 6), but it can be noticed that both reactions with hydrogen or organic peroxides are faster on the solid prepared with phenyltriethoxysilane. A lower activity for hydration of the epoxide is observed on an hydrophobic surface, which is indeed consistent with a lower concentration of water at the interface. However, hydrophobicity has only a limited effect on the selectivity of epoxidation versus allylic attack. When compared to TS-1 these mixed oxides appear then to show rather different properties that are not simply related to hydrophobicity, as proposed by others (7). The different behaviour is more likely related to the different coordination of Ti. The different selectivities observed in the epoxidations of norbornene and α-pinene with hydrogen peroxide confirm that the specific reactivity of these solids is related to their ability to decompose TiOOH species into radicals. The possible applications are then limited to the epoxidation with organic peroxides, or to those substrates which cannot suffer allylic attack with H_2O_2.

In conclusion, if an organic hydroperoxide is used as the oxidizing agent, these mixed gels are good catalysts, reaching >95% yield for cyclohexene oxide. With hydrogen peroxide a selectivity of about 80% for the attack of the double bond can be reached with cyclohexene, by optimizing the solvent, but the hydration of the resulting epoxide is fast and can be slightly decreased but not suppressed, even on hydrophobic surfaces. This is consistent with the idea that the site active for epoxidation is a strong Lewis site; the *selective* inhibition of the secondary reaction is then practically impossible.

REFERENCES

1. Sheldon, R. A., and Dakka, J., *Catal. Today* **19**, 215 (1994).
2. Tatsumi, T., Nakamura, M., Yuasa, K., and Tominaga, H., *Catal. Lett.* **10**, 259 (1991).
3. Wulff, H. P., Shell Oil Co., U.S. Pat. 3,923,843 (1975).
4. Fraile, J. M., García, J. I., Mayoral, J. A., de Mènorval, L. C., and Rachdi, F., *J. Chem. Soc., Chem. Commun.*, 539 (1995).
5. Maschmeyer, T., and Thomas, J. M., *in* "Proc. 11th Int. Cong. Catal., Baltimore, June 30–July 5, 1996." [Poster Po-99]
6. Jorda, E., Tuel, A., Teissier, R., and Kervenal, J., *J. Chem. Soc. Chem. Commun.*, 1775 (1995).
7. Klein, S., Thorimbert, S., and Maier, W. F., *J. Catal.* **163**, 476 (1996).
8. Blasco, T., Camblor, M. A., Corma, A., Esteve, P., Martinez, A., Prieto, C., and Valencia, S., *J. Chem. Soc. Chem. Commun.*, 2367 (1996).
9. Toba, M., Mizukami, F., Niwa, S-I., Sano, T., Maeda, K., Annila, A., and Komppa, V., *J. Mol. Catal.* **91**, 277 (1994).
10. Brown, J. F., *J. Polymer Science, Part C1* **83**, 1 (1963).
11. Guyot, A., and Bartholin, M., *Compt. Rend. Acad. Sci.* **264**, 1232 (1967).
12. Danforth, J. D., and Roberts, J. H., *J. Catal.* **10**, 252 (1968).
13. Klein, S., and Maier, W. F., *Angew. Chem. Int. Ed. Engl.* **35**, 2230 (1996).
14. Dutoit, D. C. M., Schneider, M., and Baiker, A., *J. Catal.* **153**, 165 (1995).
15. Corma, A., Esteve, P., and Martinez, A., *J. Catal.* **161**, 11 (1996).
16. Geobaldo, F., Bordiga, S., Zecchina, A., and Giamello, E., *Catal. Lett.* **16**, 109 (1992).
17. Boccuti, M. R., Rao, K. M., Zecchina, A., Leofanti, G., and Petrini, G., *Stud. Surf. Sci. Catal.* **48**, 133 (1989).
18. Aizawa, M., Nosaker, Y., and Fujii, N., *J. Non. Crys. Solids* **128**, 77 (1991).
19. Keshavaraja, A., Ramaswamy, V., Soni, H. S., Ramaswamy, A. V., and Ratnasamy, P., *J. Catal.* **157**, 501 (1995).
20. Neumann, R., Chava, M., and Levin, M., *J. Chem. Soc. Chem. Commun.*, 1685 (1993).
21. Deo, G., Turek, A. M., Wachs, I. E., Huybrechts, D. R. C., and Jacobs, P. A., *Zeolites* **13**, 365 (1993).
22. Liu, Z., and Davis, R. J., *J. Phys. Chem.* **98**, 1253 (1994).
23. Wu, P., Komatsu, T., and Yashima, T., *J. Phys. Chem.* **100**, 10316 (1996).
24. Bartok, M., and Lang, K. L., *in* "Small Ring Heterocycles" (A. Hassner, Ed.), Part 3, p. 71. Wiley, New York, 1985.
25. Tanev, P. T., Chibwe, M., and Pinnavia, T. J., *Nature* **368**, 321 (1994).
26. Sheldon, R. A., and van Doorn, J. A., *J. Catal.* **31**, 427 (1973).
27. Giamello, E., Rumori, P., Geobaldo, F., Fubini, B., and Paganini, M. C., *Appl. Magn. Reson.* **10**, 173 (1996).
28. Shvets, V. A., and Kazanski, V. B., *J. Catal.* **25**, 123 (1970).
29. Hutter, R., Mallat, T., and Baiker, A., *J. Catal.* **153**, 177 (1995).
30. Corma, A., Camblor, M. A., Esteve, P., Martinez, A., and Perez-Pariente, J., *J. Catal.* **145**, 151 (1994).
31. Jorda, E., personal communication.
32. Fusi, A., Ugo, R., and Zanderighi, G. M., *J. Catal.* **34**, 175 (1974).
33. Auroux, A., Gervasini, A., Jorda, E., and Tuel, A., *in* "Zeolites and Related Microporous Materials: State of the Art 1994" (J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Eds.), Garmisch-Partenkirschen 1994, *Stud. Surf. Sci. Catal.* **84**, 653 (1994).
34. Bellussi, G., Carati, A., Clerici, M. G., and Maddinelli, G., *J. Catal.* **133**, 220 (1992).
35. Clerici, M. G., and Ingallina, P., *J. Catal.* **140**, 71 (1993).
36. Sato, T., Dakka, J., and Sheldon, R. A., "Zeolites Related Microporous Materials," *Stud. Surf. Sci. Catal.* **84**, 1853 (1994).