Tetraneopentyltitanium Derived Silica Supported Complexes

Part 2. Influence of the Hydrophobic Character of Silica on the Catalytic Properties

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Titanium containing catalysts were synthesized using hydrophobic silicas as support; they were tested for the epoxidation of cyclohexene with aqueous H_2O_2. It is shown that, despite the low number of surface silanols and the presence of surface hydrophobic methylsilane entities, tetraneopentyltitanium $TiNp_4$ reacts with the surface silanols, with formation of the complex $\equiv SiOTiNp_3$, **1**, chemically bonded to the surface. Hydrolysis of this surface complex **1** leads to the formation of $\equiv SiOTi(OH)_3$; contrary to what was observed with hydrophilic silica supports, the anchoring bond $\equiv SiO-Ti$ is maintained. Calcination of **1** decomposes the silica surface modifying methyl groups, $SiMe_3$ to $Si(OH)_3$; the chemical environment of Ti is then no longer hydrophobic in character; titanium remains very well dispersed. The two types of solids catalyze the epoxidation of cyclohexene with aqueous H_2O_2, with an epoxidation yield and selectivity significantly higher than those obtained with the analogs supported on hydrophilic silicas. A zirconium containing catalyst synthesized in a similar manner from $ZrNp_4$ and a hydrophobic silica shows also enhanced selectivity or epoxide formation; interestingly, the rate of the successive decomposition of the epoxide is lowered. These properties are explained by the achievement of a better isolation of the Ti and Zr active sites on the hydrophobic silicas. © 1998 Academic Press

INTRODUCTION

We have previously shown that the complex tetraneopentyltitanium presents some advantages over other titanium complexes such as $Ti(OR)_4$, $TiCl_4$ for example, as a precursor of active sites for the catalytic epoxidation of olefins (1). Thus, when this alkyl complex is reacted with a partially dehydroxylated silica, isolated mononuclear titanium surface complexes $(\equiv SiO)TiNp_3$, $Np = neopentyl$, are formed; contrary to what occurs when alkoxytitanium complexes are taken as precursors, in our case no complex association is possible at this stage of the synthesis. These silica grafted neopentyltitanium complexes are transformed

by mild hydrolysis or calcination into easy-to-handle catalysts, active for the epoxidation of cyclohexene. As is generally observed for most Ti supported catalysts, epoxide selectivity close to 100% is achieved when using an organic hydroperoxide such as ^tBuOOH. These solids are active and stable when aqueous hydrogen peroxide is used as oxidant, although their selectivity and oxidation yield are only moderate; formation of products of formal allylic oxidation of cyclohexene and partial decomposition of H_2O_2 are observed (1). Two structural parameters are generally considered of prime importance for this type of catalysts, because they are suspected to be responsible for the high selectivities of catalysts such as TS-1: titanium site isolation and/or a hydrophobic environment (2). For the reaction of epoxidation of propene, it was shown earlier that postsynthesis silylation of some Ti/SiO_2 catalysts improved considerably the selectivity for the epoxide (3). This treatment was supposed to remove the surface Bronsted acid sites, the proposed catalysts of the epoxide ring opening reaction. In the present work, our objective is to synthesize in an hydrophobic environment isolated titanium sites which can be used with aqueous H_2O_2; therefore we have performed the reaction of the titanium precursor complex directly with a presilylated silica.

EXPERIMENTAL PART

The reagents and techniques used are those previously described (1). Three commercially available hydrophobic silicas (from Degussa) were used: two of them are silylated Aerosil silicas, i.e. R812 (noted **SA1**) and R974 (noted **SA2**); the third is a precipitated silica, Sipernat D17 (noted **SP**), for which the precise nature of the modification is not given. Their specific surface areas, determined by the BET method, are 260, 170, and 100 m^2/g, respectively. The silylation procedures use either hexamethyldisilazane, $(Me_3Si)_2NH$ (**SA1**), or dichlorodimethylsilane, Cl_2SiMe_2 (**SA2**), as reactants and result in the partial substitution

of the silanol surface groups by either $\equiv$SiOSiMe$_3$ or ($\equiv$SiO)$_2$SiMe$_2$ entities (4). In this latter case, the main surface entities are, according to solid state ^{29}Si NMR studies (4), those represented as
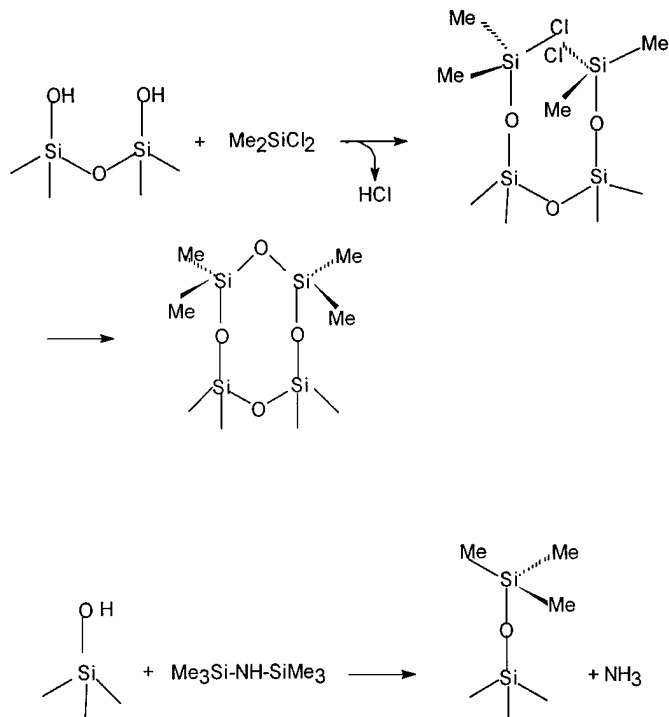
The degree of hydrophobicity is correlated to the number of residual surface silanol groups; it increases when this number decreases. The decreasing order of hydrophobicity of the three silicas used in this study is:

$$SP \gg SA1 > SA2.$$

The reaction of TiNp$_4$ with these silicas was performed under the conditions given for the hydrophilic silicas used in Ref. (1), but lower amounts of complex were engaged with these solids. The catalytic solids were obtained either by room temperature controlled hydrolysis (type **H**) or calcination under O$_2$ at 673 K (type **C**) of the precursor surface complex ($\equiv$SiO)TiNp$_3$ (1).

The catalytic tests of epoxidation of cyclohexene were performed under the following conditions: the solid (0.400 g) was taken in diglyme (20 ml) in a round bottomed flask (50 ml) fitted with a condenser and a septum. Cyclohexene (5 ml, 50 mmol) was added by syringe and the contents of the flask were heated to reflux (388 K) with stirring. Aqueous hydrogen peroxide (70% wt/wt, 0.266 g, 5 mmol) in diglyme (10 ml) was added over a period of ca 15 min by syringe. The reaction was stopped after 2 h 30 min, after the end of the addition of H$_2$O$_2$. The solution was analyzed by GPC for the products and the H$_2$O$_2$ content was titrated against Na$_2$S$_2$O$_3 \cdot$5H$_2$O (5). These conditions

are those used previously in order to facilitate comparison of the different solids (1). No optimization was attempted, although parameters such as solvent and temperature for example are known to be essential.

The catalytic properties of the different solids for the reaction of epoxidation of cyclohexene with H$_2$O$_2$ are expressed as:

$$\%\text{conv.} = \{[H_2O_2]^o - [H_2O_2]^f\} * 100/[H_2O_2]^o$$
$$\%\text{yield} = [P_i] * 100/[H_2O_2]^o.$$

The difference between the H$_2$O$_2$ conversion and the sum of the yields of the four analyzed products, i.e. cyclohexene oxide, 1,2-cyclohexanediol, 2-cyclohexen-1-ol, and -1-one gives an idea of the productive oxidation; we assume implicitly that this difference corresponds to the nonproductive degradation of H$_2$O$_2$ into H$_2$O and O$_2$.

RESULTS

Reactivity of TiNp$_4$ with Hydrophobic Silicas

All silicas used in this study are modified with organosilanes to a certain extent; we have thus first checked if, despite the presence of surface methylsilanes, a reaction occurs between the residual silanol groups and the tetraneopentyl complex.

When a solution of TiNp$_4$ in n-hexane is put into contact with any among the three hydrophobic silicas, preevacuated at 753 K (10^{-4} Torr, 16 h), the initially yellow solution does not entirely decolorize as was observed with hydrophilic silicas (1). That only a small fraction of the amount of TiNp$_4$ introduced reacts chemically with the silica surface is further evidenced by the formation of a yellow powder on the walls of the reactor when the solid is evacuated at 333 K; excess TiNp$_4$ sublimes easily. Elemental analysis of the different solids, after hydrolysis or calcination, reveals that only a small quantity of titanium can be deposited by this procedure (Table 1).

In situ IR spectroscopic studies further confirm that a true chemical reaction has occurred. Thus, when TiNp$_4$ is sublimed on a disk of silica **SA1**, dehydroxylated at 753 K,

TABLE 1

Titanium Content of the Solids

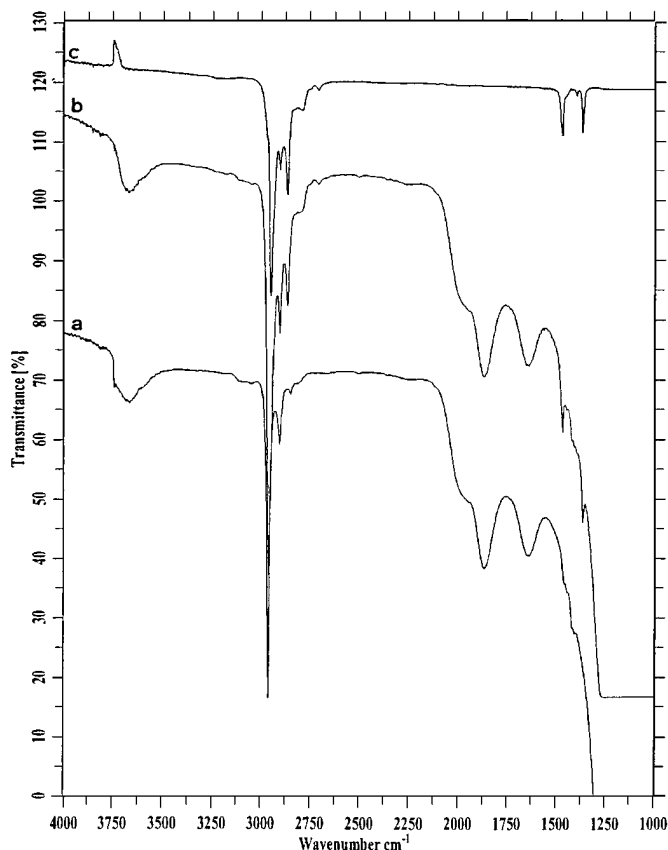| Silica	Postgrafting treatment	Ti$_{intro.}$ (wt%)	Ti$_{anal}$ (wt%)
SP	**H**	0.36	0.33
	C	0.36	0.19
SA1	**H**	0.5	0.27
	C	0.5	0.3
SA2	**H**	1.3	0.83

Note. **H**: hydrolysis; **C**: calcination.

FIG. 1. Infrared spectra in the 4000–1000 cm^{-1} region of (a) silica **SA1**, evacuated at 753 K (10^{-4} Torr, 16 h); (b) (a), after sublimation of TiNp$_4$, followed by evacuation at 333 K (2 h, 10^{-4} Torr); (c) difference spectrum (b)–(a).

the sharp weak shoulder at 3746 cm^{-1}, attributed to isolated surface silanol groups, disappears but the broad band, corresponding to hydrogen bonded silanols, is not affected by the reaction (Fig. 1). Simultaneously, the intensity of the ν(CH$_3$) bands at 2965 and 2907 cm^{-1} increases and bands at 2867, 1465, and 1364 cm^{-1} attributed to ν(CH$_2$) and δ(CH$_2$) vibrations appear (Fig. 1c), indicating the presence on the surface of neopentyl ligands (6, 7). These observations, i.e. simultaneous consumption of hydroxyl groups and appearance of neopentyl groups, are strong evidence for the onset of the reaction:

$$\equiv\text{SiOH} + \text{TiNp}_4 \rightarrow \equiv\text{SiOTiNp}_3 + \text{NpH}. \qquad [1]$$

1
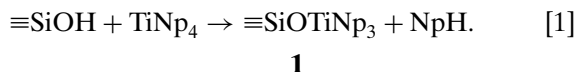
We assume here that the stoichiometry of the surface reaction is that represented in Eq. [1], by analogy with what was demonstrated previously on the hydrophilic silica **D** (1). The low density of surface silanols in the present case should indeed favor the anchoring of the titanium complex *via* only one $\equiv$SiO–Ti bond.

In conclusion, despite the low number of available silanol surface groups, it is possible to chemically graft TiNp$_4$ on

the surface of silica **SA1**. We have checked that the same reaction takes place on the surface of silica **SA2** under the same experimental conditions. We were not able to follow the reaction on silica **SP** by IR spectroscopy; our attempts to press this silica into a transparent disk were not successful.

Catalytic Properties of the Titanium-Based Catalysts

Influence of the nature of the support. The catalytic properties of three Ti containing solids prepared by hydrolysis of the tris(neopentyl)titanium complex **1** anchored to the three hydrophobic silicas, i.e. **H** type catalysts, were tested. We have first followed the evolution with time of the composition of the reaction solution during the first 2 h following the end of the introduction period of H$_2$O$_2$. Figure 2 shows the results of this study in the case of Ti/**SA1**, **H** type. Clearly no successive reactions occur after 0.5 h approximately; this behavior is very similar to that observed with hydrophilic silica **D** as support (1). It is particularly worthwhile to mention here that no epoxide ring opening by hydrolysis occurs during this period of time as no increase of the diol concentration is observed.

The catalytic properties of the three **H**-type solids, differing by the nature of the silica support, were compared with those of Ti supported on the hydrophilic silica **D** (results from Ref. (1)). At near complete conversion of H$_2$O$_2$ dramatic differences in the selectivities are observed (Table 2). Thus, with Ti/silica **SP** (Table 2, entry 5), very low selectivities for the epoxidation of cyclohexene are obtained, significant amounts of allylic oxidation products are formed and the overall oxidation yield is poor. Solid Ti/**SA2** shows a global epoxidation yield very similar to that observed with Ti/silica **D**, but the epoxide/diol ratio is much higher (Table 2, entries 3, 6). Solid Ti/**SA1** is the best among all tested catalysts; it has the highest epoxide yield and highest
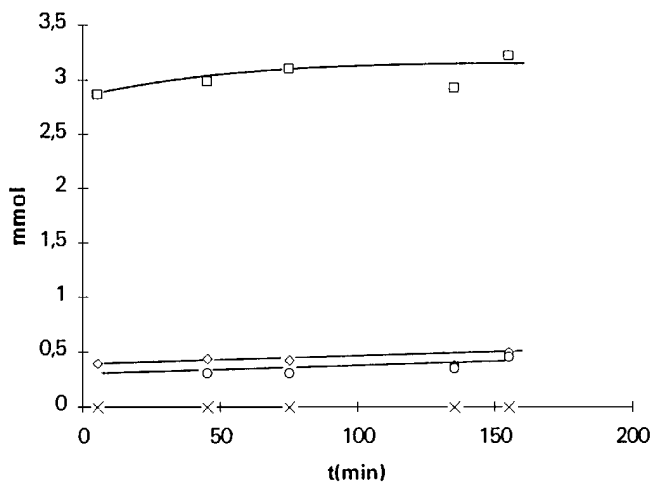

FIG. 2. Catalytic properties of Ti/**SA1**, **H** type: evolution with time of the amounts of ($\square$), cyclohexene oxide; ($\diamond$), cyclohexane-1,2-diol; ($\bigcirc$), 2-cyclohexen-1-ol; ($\times$), 2-cyclohexen-1-one. $m_{\text{cata}} =$, 0,406 g; H$_2$O$_2$, 4.99 mmol; cyclohexene, 5 ml.

TABLE 2

Catalytic Properties of Ti/Silica and Blank Tests

Entry	Solid	m(cata)	%Ti	Run	%conv.[a]	%epoxide	%diol	Cyclohexen-1-ol	%cyclohexen-1-one	$\sum$yield
								Yield		
1	SA1-H	0.406	0.27	1	96	64	10	9	0	83
2				2	94	56	6	12	3	77
3	SA2-H	0.400	0.83	1	96	47	13	7	2	69
4				2	95	48	10	10	3	70
5	SP-H	0.407	0.33	1	90	20	7	18	6	51
6	TiH-D	0.403	1.0	1	95	37	21	4	0	62[b]
7	SA1-C	0.407	0.30	1	93	63	15	8	0	86
8				2	95	70	9	14	3	96
9	SP-C	0.399	0.19	1	93	36	0	20	3	59
11	silica-SA1	0.401	0	1	21	8	0	6	6	20
12	silica-SP	0.403	0	1	92	5	0	19	5	29
13	silica-D	0.404	0	1	35	10	0	6	4	20[b]
14	none	0	0	1	15	6	0	6	5	15[b]

[a] H_2O_2 conversion.

[b] Taken from Ref. (1). Exp. cond. T = 388 K, 30 ml diglyme, 50 mmol cyclohexene, 5 mmol H_2O_2, t_R = 2 h 30 min.

epoxide/diol ratio. The overall oxidation yield is well above that observed with the other solids (Table 2, entry 1).

The differences in the catalytic properties of the three solids can clearly not be simply and only correlated to the degree of hydrophobicity of the different silica supports. Indeed, the most hydrophobic silica, **SP**, shows the poorest epoxidation selectivity. In order to reach a better understanding of these observations, we have first determined the catalytic behavior, under the same reaction conditions, of two of the supports, without introduced Ti; we have tested the worst support, **SP**, and the best one, **SA1** (Table 2, entries 11, 12). Silica **SP** activates efficiently H_2O_2, but is nonselective for the formation of cyclohexen oxide. The total oxidation yield is very low, suggesting that **SP** catalyzes essentially the decomposition of H_2O_2. The presence of nonnegligible amounts of Fe (0.03% as Fe_2O_3) in this solid might be at the origin of these properties (2b). The low activity and selectivity for epoxidation of pure silica **SA1** compare well with those observed in the homogeneous phase reaction without the solid. This strongly suggests that **SA1** is inactive. The comparison between the behavior of silica **SA1** and **D**, on one hand, and the homogeneous noncatalyzed system, on the other hand, suggests that the surface silanols may intervene essentially in the nonproductive decomposition of H_2O_2 into H_2O and O_2. These groups are present in very different concentrations on the surface of the two silicas (0.44 and 2.5 OH/nm^2 respectively for **SA1** and **D** (4). It is essential to notice that none of the silicas tested here catalyzes the hydrolysis of the epoxide ring, suggesting that the formation of cyclohexane-1,2-diol is catalyzed by Ti centers and not by the weakly acidic Bronsted sites of silica.

Influence of the method of preparation of the catalysts. We have synthesized the active entities using the two

methods described previously (1), i.e. hydrolysis (**H**-type catalysts) or calcination (**C**-type catalysts) of the precursor silica-anchored $\equiv$SiOTiNp$_3$ complex **1**. As can be seen in the case of Ti/**SA1**, the method of preparation has no significant effect on the catalytic properties; at full conversion of H_2O_2, similar product yields and similar total oxidation yields are obtained (Table 2, entries 1, 7). These properties are not significantly different with the recycled solids (Table 2, entries 2, 8).

Influence of oxidant concentration and olefin/oxidant ratio on the catalytic properties of Ti/SA1. The dependence of the catalytic properties on the rate of addition of H_2O_2 is clearly shown on Fig. 3, with Ti/**SA1**, **C** type; drastically
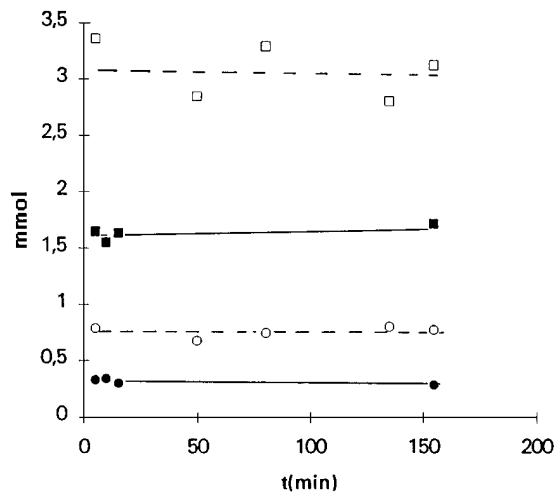

FIG. 3. Influence of the mode of oxidant addition on the catalytic properties of Ti/**SA1** (**C** type): variation of the amount of epoxide (□) and diol (○) with time (t = 0 at the end of the period of introduction of H_2O_2). Open symbols, H_2O_2 added slowly; black symbols, H_2O_2 added at once.
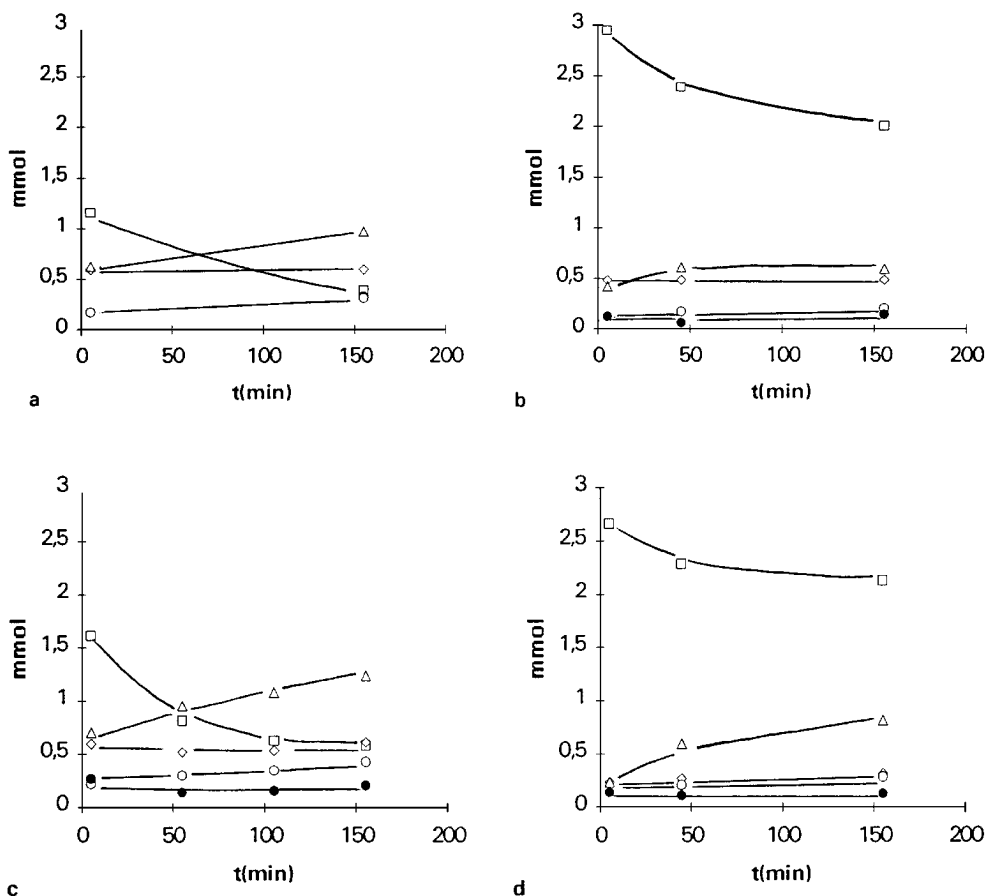
FIG. 4. Catalytic properties of Zr based catalysts (**H** type) for the epoxidation of cyclohexene: (a) Zr/silica **D**; (b) Zr/**SA1**; (c) (a) recycled; (d) (b) recycled. Evolution of the composition of the reaction solution with time. □, cyclohexen oxide; ◇, cyclohexane-1,2-diol; ○, 2-cyclohexen-1-ol; ●, 2-cyclohexen-1-one; △, unknown product.

higher epoxidation yields are obtained for a slow addition of the oxidant. With a ratio [cyclohexene]/[H_2O_2] close to 1 and the oxidant added at once, the epoxide yield becomes as low as 11% and the decomposition of H_2O_2 is favored. This shows that an instantaneous low ratio [H_2O_2]/[catalyst], a low H_2O_2 concentration, and a high ratio [olefin]/[H_2O_2] favor the selectivity for the epoxide. These observations are in close agreement with reported data on TS-1 for example (2b).

Catalytic Properties of Zirconium Containing Catalysts

We have synthesized the zirconium-containing catalyst, analog to Ti/**SA1**, **H** type. Its catalytic properties are compared with the previously reported Zr/silica **D** for the first run and a second one (Fig. 4). The most interesting result is the sharp increase of the "initial" selectivity for the formation of cyclohexene oxide with the replacement of the hydrophilic silica by a hydrophobic one. Simultaneously, the ratio epoxide/diol is higher and the consumption of cyclohexene oxide by a successive reaction (1) is slowed down. These enhanced properties are maintained with the

recycled solid (Figs. 4c, d). These results parallel closely those obtained with titanium.

Characterization of the Titanium-Containing Catalysts

In order to get some insight into the proximate environment of the Ti sites, we have tried to characterize, on one hand, the surface of silica **SA1**, at least as far as silanol groups are concerned, and on the other hand the environment and coordination sphere of Ti.

The silica surface. An *in situ* infrared spectroscopic study of the process of thermal dehydroxylation of silica **SA1** gives some indications on the surface state of this modified silica. It is compared to the behavior of the hydrophilic silica **D** for which this process is well known (8). After evacuation of the solids at ambient temperature, two main features are observed (Fig. 5). First, the overall intensity of the OH vibrational bands between 3750 and 3300 cm^{-1} is much lower on **SA1** than on **D**, the intensity of the SiOSi skeletal vibrations around 2100–1800 cm^{-1} being considered as constant. This is in agreement with the consumption of surface silanol groups by the reaction with methylorganosilanes,
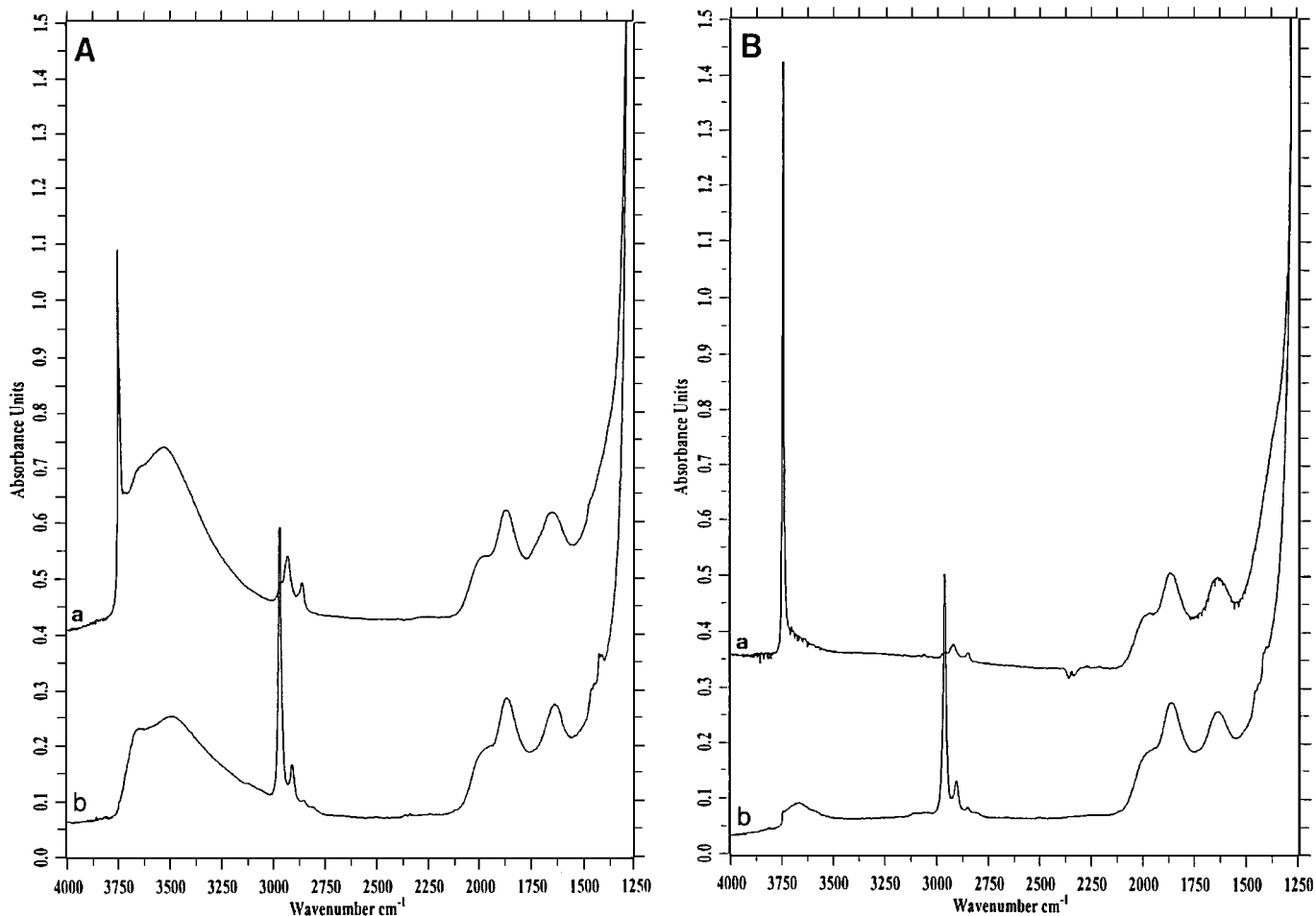
FIG. 5. Infrared spectra in the 4000–1250 cm^{-1} region of: (a) silica **D**; (b) silica **SA1** after evacuation at (**A**) 298 K and (**B**) 753 K.

a reaction confirmed by the presence of vibrational bands at 2965 and 2907 cm^{-1}, assigned to $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$, respectively. Second, no isolated silanol groups can be detected on **SA1** (absence of a band at 3745 cm^{-1}), while on silica **D** their number is large; hydrogen bonded silanol groups and molecularly adsorbed water, characterized by bands at 3650 and 3500 cm^{-1} (8), are present on both solids, showing clearly that some silanol groups are left on the surface of **SA1**. When increasing the temperature to 753 K, a very small number of isolated silanol groups appear on **SA1**, evidenced by a weak sharp shoulder at 3745 cm^{-1}; simultaneously on silica **D**, only isolated silanol groups are left. In both cases, the very weak band at ca 3650 cm^{-1}, corresponds to hydrogen bonded silanols, not accessible to dehydroxylation and, thus, very often considered as occluded silanol groups (8). Increasing the temperature of evacuation from 298 K to 753 K raises the number of isolated silanol groups considerably, a phenomenon, where hydrogen bonded groups condense and leave isolated silanol groups.
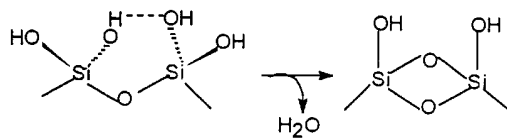
Such an intensity increase is not observed on silica **SA1**, suggesting that initially the number of neighboring silanols is limited; the modification of the surface is rather homogeneous, in the sense that no microdomains of hydrophilic-like silica are left.

The titanium sites. The reaction of hydrolysis of ≡SiOTiNp$_3$ was followed by *in situ* IR spectroscopy (Fig. 6). When oxygen-free H$_2$O (5 Torr, 298 K) is introduced on a disk of ≡SiOTiNp$_3$ on **SA1** (Figs. 6a, b), the neopentyl ligands are immediately hydrolyzed. This reaction is evidenced by examination of the difference spectrum (Fig. 6c); the disappearance of the $\nu(CH_2)$ and $\delta(CH_3)$ vibrational bands at 2867, 1465, and 1364 cm^{-1} of the neopentyl ligands,
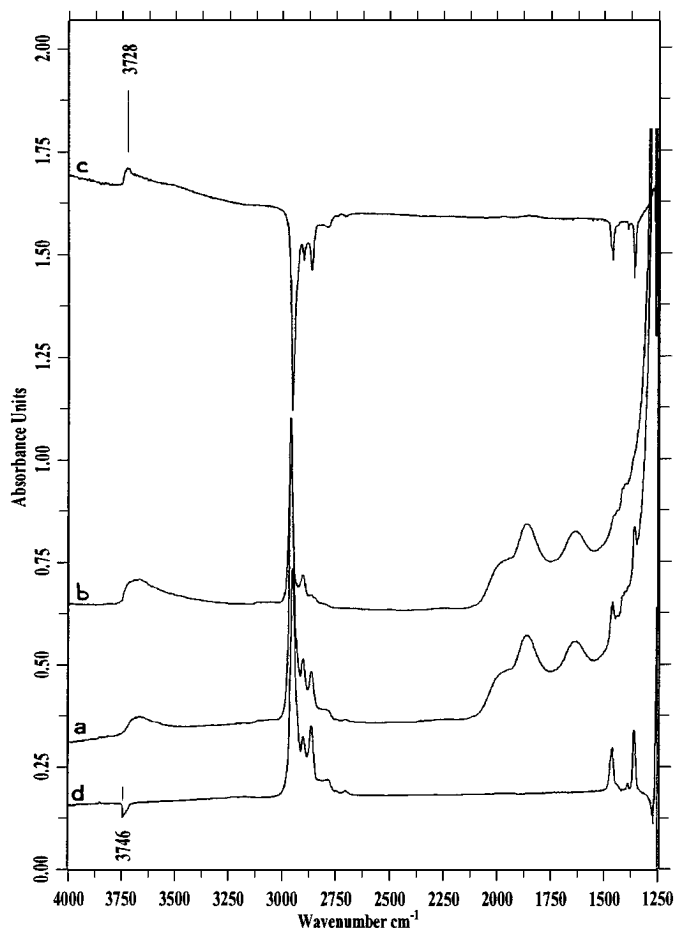
FIG. 6. Infrared spectrum in the 4000–1250 cm^{-1} region of: (a) ($\equiv$SiO)TiNp$_3$ supported on silica **SA1**; (b) (a), after treatment with H$_2$O (5 Torr, 298 K), followed by evacuation at 373 K (16 h); (c) (b)–(a); (d) same as spectrum Fig. 1c.

the concomitant appearance of new hydroxyl groups, characterized by a band at 3728 cm^{-1} and the fact that no band at 3747 cm^{-1} is restored, suggest the formation of a hydroxytitanium complex covalently bonded to the surface ($\equiv$SiO)Ti(OH)$_3$. The nonformation of silanol groups is deduced from the comparison between the spectra of Figs. 6c and d. Assignment of the 3728 cm^{-1} to ν(TiOH) vibrations is reasonable, although to our knowledge, no molecular titanium hydroxyl complex has so far been isolated <u>and</u> characterized by IR spectroscopy. Isolated TiOH groups on the surface of TiO$_2$ anatase particles are characterized by a band at 3715 cm^{-1} (9), while others report the presence of at least four bands, among which a band at 3730 cm^{-1} is assigned to such groups (10). The presence of two bands at 1710 and 1750 nm, assigned to the second mode 2ν(C–H) in CH$_3$ of the silane modifier (Fig. 7a) shows that hydrolysis **does not** (i) remove the silica modifier groups, a fact in agreement with the known stability of the Si–C bonds, and (ii) break the bond which anchors Ti to the surface of silica,

a fact which seems to be correlated to the hydrophobicity of the close environment of titanium.

The near-infrared spectrum of Ti/**SA1, C**-type (Fig. 7b) is characterized by the absence of the bands [2ν(CH$_3$)] and the presence of a strong band at 1370 nm with a broad shoulder towards lower energies, characterizing isolated and hydrogen bonded silanol groups (11). These observations attest for the complete removal of the surface methyl groups, i.e. the hydrophobic groups, under calcination. The number of silanol groups formed during the calcination procedure is much larger than the number of silanol groups present initially on the surface of **SA1**, in agreement with the occurence of reaction (2):

$$\equiv SiOSiMe_3 \xrightarrow[\Delta]{O_2} \equiv SiOSi(OH)_3. \qquad [2]$$
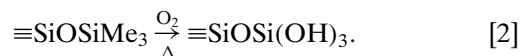
It is not possible from this experiment to conclude the fate of the SiO–Ti bond, the Ti anchoring bond; its hydrolysis would result in the formation of surface silanols (SiOH) which cannot be distinguished spectroscopically (IR, NMR) from the former ones (Eq. [2]).

Finally, the UV spectra of both solids, Ti/**SA1, H** and **C** types, respectively, show bands centered at 240 and 235 nm (Fig. 8). These bands are significantly shifted toward high energies when compared to Ti/silica **D**, **C** type, obtained by calcination of the same precursor complex (Fig. 8c, from Ref. (1); they are also less broad and, in particular, the absorption near 320 nm is very weak. These spectra are in favor of the presence on the surface of silica of titanium, essentially in an octahedral environment (13, 14) which would result from coordination of water to Ti(IV), the spectra being recorded in air.

DISCUSSION AND CONCLUSIONS

The substitution of the conventional silica, hydrophilic in character, by a silylated silica, hydrophobic in nature, as support for catalytic systems prepared by reaction of tetraneopentyltitanium TiNp$_4$ with the surface silanol groups induces a dramatic increase of the selectivity for epoxide formation and the concomitant reduction of the formation of cyclohexane-1,2-diol. The same positive effect of support substitution is revealed with the system ZrNp$_4$/silica, but, as observed with hydrophilic silicas as well, cyclohexene oxide is progressively consumed with time, but with a lower rate (1). Among the tested, commercially available, hydrophobic silicas, a silica modified via reaction with hexamethyldisilazane leads to the best catalysts. As already observed previously, the silicas must be of high purity, and in particular should not contain even trace amounts of Fe, which seem to be responsible for nonproductive activation of H$_2$O$_2$.

The results obtained demonstrate that, despite the low number of available surface silanol groups, the organometallic complex TiNp$_4$ reacts chemically, exactly as
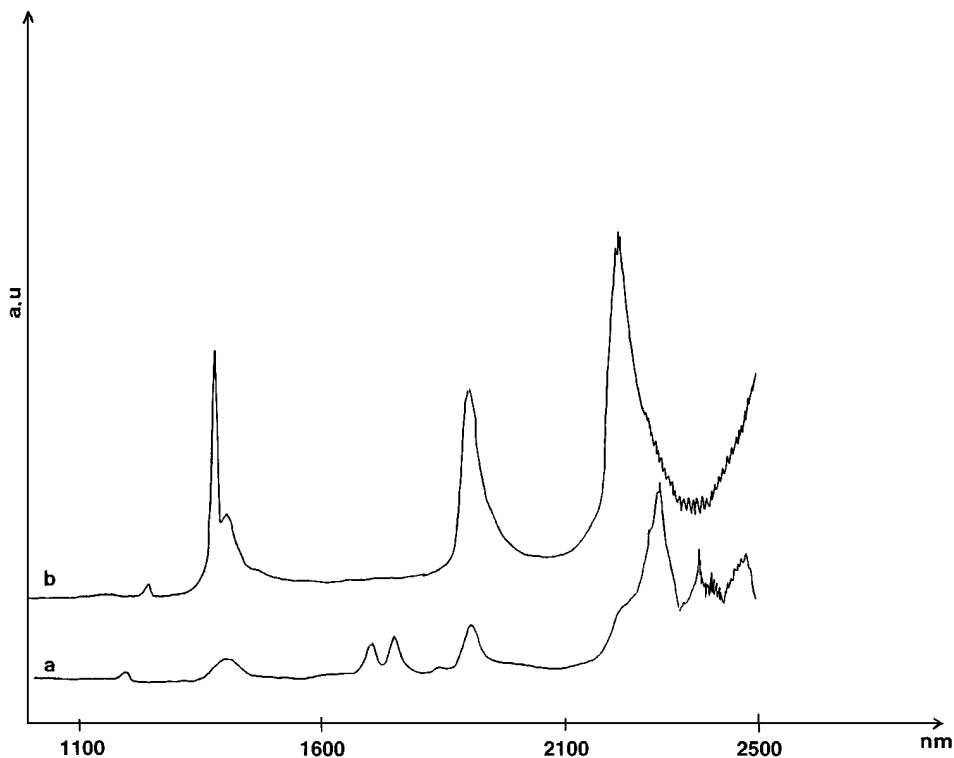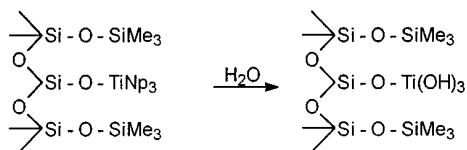
FIG. 7. Near infrared spectra in the 1000–2500 nm region of Ti/**SA1**: (a) **H** type; (b) **C** type. All spectra were recorded in air.

it does with surface silanols of a hydrophilic silica (1). The silanol sites being very well dispersed on the atomic scale, the resulting surface complexes, identified as ($\equiv$SiO)TiNp$_3$, are truly isolated and surrounded by hydrophobic methyl-silane entities.

The presence of such an hydrophobic environment in the close vicinity of Ti is certainly responsible for the high stability of the titanium-anchoring bond, $\equiv$SiO–Ti, toward water under our conditions. Hydrolysis of the trisneopentyl-surface complex results in the formation of $\equiv$SiOTi(OH)$_3$ surface complexes (as shown above).

Calcination of the precursor system ($\equiv$SiO)TiNp$_3$ removes totally the hydrophobic methylsilane species which are replaced by surface silanol groups.
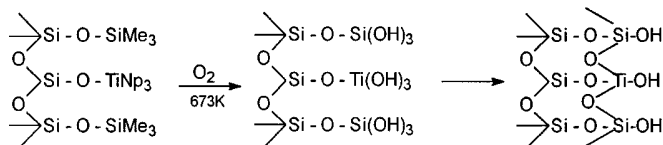
In this case, the Ti environment is no longer hydrophobic, but, provided that the Ti surface anchoring is not broken (which we have not yet fully demonstrated), at these temperatures condensation between SiOH and TiOH groups can occur, thus preserving Ti as isolated sites. On the surface one would thus have a structure approaching closely that of a Ti incorporated in a silica overlayer. The UV spectrum of this solid is shifted to higher energies when compared to the hydrolyzed sample, suggesting that Ti remains essentially well dispersed and that no TiO$_2$ particles are present.

The absence of significant differences in the catalytic properties of the solids obtained either via hydrolysis or via calcination of the precursor neopentyltitanium-supported complex suggests that the catalytically active entities must be closely related. Indeed under catalytic conditions, opening some of the Si–OTi bonds by water may occur in the case of the calcined sample, a reaction which is often proposed to explain certain properties of TS-1 (solvent effect, for example) (15); this would lead to very similar Ti sites with the two solids.

The properties of the analog Zr catalyst supported on hydrophobic silica are interesting. The "initial" selectivity for epoxide formation is very close to that of the Ti based catalysts, a property fully unexpected from the literature data, but consistent with the results that we have obtained recently (1). We are considering now different means for suppressing the successive reaction of epoxide ring
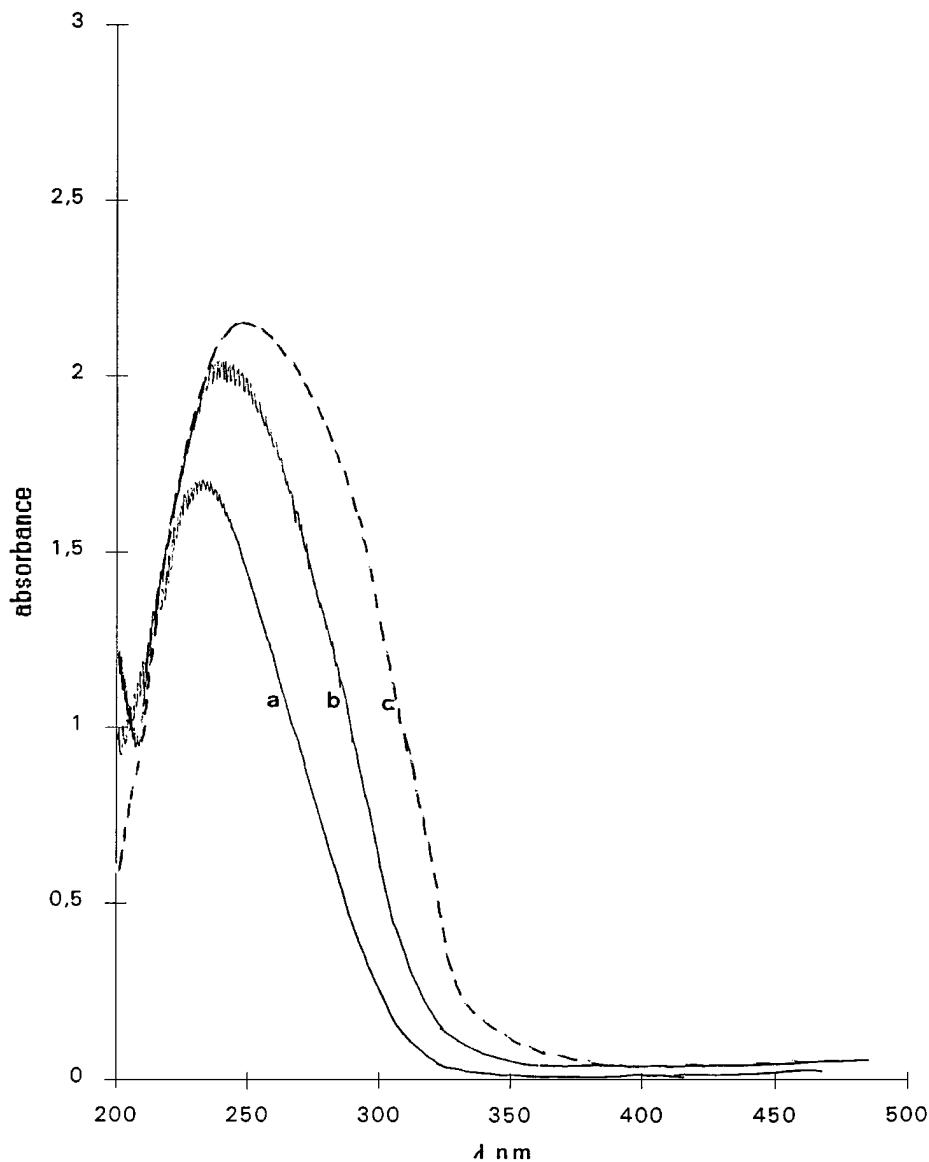
FIG. 8. UV spectra of: (a) Ti/**SA1**, **C** type; (b) Ti/**SA1**, **H** type; (c) Ti/**D**, **C** type. All spectra were recorded in air.

opening, which is apparently catalyzed by the Zr centers themselves.

In conclusion, our approach for the synthesis of Ti or Zr catalysts anchored on the surface of hydrophobic silicas leads to catalysts that are active and stable for the reaction of epoxidation of cyclohexene with aqueous H_2O_2. When taken all together, the data strongly suggest that the role of hydrophobic entities, such as methylsilanes, on the surface of silica is to allow precise control of the dispersion of titanium on the surface of the support. This factor determines the initial selectivity. This is achieved on silica **SA1**, where a subtle compromise between the number of surface silanol groups, necessary for the attachment of the metal, and their degree of isolation, is reached.

REFERENCES

1. Holmes, S. A., Quignard, F., Choplin, A., Teissier, R., and Kervennal, J., *J. Catal.* **176**, 173 (1998).
2. (a) Clerici, M. G., Bellussi, G., and Romano, U., *J. Catal.* **129**, 159 (1991).
2. (b) Notari, B., *Catal. Today* **18**, 163 (1993).
2. (c) Corma, A., Esteve, P., and Martinez, A., *J. Catal.* **161**, 11 (1996).
3. Sheldon, R. A., *J. Mol. Catal.* **7**, 107 (1980). [Wulff, H. P., U.S. Patent, 3,923,843 (1975) to Shell Oil]
4. Technical note from Degussa, 1995, n 11.
5. Jeffery, G. H., Bassett, J., Mendham, J., and Denney, R. C. (Eds.), *in* "Vogel's Textbook of Quantitative Inorganic Analysis," p. 372. Wiley, New York, 1989.
6. Silverstein, R. M., Bassler, G. C., and Morrill, T. C. (Eds.), *in* "Spectroscopic Identification of Organic Compounds," 4th ed. Wiley, New York, 1981.

7. Quignard, F., Lecuyer, C., Bougault, C., Lefebvre, F., Choplin, A., and Basset, J. M., *Inorg. Chem.* **31**, 928 (1992).

8. Hoffmann, P., and Knözinger, E., *Surf. Sci.* **188**, 181 (1987). [Morrow, B. A., Cody, I. A., and Lee, L. S. M., *J. Phys. Chem.* **80**, 2761 (1976); Boccuzzi, F., Coluccia, S., Ghiotti, G., Morterra, C., and Zecchina, A., *J. Phys. Chem.* **82**, 1298 (1978); Vansant, E. F., Van der Voort, P., and Vrancken, K. C., *Stud. Surf. Sci. Catal.* **93**, 59 (1995)]

9. Primet, M., Pichat, P., and Mathieu, M. V., *J. Phys. Chem.* **75**, 1216, (1971).

10. Munuera, G., Moreno, F., and Gonzalez, F., *in* "Proc. Int. Symp. Reactiv. Solids, 7th, Bristol, 1972," p. 681.

11. Liu, T. C., Forissier, M., Coudurier, G., and Vedrine, J., *J. Chem. Soc., Faraday Trans. 1* **85**, 1607 (1989).

12. Geobaldo, F., Bordiga, S., Zecchina, A., Giamello, E., Leofanti, G., and Petrini, G., *Catal. Lett.* **16**, 109 (1992). [Huybrechts, D. R. C., Buskens, P. L., and Jacobs, P. A., *J. Mol. Catal.* **71**, 129 (1992)]

13. Dutoit, D. C. M., Schneider, M., and Baiker, A., *J. Catal.* **153**, 165 (1995).

14. Klein, S., Thorimbert, S., and Maier, W. F., *J. Catal.* **163**, 476 (1996).

15. Bellussi, G., Carati, A., Clerici, M. G., Maddinelli, G., and Millini, R., *J. Catal.* **133**, 220 (1992).