

Tetraneopentyltitanium Derived Supported Catalysts

Part 1. Synthesis and Catalytic Properties for the Epoxidation of Cyclohexene with Aqueous Hydrogen Peroxide

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The reaction between tetraneopentyltitanium and the isolated hydroxyl groups of the surface of a silica partially dehydroxylated at 753 K leads to the formation of isolated surface complexes ($\equiv\text{SiO}$)TiNp₃, Np = neopentyl. A mild hydrolysis at 298 K or a calcination at 673 K of these silica-bonded trisneopentyl titanium complexes both lead to surface species, H and C types, catalytically active for the epoxidation of cyclohexene by organic hydroperoxides or aqueous hydrogen peroxide. The origin and, thus, the purity of the silica support, the treatment performed on the precursor anchored trisalkyl complex, and the nature of the oxidant are all important parameters. Thus, with 'BuOOH, the selectivity of these Ti/silica catalysts for the epoxide is very good (ca 95%); but with aqueous H₂O₂, the epoxide yields are only moderate and partial decomposition of the oxidant is occurring. All solids could be recycled by simple filtration and only very minor leaching of titanium into the solution is detected. The related H-type Zr catalyst, prepared from ZrNp₄ and silica, shows an unexpected activity, similar to that observed with the analog titanium catalysts. The low epoxide selectivity is correlated to the fact that the same Zr centers catalyze both the formation and the decomposition of the epoxide. The greater stability towards hydrolysis of the $\equiv\text{SiO}$ -Zr bond when compared to the $\equiv\text{SiO}$ -Ti bond may explain the catalytic properties observed, which must be at least partially correlated to a higher concentration of isolated, mononuclear Zr sites than Ti sites, the latter coexisting with nanosized particles of TiO₂. © 1998 Academic Press

INTRODUCTION

The outstanding catalytic performances of titanosilicalite (TS-1) (1–6) for a number of reactions, including the epoxidation of olefins with H₂O₂, are generally attributed to some very special structural features not encountered in other Ti-based solids, i.e. those prepared either by deposition/anchoring of a Ti complex on the surface of a silica (7–9) or by sol-gel or precipitation methods (formation of

titania-silica mixed oxides) (10–13). One of the observed differences is the presence in TS-1 of isolated Ti located in the framework (substitutional Ti) of silicalite; such sites ($\equiv\text{Si-O}$)₄Ti are suspected to be responsible for the high epoxide yield. It was indeed demonstrated that particles of TiO₂ decompose H₂O₂ by dismutation to H₂O and O₂ (14); such particles are generally present in solids with a high Ti content. Nevertheless titanosilicalites show steric limitations, so that applications to bulky substrates or oxidants are not possible. The research into either systems with larger pores, such as zeolite beta or MCM type silicalites (15–21), or amorphous and/or nonmicroporous materials is, therefore, very active (11–13, 21–24).

One of the main advantages of titanium catalysts deposited or anchored on the surface of a nonmicroporous solid is an easy access of the reactants to the active species. Nevertheless, very few examples have so far been reported using the complex anchoring approach, and none has used aqueous H₂O₂ as the oxidant (7, 9). The recently reported TiF₄/SiO₂ catalysts are interesting in this regard; they are both stable and efficient with H₂O₂ (23). Although the reasons for such behaviour are not yet fully understood, one can suspect the fluoride anion to be implied in the process of site isolation through the formation of surface SiF species which may block any migration and/or dimerization of Ti species, even under oxidizing conditions.

We wish to report here our attempts to synthesize isolated Ti sites on a silica surface which would be active for the epoxidation of olefins with aqueous H₂O₂. We have used an approach which *a priori* takes into account the following criteria for the choice of the precursor complex and the support: (i) the complex must react cleanly with the surface; e.g., only one surface complex can form and the reaction liberates no reactive products; (ii) the surface of the solid support must have functional groups sufficiently remote from each other so that no dimerisation/condensation reactions of the surface complexes can occur; (iii) the surface complex must have ligands which are easy to hydrolyse and the

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surface-anchoring bond must be maintained under the reaction conditions. Preliminary experiments using as a precursor the complex tetraeopentylzirconium and a silica, partially dehydroxylated so as to present only isolated surface silanols, lead to solids with unusual properties when compared with either homogeneous or heterogeneous Zr-based catalysts (25, 26). We have now extended this approach to titanium, known in general to show better catalytic performance than zirconium in terms of activities and selectivities for the epoxidation of olefins.

EXPERIMENTAL

Reagents

Hydrogen peroxide was provided as an aqueous solution (70% wt/wt) by Elf Atochem. *ter*-butylhydroperoxide, $t\text{-BuOOH}$, was purchased from Aldrich as a solution 3 M in isooctane. Cyclohexene (99%, from Janssen Chemicals) was used as received, except when used with $t\text{-BuOOH}$, where it was dried over molecular sieves (4A). Diglyme (99%), isooctane (99.8%, anhydrous), diethylether (99%, anhydrous), *n*-hexane (95%, anhydrous), neopentylchloride (99%), titanium tetrachloride (99.9%), cyclohexene oxide (epoxide), 1,2-cyclohexanediol, 2-cyclohexen-1-one, 2-cyclohexen-1-ol, and anhydrous hydrogen chloride (1 M in Et_2O) were all purchased from Aldrich and used as received.

Supports

Two different silicas were tested as supports of the catalysts. The Shell silica (noted **S**) is a mesoporous silica (pore diameter 15 nm), processed as small spheres; its specific surface is $350 \text{ m}^2/\text{g}$ as determined by the BET method. The silica Aerosil 200 from Degussa (noted **D**) is essentially nonporous and has a specific surface of $200 \text{ m}^2/\text{g}$. Both silicas are reported as hydrophilic.

Physical Techniques

Infrared spectra were recorded on a Brüker VECTOR 22 FT spectrometer. A Perkin-Elmer Lambda 9 spectrophotometer working in the diffuse reflectance mode with BaSO_4 as reference was used to record the UV spectra of the samples. The powder samples (ca 200 mg) were introduced between two plates, one being a quartz plate; the spectra were recorded in air.

The solution NMR spectra were recorded on a 100 MHz Brüker spectrometer.

The determination of the metal loading of the solid samples was performed by AES-ICP spectroscopy, after dissolution of silica in HF/HCl ; the *relative errors* are estimated to be 1%.

Analysis of the catalytic solutions was performed by gas chromatography, using a HP 5890 Series Chromato-

graph, fitted with a polar capillary column, BP20 (l = 25 m, 0.32 mm) and equipped with a FID detector. The experimental conditions for analysis were the following: $T_{\text{inj}} = 513 \text{ K}$, $T_{\text{det}} = 553 \text{ K}$, $T_{\text{column}} = 343 \text{ K}$ (for 2 min); then increase up to 523 K at the rate of $10 \text{ K} \cdot \text{min}^{-1}$.

Synthesis of the Catalysts

All experiments were performed under strict exclusion of air and water using standard high vacuum line equipment and break seal techniques (27).

The complex was synthesized according to a published procedure (28), purified by sublimation (333 K , 10^{-3} Torr) prior to use and characterized by ^1H NMR spectroscopy: (C_6D_6) $\delta(\text{ppm})$: 1.17 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$); 2.21 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$); lit. (28) $\delta(\text{ppm})$ 1.28 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$); 2.32 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$). Only trace amounts of tetraeopentoxytitanium were detected: ^1H NMR: C_6D_6 $\delta(\text{ppm})$ 0.99 ($-\text{OCH}_2\text{C}(\text{CH}_3)_3$); 4.06 ($-\text{OCH}_2\text{C}(\text{CH}_3)_3$); lit. (28) $\delta(\text{ppm})$ 1.12 ($-\text{OCH}_2\text{C}(\text{CH}_3)_3$); 4.17 ($-\text{OCH}_2\text{-C}(\text{CH}_3)_3$). The complex is photosensitive in solution and was thus protected from light where appropriate.

The synthesis and purification of tetraeopentylzirconium was performed according to the same procedure (28) and characterized by ^1H NMR spectroscopy: (C_6D_6) $\delta(\text{ppm})$: 1.28 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$); 1.48 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$); lit. (28) $\delta(\text{ppm})$ 1.28 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$); 1.52 ($-\text{CH}_2\text{C}(\text{CH}_3)_3$).

The experimental conditions for the reaction between TiNp_4 and silica were determined using *in situ* IR spectroscopy; they were then extrapolated for the synthesis of a larger sample of catalyst. The *in situ* IR spectroscopic studies were performed in a cell especially designed so as to allow for sublimation of the complex on the silica surface, as well as for vacuum, thermal, and/or chemical treatments, under strict exclusion of air (Fig. 1, Ref. (29)).

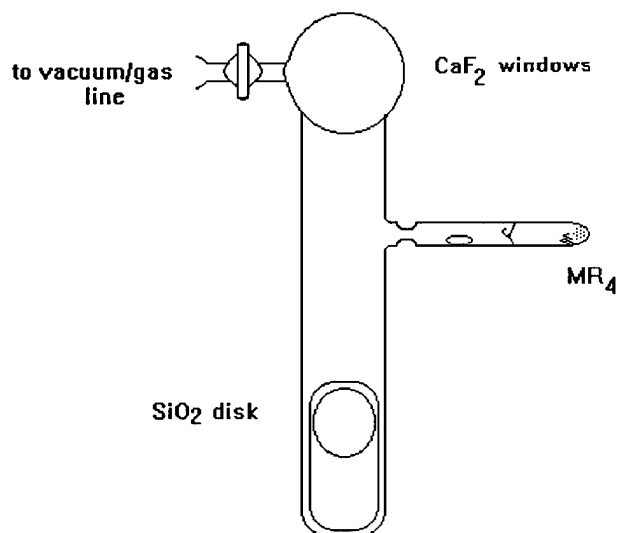
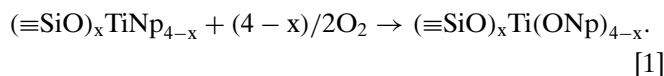


FIG. 1. Scheme of the IR cell used for the *in situ* experiments.

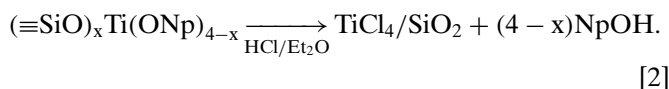
A large sample of supported titanium catalyst was prepared as follows: silica (3 g) was evacuated at 753 K (10^{-4} Torr) for 10 h. TiNp_4 (185 mg, 0.56 mmol) in hexane (10 ml) was introduced onto the surface of the silica under an atmosphere of dry argon and allowed to diffuse through the solid. The slurry was heated to ca 333 K for 15 min until the initially yellow solution is fully decolorized. The liquid was then removed *via* a cannula and the solid evacuated (10^{-2} Torr, 298 K) until a dry yellow powder was obtained, and then further evacuated (10^{-4} Torr) at 333 K for 3 h, conditions under which TiNp_4 sublimes easily. All solids were prepared so as to present a Ti content close to 1 wt% (see legends of figures for the precise values). This solid was then split under argon into two parts: one was contacted with H_2O (22 Torr, 298 K), then evacuated at 333 K (10^{-4} Torr, 1 h) (**H**-type catalyst); the second part was calcined under flowing oxygen at 673 K (**C**-type catalyst). Both samples were stored in a closed vessel under air.

Characterization of the Precursor Silica-Supported Neopentyltitanium Complex

Hydrolysis of $(\equiv\text{SiO})\text{TiNp}_3$ with water and analysis of the liberated neopentane is one of the methods to determine the number of neopentyl ligands around the titanium atom. Nevertheless, this method is not accurate because any accidental introduction of O_2 leads to the neopentoxy complex, which can only be hydrolyzed under acidic conditions. We have thus first transformed the surface neopentyltitanium complex quantitatively into the corresponding neopentoxytitanium complex under dry oxygen (400 Torr, 313 K, 4 h), using a procedure previously described (30) (Eq. [1]):



On this sample, both elemental analysis of the solid (Ti, C) and acidic hydrolysis using a 1 M solution of HCl in Et_2O were performed. The neopentanol liberated by this latter reaction (Eq. [2]) is quantitatively analyzed by GPC, using a calibration curve established, in presence of silica, with cyclohexanol as the internal standard:



This analysis was duplicated.

The synthesis of the supported zirconium catalysts is done according to the same procedure (30).

Catalytic Testing

All catalytic tests were performed using diglyme (bis(2-methoxyethyl)ether) as solvent. No optimization of the procedure was attempted; in particular, the temperature of the reaction was maintained at the temperature of the reflux of

the reaction mixture, ca 388 K, and the addition of H_2O_2 was slow. These conditions allowed for a good reproducibility of the experiments and an easy comparison with different solids previously tested in the laboratory.

Oxidation with H_2O_2 . 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. Hydrogen peroxide (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_2O_2). After decantation, 1 ml of the reaction mixture is taken off and filtered through a 13-mm teflon 0.45- μm membrane syringe filter. A 0.5-ml portion of this latter sample was used for CPV analysis after the addition of 1 μl of octan-2-ol as an internal standard. Quantitative data were deduced from the calibration curves performed with analytically pure samples of cyclohexene oxide, cyclohexane-1,2-diol, 2-cyclohexen-1-one, and 2-cyclohexen-1-ol. The H_2O_2 content was titrated against $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (31).

Oxidation with $^t\text{BuOOH}$. The apparatus is similar to the one described above. The solid (0.500 g) was treated under vacuum (10^{-4} Torr) at 373 K (1 h) before being transferred into the flask under an atmosphere of Ar and suspended in isooctane (27 ml) and cyclohexene (6 ml, 60 mmol). $^t\text{BuOOH}$ (2 ml, 6 mmol) in isooctane was added over a period of 15 min. The reaction was stopped after a period of 2 h 30 min following the addition. Unreacted $^t\text{BuOOH}$ was titrated against $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (31).

Conversions are expressed towards the oxidant; we have systematically checked that the cyclohexene conversion never exceeded significantly that corresponding to its oxidation: oligomerization can thus be excluded. Yields of the four products quantitatively analyzed by GC, i.e. cyclohexene oxide, 1,2-cyclohexanediol, 2-cyclohexen-1-one, and 2-cyclohexen-1-ol, are given, assuming the consumption of 1 mole H_2O_2 per mole product formed. The comparison of the sum of the yields of these our products and the total H_2O_2 consumption gives an idea of the importance of side reactions.

Conversion of the oxidant and yields for the products, P_i , are defined as follows:

% conv. = $\{[\text{H}_2\text{O}_2]^0 - [\text{H}_2\text{O}_2]^f\} * 100/[\text{H}_2\text{O}_2]^0$, where $[\text{H}_2\text{O}_2]^0$ and $[\text{H}_2\text{O}_2]^f$ are respectively the initial and final H_2O_2 concentration;

%yield = $[\text{P}_i] * 100/[\text{H}_2\text{O}_2]^0$.

RESULTS

Synthesis of the Catalysts

The reaction between TiNp_4 and the surface of silica was followed by *in situ* IR spectroscopy. Silica was first

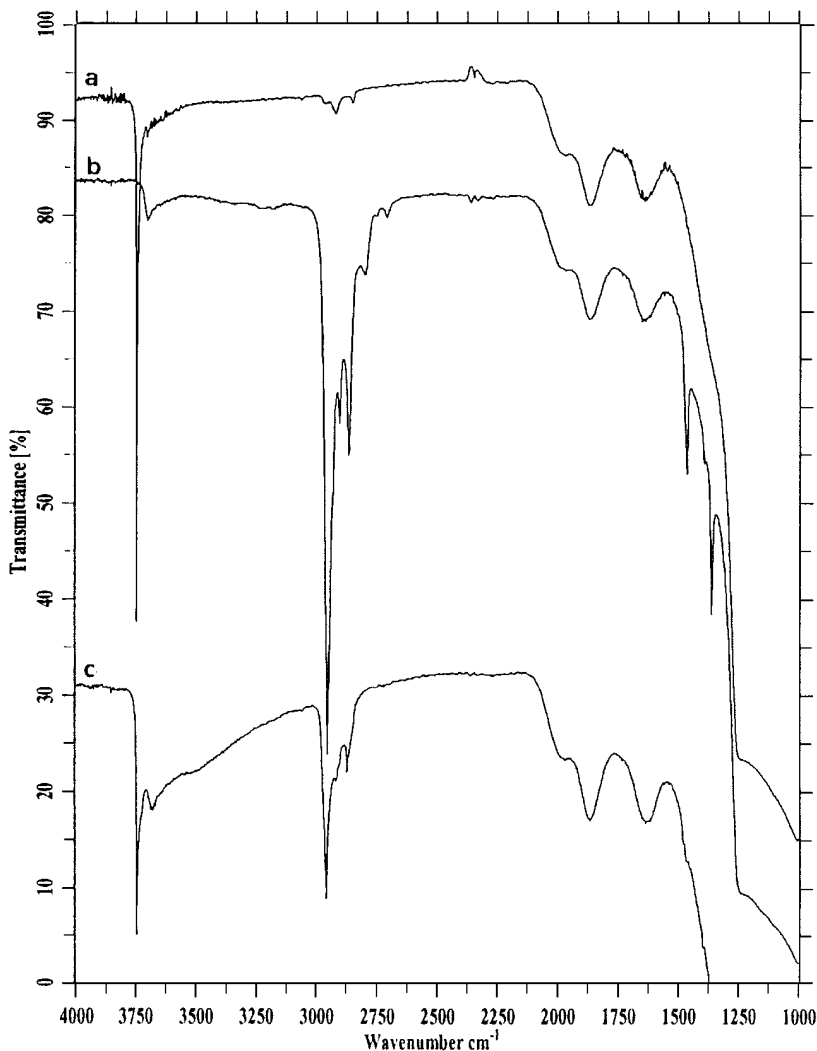


FIG. 2. Infrared spectra in the region 4000–1000 cm^{-1} of: (a) a disk of silica **D** evacuated at 753 K (16 h, 10^{-4} Torr); (b) (a) after sublimation of TiNp_4 , followed by evacuation (333 K, 10^{-4} Torr, 1 h); (c) (b) after introduction of H_2O (5 Torr, 298 K, 15 min) followed by evacuation (298 K, 10^{-4} Torr, 1 h).

evacuated at 753 K (10^{-4} Torr, 16 h); under these conditions, only isolated silanol groups, characterized by a sharp band at 3747 cm^{-1} , are present on the surface (Fig. 2a) (32). The sublimation of TiNp_4 , followed by evacuation at the same temperature, leads to the total disappearance of the $\nu(\text{SiOH})$ band at 3747 cm^{-1} and to the simultaneous appearance of new bands at 2957, 2905, 2867 cm^{-1} and 1465, 1365 cm^{-1} , assigned to $\nu(\text{C-H})$ and $\delta(\text{CH}_x)$ vibrations of the neopentyl ligands, respectively (Fig. 2b) (33). These observations are strongly in favor of the occurrence of the reaction (Eq. [3]):



The surface titanium species was further characterized by determining the number of neopentyl ligands per surface Ti atom. This study was performed on a larger sample,

synthesized by impregnation of a pretreated silica with a solution of TiNp_4 in n-hexane. Acidic hydrolysis liberates 3.0 ± 0.1 mol neopentanol/mol $[\text{Ti}]_s$; and elemental analysis (% Ti = 0.76, % C = 2.4, i.e., C/Ti = 12.6) confirms that the main surface species is $(\equiv\text{SiO})\text{TiNp}_3$ (**1**). This type of surface reaction, a partial solvolysis of an alkyl complex by surface silanols, is already well documented (34–36); in the case of ZrNp_4 and HfNp_4 , the formation of $(\equiv\text{SiO})\text{MNp}_3$ (M = Zr, Hf) as the major surface complex was unambiguously demonstrated (37, 38).

Two methods were employed for the synthesis from complex **1** of the catalytically active surface sites: hydrolysis (type **H** catalysts) and calcination (type **C** catalysts). The first method is justified by the fact that hydroxytitanium complexes are involved at some stage in most mechanisms proposed for the epoxidation by group-4-based catalysts. The second method would allow for easy regeneration of

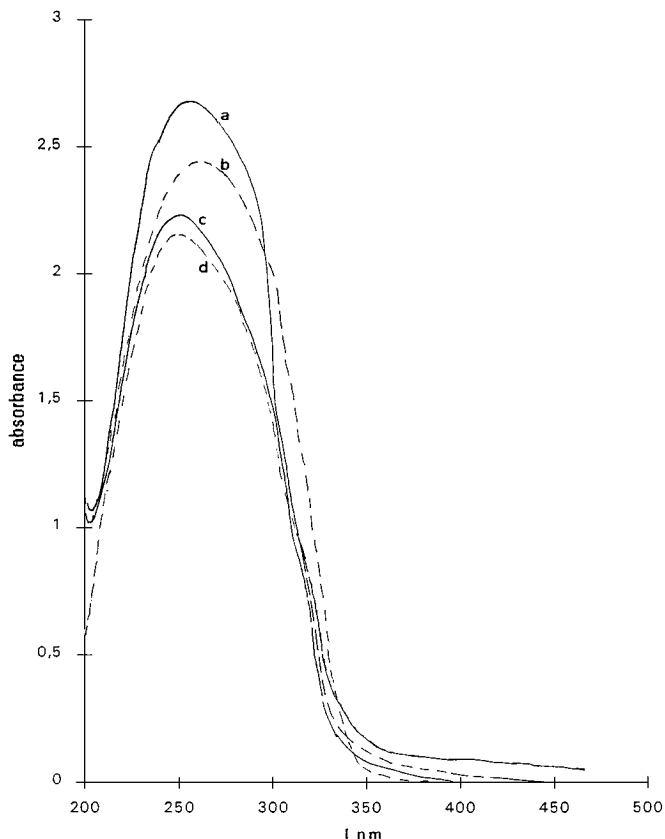
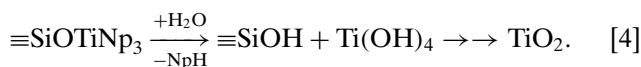


FIG. 3. Diffuse reflectance UV spectra of: (a) **Ti_H-D** (% Ti = 1.00 wt); (b) **Ti_C-D** (% Ti = 1.2 wt); (c) **Ti_H-S** (% Ti = 0.85 wt); (d) **Ti_C-S** (% Ti = 0.86 wt). All spectra were recorded in air.

the catalyst by removal of any surface carbonaceous species formed during catalysis.

The transformation of complex **1** in presence of water was followed by IR spectroscopy. The sharp intensity decrease of the $\nu(\text{C-H})$ and $\delta(\text{CH}_x)$ vibrational bands confirms the easy hydrolysis of the Ti-C bonds, but the concomitant intensity increase of the $\nu(\text{SiOH})$ band at 3747 cm^{-1} is evidence for simultaneous partial hydrolysis of the anchoring $(\equiv\text{SiO})\text{-Ti}$ bonds (Fig. 2c). Two broad bands at ca 3686 and 3500 cm^{-1} may be assigned to hydrogen bonded silanols and to water physisorbed on the surface; they are still present after evacuation at 373 K . The $\nu(\text{TiOH})$ bands, expected at $3715\text{--}3730\text{ cm}^{-1}$ (39, 40) cannot be identified; nevertheless partial formation of $\text{Ti}(\text{OH})_4$ and TiO_2 must be considered (Eq. [4]):



The UV spectra of these solids **Ti_H-D** and **Ti_H-S** present a broad band centered at $250\text{--}260\text{ nm}$ (Figs. 3a, c). This clearly shows the absence of both isolated $[\text{TiO}_4]$ or $[\text{TiO}_3(\text{OH})]$ tetrahedral units, characterized by an absorption maximum

at 212 nm (41, 42) and large particles of anatase, which show absorption edge close to 360 nm . A high energy shift of this band is characteristic for small particles ($<6\text{--}8\text{ nm}$), a phenomenon interpreted as a quantum size effect (43, 44). A band near $240\text{--}260\text{ nm}$ is generally attributed to Ti(IV) in an octahedral environment (45). The observed spectra therefore suggest a good overall dispersion of Ti on the surface of silica.

The second method was calcination of **1** under O_2 : The solids, **Ti_C-D** and **Ti_C-S**, show UV spectra centered at $250\text{--}260\text{ nm}$ (Figs. 3b, d), very similar to that of the **H**-type solids. These observations suggest that the dispersion and state of Ti on the surface is very similar for all solids, **H** type or **C** type. A slight broadening of the absorption band towards the lower energies could reflect an increase of the amount of TiO_2 nanoparticles (Fig. 3b).

Catalytic Properties

In a preliminary test, we have followed the formation of the products with time (Fig. 4). The catalyst was a type **H** Ti/silica Degussa, **Ti_H-D**. We commenced the solution analysis 5 min after the end of the period of addition of H_2O_2 . During the first hour, the conversion of H_2O_2 and the amounts of the products formed, i.e. cyclohexene oxide, 1,2-cyclohexanediol, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one increase. No significant evolution of the composition of the reaction mixture occurs afterwards, suggesting that the titanium sites present on the surface are not good catalysts for the epoxide ring hydrolysis. For the subsequent tests, we have compared the performances of the different solids at $t_{\text{R}} = 2\text{ h } 30\text{ min}$ ($t_{\text{R}} = 0$ when starting H_2O_2 addition).

We have determined the influence of the following parameters on the catalytic properties of all Ti solids synthesized as described above: (i) nature of the oxidant,

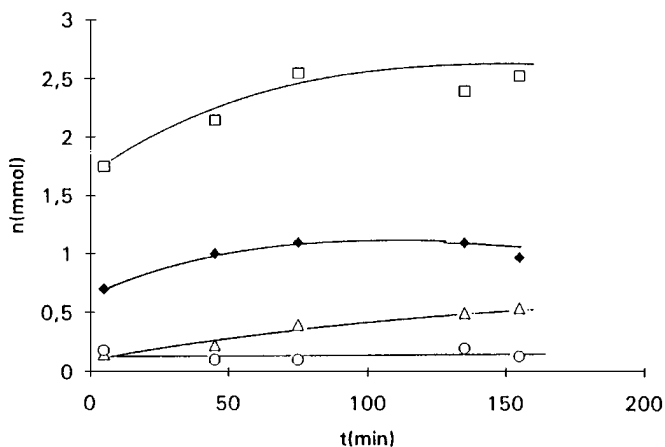


FIG. 4. Catalytic properties of **Ti_H-D** (Ti, 1 wt%) cyclohexene oxide (\square); 1,2-cyclohexanediol, (\blacklozenge); 2-cyclohexen-1-ol (\triangle); 2-cyclohexen-1-one (\circ). Exp. cond. $m_{\text{cata}} = 0.400\text{ g}$; H_2O_2 : 5.1 mmol , cyclohexene: 50 mmol , 30 ml diglyme, $T = 388\text{ K}$; $t = 0$ at the end of period of H_2O_2 introduction.

TABLE 1
Catalytic Properties of Different Titanium-Supported on Silica Solids and Blank Tests

Entry	Solid	m(cata) (g)	%Ti	Run n ^o	Oxidant ^a	% conv. ^c	% yield				∑ yield
							Epoxide	Diol	2-cyclohexen-1-ol	2-cyclohexen-1-one	
1	Ti_H-S	0.403	0.86	1	H ₂ O ₂	93	23	15	9	3	50
2				2	H ₂ O ₂	84	25	10	11	3	49
3	Ti_H-S	0.536	0.86	1	^t BuOOH ^b	97	89	2	0	0	91
4				2	^t BuOOH ^b	99	98	2	0	0	100
5	Ti_H-D	0.403	1.00	1	H ₂ O ₂	95	37	21	4	0	62
6				2	H ₂ O ₂	94	50	5	14	2	71
7	Ti_C-D	0.403	1.2	1	H ₂ O ₂	95	42	15	10	0	67
8				2	H ₂ O ₂	95	41	16	109	2	68
9	No	0	0	1	H ₂ O ₂	15	6	0	6	5	17
10	Silica S	0.398	0	1	H ₂ O ₂	70	13	0	13	4	30
11	Silica D	0.404	0	1	H ₂ O ₂	35	10	0	6	4	21
12	TiF ₄ /SiO ₂	0.401	1.0	1	H ₂ O ₂	93	70	7	5	2	84

^a 5.1 mmol H₂O₂, 50 mmol cyclohexene, 30 ml diglyme.

^b 6 mmol ^tBuOOH, 60 mmol cyclohexene, 29 ml isooctane.

^c Based on oxidant. Exp: cond: T = 388 K, t_R = 2 h 30 min.

(ii) nature of the silica, (iii) method of preparation of the catalytically active species (**Ti_H** and **Ti_C** solids). Finally, we have compared these Ti-containing solids with similar Zr-containing solids. The results are presented in Table 1.

Influence of the nature of the oxidant. An **H**-type Ti/silica Shell, **Ti_H-S**, was tested using either ^tBuOOH or H₂O₂ as oxidant. Both oxidants are totally converted in less than 2 h 30 min (Table 1, entries 1–4). With H₂O₂, the epoxide yield is low; 1,2-cyclohexanediol, of 2-cyclohexen-1-ol, and 2-cyclohexen-1-one form and the total oxidation yield, based on H₂O₂, is close to 60%. Although we did not systematically determine the amount of O₂ liberated, because of the poor reproducibility of this determination, we observed in a number of experiments the evolution of O₂ in various amounts. With ^tBuOOH, the epoxide selectivity and yield are both close to 90% (Table 1, entry 3).

In both types of experiments, the solids were engaged in a second test after filtration and careful washing of the solid with solvent. No significant differences in the catalytic properties are observed (entries 2, 4), suggesting that the active species are stable under the experimental conditions, both under protic and nonprotic media.

Influence of the nature of the silica support. Two **H**-type solids, supported on silica Degussa and silica Shell, respectively, **Ti_H-S** and **Ti_H-D**, were tested with H₂O₂ as oxidant (Table 1, entries 1, 5). With both solids, full conversion of H₂O₂ is reached after less than 2 h 30 min. A closer inspection of the data reveals that the total epoxidation yield is significantly larger with **Ti_H-D** than with **Ti_H-S**.

Both solids were engaged in a second catalytic run (entries 2, 6). Only small differences are observed with **Ti_H-S**; a slight increase of the amount of allylic oxidation prod-

ucts and a higher epoxidation yield (50%), due to reduced hydrolysis of the epoxy ring, are observed.

The elemental analysis of the reaction solution at the end of the catalytic tests (entries 2, 5) reveals the presence of traces of Ti, i.e. 0.3 and 0.6 ppm, respectively. These amounts correspond to the leaching of no more than ca 0.26% and 0.6%, respectively, of the amount of titanium initially introduced.

The differences observed for the catalytic properties when changing the support cannot reasonably be explained by differences in the morphology of the two silicas: the size of the mesopores for silica Shell is very large compared to the size of the molecules involved in the reaction. They, nevertheless, must be attributed to the supports, as shown by the following control experiments. The homogenous phase reaction, i.e. without any solid (Table 1, entry 9), is, under our conditions, very slow; only 15% H₂O₂ is converted after 2 h 30 min. The main products result from formal allylic oxidation and to a lesser extent from epoxidation. The sum of these four products accounts for all H₂O₂ converted, suggesting that no significant decomposition of H₂O₂ takes place under our experimental conditions. With the Shell silica, ca 70% of H₂O₂ is consumed, the epoxide yield is low and the total oxidation yield accounts for only ca 30% of converted H₂O₂ (Table 1, entry 10). The Degussa silica is much less active: only ca 35% of H₂O₂ is converted; epoxide and allylic oxidation products are obtained in approximately equivalent amounts and they account for ca 60% of the consumed hydrogen peroxide (Table 1, entry 11). It is worth mentioning here that we never observe the formation of cyclohexane-1,2-diol, neither in the homogeneous liquid phase nor in presence of silica alone.

These experiments show that the silica supports activate H₂O₂, essentially through its degradation into H₂O and O₂.

This latter reaction is only minor with silica **D**. The surprisingly high activity of silica **S** may be correlated to some of the impurities detected in this solid: 0.05% Ti, 0.02% Fe, and 0.02% Al (silica **D** is reported to contain less than 0.003% Fe_2O_3) or to the difference in the surface state. Whatever the precise reason, the supports may thus account, at least partially, for the moderate oxidation yields observed for the Ti based catalysts.

Influence of the method of synthesis. The catalytic properties of the solids obtained either by hydrolysis or by calcination of the silica-anchored trisneopentyltitanium complex are very similar (Table 1, entries 5–8). This is at first sight surprising because one suspected calcination to favor sintering of titanium into TiO_2 particles *a priori* more than a mild hydrolysis. But the results are in agreement with the UV data (Fig. 3).

We have compared our catalysts with a silica-supported catalyst, synthesized from TiF_4 (22) and calcined at 673 K. Clearly this solid is more efficient than ours (Table 1, entry 12).

Catalytic Properties of Zr-Based Solids

Zr-based solids are reportedly poor catalysts for the epoxidation of olefins; this is generally interpreted on the basis of its lower Lewis acidity (47). Recently, we have shown that Zr based catalysts, prepared by the method described here, are unexpectedly active (25, 26). These solids were prepared with a very low Zr content (<1.0 wt%) and, thus, a formal dispersion of the active element is very different from those used with the Ti catalysts studied here. We have now synthesized catalysts from ZrNp_4 and silica Degussa having a Zr content close to 2 wt%. The evolution with time of the amount of the different products formed on the **H**-type catalyst, **Zr_H-D**, is rather surprising (Fig. 5). Initially, epoxide (32% yield), cyclohexene-1,2-diol (12%), and an unidentified product (ca 14%) are formed. With time, the epoxide is rapidly transformed, essentially into this new product; equimolar amounts of cyclohexene oxide and H_2O_2 introduced on **Zr_H-D** leads to the fast formation of similar amounts of 1,2-cyclohexanediol and of this new product. Preliminary mass spectroscopy data suggest that this new product may be 2-methoxy-cyclohexan-1-ol, whose formation would imply a partial decomposition of diglyme.

It is essential to mention here that the formation of this latter product was never observed with any of the Ti-based catalysts. The Zr-based solids are thus as efficient as the Ti-based solids for the oxidation of cyclohexene with H_2O_2 , if one takes all together the products which result directly from epoxidation.

DISCUSSION AND CONCLUSIONS

Our approach for the synthesis of silica-supported molecularly dispersed titanium catalysts for the epoxidation of

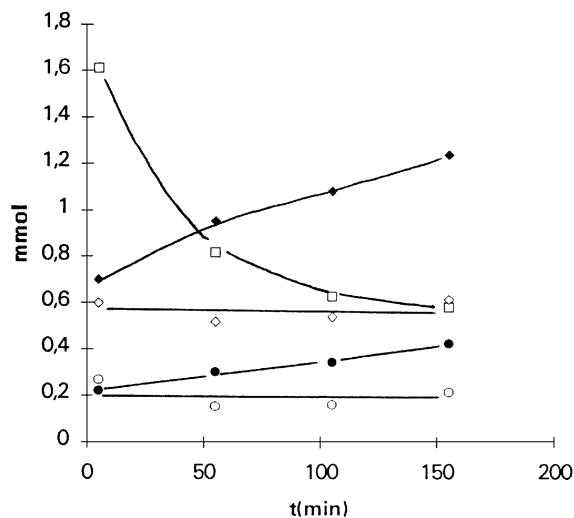


FIG. 5. Catalytic properties of **Zr_H-D** (Zr=2 wt%) cyclohexene oxide (□), 1,2-cyclohexanediol (◇), 2-cyclohexen-1-ol (●), 2-cyclohexen-1-one (○) and unknown product of epoxide degradation (◆). Exp. cond.: $m_{\text{cata}} = 0.400$ g, H_2O_2 : 5.1 mmol, cyclohexene: 50 mmol, 30 ml diglyme, $T = 388$ K, $t = 0$ at the end of H_2O_2 addition.

olefins with aqueous hydrogen peroxide includes essentially two steps. The first step is the reaction between a homoleptic alkyl, mononuclear, and hydrolyzable complex, TiNp_4 , and the surface of a silica having only isolated surface silanol groups. It successfully yields well-defined mononuclear surface complexes, $\equiv\text{SiOTiNp}_3$, covalently bonded to surface oxygen atoms via one Ti–O bond. Titanium is thus effectively atomically dispersed and no Ti–O–Ti bonds are formed. The dispersion of these complexes is probably reinforced by the use of substoichiometric amounts of TiNp_4 in this reaction (Ti < 1 wt%); an amount of 3% Ti is necessary to achieve full consumption of the surface silanol groups (48).

The second step is either a controlled hydrolysis or a calcination of these surface complexes; it leads to active and recyclable catalysts for the epoxidation of cyclohexene with either $t\text{BuOOH}$ or aqueous H_2O_2 . With the former oxidant, epoxide yields close to 95% are obtained under conditions of strict exclusion of water. With H_2O_2 , the best catalyst, **Ti_H-D**, reaches an epoxide yield of ca 50%, which is limited by significant decomposition of H_2O_2 . Among the secondary products, cyclohexane-1,2-diol is formed; it results from the epoxide ring opening hydrolysis, which is catalyzed by Ti sites. Indeed, this reaction is observed neither in the homogeneous phase reaction nor in the presence of silica alone. As evidenced by *in situ* IR experiments, water causes the partial rupture of the Ti-anchoring bonds, $\equiv\text{SiO-Ti}$, a process which favors partial aggregation of titanium into TiO_2 under the catalytic conditions. Given the low titanium content, one expects these particles to be small, a fact in agreement with the

UV-diffuse reflectance spectra observed, which show an absorption edge shifted to the high energies, compared to that of anatase. These particles would be responsible of the significant decomposition of H₂O₂. The observed epoxide selectivity of our supported Ti catalysts may then be correlated to the remaining isolated Ti sites, which are in an octahedral environment in the presence of water.

The related supported Zr catalyst shows unexpected properties. This catalyst is indeed as active for the epoxidation of cyclohexene as the related titanium one, a situation very different from that reported for the homogeneous alkoxide analogs, Ti(OBu)₄ and Zr(OPr)₄ (47). This catalyst is less selective because the same sites catalyze the epoxide ring opening reactions. The higher resistance of the anchoring bond, ≡SiO–Zr, to hydrolysis (26), which maintains the molecular dispersion of Zr on the surface, may be at the origin of this behavior.

In order to improve our titanium catalysts, it seems thus necessary to increase the concentration of isolated active sites by hindering the hydrolysis of the Ti anchoring bond. We have thus considered two possibilities. One involves the grafting of the same precursor of titanium, TiNp₄, *via* at least three bonds to the surface of silica. The requirement of a multi-attachment of Ti to the support is suggested by the mechanisms which involve hydrolysis of a titanium siloxy bond (48, 50–52) and was elegantly demonstrated recently by the study of the reactivity of two molecular titanium silasesquioxanes towards water (49). The simplest way to achieve this goal in the present case would be the use of a less dehydroxylated silica. Nevertheless, results obtained previously with the related ZrNp₄ supported on silicas evacuated at different temperatures so as to present various degrees of dehydroxylation show that a mixture of tri-, di-, but also mono-bonded surface zirconium neopentyl complexes is always obtained (34, 53). If one extrapolates these data to the titanium analogs, a partial, noneasy to control removal of Ti from the surface is highly probable in the presence of water. The creation of supplementary bonds between surface oxygen atoms and the metal was successfully achieved in the case of zirconium by reacting the supported complex ≡SiO–ZrNp₃ with hydrogen (54, 55) (Eq. [4]):



Unfortunately, preliminary attempts to perform this same reaction with ≡SiO–TiNp₃ clearly show the formation of a mixture of Ti(III) and Ti(IV) hydrides, in agreement with published data (56). The observed concomitant partial rupture of the ≡SiO–Ti bonds definitely leads us to reject this type of synthesis.

The second means for increasing the concentration of isolated Ti active sites consists in stabilizing the Ti–O anchoring bond towards hydrolysis by introducing an hydrophobic

environment in the close vicinity of the titanium center. This is developed in Part 2 of this work.

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