Mono- and Dinuclear Silica-Supported Titanium(IV) Complexes and the Effect of TiOTi Connectivity on Reactivity

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Abstract: The room-temperature reactions of excess $Ti(O^iPr)_4$ with the hydroxyl groups of a nonporous silica yield *dinuclear* surface complexes regardless of the degree of partial dehydroxylation of the silica. The surface reactions were studied by in situ IR transmission spectroscopy, ^{13}C CP/MAS NMR, GC/MS, and elemental analysis. The spontaneous stoichiometric formation of both 2-propanol and propene during grafting indicates that interaction of $Ti(O^iPr)_4$ with the silica surface induces disproportionation of alkoxide ligands with concomitant formation of Ti−O−Ti bridges. A synthetic route to *mononuclear* silica-supported Ti alkoxide complexes was developed by reaction of grafted amide complexes $(\equiv SiO)_nTi(NEt_2)_{4-n}$ ($n = 1$ or 2) with alcohols. Subsequent reactions of the mononuclear surface alkoxide complexes with $Ti(O^iPr)_4$ yield dinuclear species identical to those prepared by the direct reaction of $Ti(O^iPr)_4$ with silica. Both mono- and dinuclear supported alkoxide complexes undergo ligand-exchange reactions with *tert*-butylhydroperoxide, but only the dinuclear alkylperoxo titanium surface complexes react with cyclohexene to generate cyclohexene oxide.

Introduction

Titanium alkoxide complexes are homogeneous catalysts for esterification,[1] olefin epoxidation,[2,3] Diels−Alder, and ene reactions.[4] Oxide-supported titanium catalysts often show even higher activity for olefin epoxidation,[5,6] esterification[7] and transesterification,[8] hydroxylation of phenol,[9] oxyfunctionalization of alkanes,[10−12] Baeyer−Villiger oxidations,[13] and ammoximation of ketones.[14] The catalyst may contain Ti in the form of a Ti(IV) overlayer on the oxide support[15] or as Ti incorporated directly into the oxidic (e.g., zeolitic) framework.[16] While the silica-supported catalyst is most active for epoxidation and is used in a commercial process for propylene oxide,[17] it is highly water-sensitive. Zeolite-based catalysts such as TS-1[18] are hydrolytically stable but are less active, presumably due to restricted access of the substrate to the active site. High catalytic activity associated with low water sensitivity was recently reported for Ti grafted onto MCM-41[19] and other Ti-substituted mesoporous materials.[20,21]

Sol−gel processes for the preparation of Ti−Si mixed oxides are plagued by TiO_2 domain formation, which leads to undesirable side reactions such as peroxide disproportionation. An alternate method for preparing highly dispersed silica-supported Ti is the reaction of readily available volatile chloride and alkoxide compounds TiX_4 with surface hydroxyl groups to form chemisorbed species. The grafting reaction has been suggested to proceed by simple ligand displacement, yielding mononuclear surface species with liberation of HCl and/or ROH.[22−24] The following reactions have been proposed:

$$\equiv SiOH + TiX_4 \rightarrow (\equiv SiO)TiX_3 + HX \qquad (1)$$

$$2 \equiv SiOH + TiX_4 \rightarrow (\equiv SiO)_2TiX_2 + 2 HX \qquad (2)$$

At a loading of $Ti(O^iPr)_4$ on silica roughly corresponding to the number of surface hydroxyl groups, monolayer coverage and molecular dispersion is assumed.[25] However, UV−vis[25] and EXAFS[26] analyses of the surface complexes are not fully consistent with the reactions shown in eqs 1 and 2. Mixed ligand precursors such as $(CH_3)Ti(O^iPr)_3$ and $(N_3)_2Ti(O^iPr)_2$ have also

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been used,[7] as well as TiF_4[27] and $Ti(CH_2{}^tBu)_4$.[28] The kind of surface Ti complex obtained thus depends critically on the precursor used, and this has important implications for reactivity,[26] although the origins of such effects are not clear since the products of such grafting reactions, after calcination, are presumed to be isolated pseudotetrahedral sites.

Proposals for the mechanisms of catalysis by supported Ti abound,[9,29−31] but in the absence of accurate knowledge about the structure of the active site(s), hypotheses are difficult to test. The activity of Ti-substituted zeolites for epoxidation is correlated with Ti dispersion.[32] This finding has been widely interpreted as evidence for a tetrahedral site-isolated active site, $(\equiv SiO)_4Ti$.[9] Similarly, the greater esterification activity of the surface complex assumed to be "$\equiv SiOTi(O^iPr)_3$" compared to homogeneous $Ti(O^iPr)_4$ was attributed to the inability of the former to dimerize due to its immobility.[7] TiOTi connectivity is believed to be detrimental to catalytic activity and selectivity. In this context, it is interesting to note that the active species in the extensively studied Sharpless homogeneous catalytic epoxidation process is a dinuclear Ti tartrate complex, which is much more active than the mononuclear complex.[33] Therefore, we decided to investigate the nuclearity of the active species in supported Ti catalysts, particularly in view of the much sought-after goal of extending the reactivity of supported metal complexes to heterogeneous enantioselective catalysis.

In this paper, we report the preparation and characterization of silica-supported titanium(IV) coordination complexes. Our results suggest that supported Ti alkoxides obtained by the direct reaction of $Ti(O^iPr)_4$ with silica are *not* mononuclear, as previously supposed. We have also succeeded in preparing the mononuclear supported complexes by an indirect route, via the reactions of supported Ti amido surface complexes with alcohols. The ability to prepare well-defined surface species allows us to assess directly the influence of an important structural feature, namely the presence or absence of TiOTi, on reactivity.

Experimental Section

Preparation and Characterization of Silica-Supported Titanium Complexes. Surface complexes were prepared from two different titanium precursors. $Ti(O^iPr)_4$ (99.999%, Aldrich) was separated from its 2-propanol impurity before each experiment by trap-to-trap distillation using liquid N_2 and salt/ice baths. A similar procedure was employed to remove $HNEt_2$ from $Ti(NEt_2)_4$ (99.99%, Alfa-Aesar). Both titanium reagents were stored in glass bulbs equipped with high-vacuum stopcocks and were transferred into reaction vessels via the vapor phase using standard breakseal and high-vacuum techniques.

A nonporous pyrogenic silica (Degussa Aerosil-200, surface area 200 m^2/g) was used as the support in all experiments. A standard pretreatment procedure was followed in order to ensure reproducibility. For transmission infrared experiments, silica was either pressed at 125 kg/cm² into a self-supporting disk of diameter 1.6 cm (2−4 mg of silica/cm²) or spread in a thin film onto a 25-mm-diameter ZnSe disk (0.1−0.5 mg of silica/cm²). In all other experiments, the silica was compacted

by pressing into pellets (20−30 mg/cm²), which were then finely ground in a mortar. Infrared experiments were performed with self-supporting disks or thin films of silica in high-vacuum in situ IR cells (volume ca. 300 mL) equipped with KCl windows. Transmission spectra were recorded on a dry-air-purged Mattson Research Series FTIR equipped with a DTGS detector. For both background and sample spectra, 32 scans were recorded at a resolution of 2 cm⁻¹.

The temperature at which the silica is heated determines the density of surface hydroxyl groups. Aerosils dehydroxylated at 200 and 500 °C contain 2.6 and 1.2 OH/nm², respectively.[34] The latter materials will be referred to as silica-200 and silica-500, respectively, where the appended number indicates the temperature at which the silica was pretreated prior to its room-temperature reaction with the titanium complexes. Silica-500 was prepared by calcination in 200-Torr O_2 (Air Products, ultrapure carrier grade) at 500 °C for at least 4 h to remove hydrocarbon impurities, followed by partial dehydroxylation for at least 4 h at 500 °C in dynamic vacuum (<10⁻⁴ Torr). To prepare silica-200, the calcination step was omitted. The silica was simply heated to 200 °C under dynamic vacuum for at least 4 h. ¹⁸O-Enrichment of the surface hydroxyl groups[35] was achieved by four cycles of exposing the silica to $H_2{}^{18}O$ vapor at 400 °C, followed by dynamic vacuum at 450 °C. The degree of enrichment was estimated from the intensity ratio of the $\nu(Si^{16}O-H)$ and $\nu(Si^{18}O-H)$ bands at 3747 and 3736 cm⁻¹, respectively, in the IR transmission spectra of self-supporting disks.

For NMR experiments, supported titanium complexes were prepared in powdered form in a Schlenk tube equipped with a high-vacuum stopcock and a 5-mm Pyrex NMR tube welded onto the tube at right angles. Samples were transferred in vacuo into the NMR tube and sealed off at 30-mm lengths with a torch, to give tubes containing approximately 50 mg of sample. The ¹³C CP/MAS (cross polarization/magic angle spinning) NMR spectra, frequency 50.32 MHz, were recorded on a Bruker ASX-200 spectrometer. Spectra were collected using a 4.4-ms 90° proton pulse with a contact time of 2 ms and a relaxation delay of 2 s.

Quantitative Analysis of Grafted Products. The quantitation of chemisorbed alkoxide ligands was achieved by calcination, which converts all the chemisorbed hydrocarbons to CO_2. The sample was heated for 2 h at 750 °C in the presence of 300-Torr O_2 in a quartz in situ IR cell, and then a gas-phase spectrum was recorded. CO_2 was determined by quantitative IR spectroscopy using the absorbance (peak height) of the narrow 667-cm⁻¹ deformation mode. A linear calibration curve was obtained using $CO_{2(g)}$ in the pressure range 1−10 Torr. The quantity of CO_2 was obtained from the calibration curve, and the ratio CO_2/Ti was calculated on the basis of the Ti analysis of the sample.

At the end of each experiment (except those in which Ti/silica samples were calcined at 750 °C), chemisorbed titanium was extracted by stirring the modified silica with an appropriate volume of 3.6 M H_2SO_4 to give solutions containing ca. 0.5 mg of Ti/mL. These solutions were treated with 30% aqueous H_2O_2 (0.03 mL/mL of sample solution) to form the yellow peroxotitanium complex.[36] The absorbance at λ_{max} = 408 nm was converted to titanium concentration using a calibration curve prepared from a 1 g/L standard Ti solution (Aldrich) under the same conditions. Extraction of Ti from calcined samples is not quantitative.[36] For these samples, a portion of the material was retrieved from the reactor for Ti analysis before the rest of the sample was heated.

Quantitative Analysis of Volatile Products. The gases liberated by reactions of TiX_4, where X is NEt_2 or O^iPr, with silica and in subsequent reactions were analyzed by quantitative gas-phase IR spectroscopy (using a pressure vs absorbance calibration curve), GC, and GC/MS. All gases except CO_2 were analyzed qualitatively by GC on a HP 5710A gas chromatograph equipped with a Porasil packed column and an FID detector. Diethylamine was quantified by IR spectroscopy using a calibration curve prepared by recording the spectra of authentic samples in the pressure range 1−10 Torr. Integration of the absorbance in the region 3050−2600 cm⁻¹ was found to depend linearly on the pressure of $HNEt_2$ in this range. Upon reaction of $Ti(NEt_2)_4$ with silica, the in situ gas-phase IR spectrum was recorded in order to determine the quantity of $HNEt_2$ present. At the end of the

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Table 1. Titanium Content of Materials Prepared by Room Temperature Chemisorption of Ti(O^{i}Pr)$_4$ on Silica

silica support[a]	wt %Ti	mmol of Ti[b]	Ti/≡SiOH[c]
silica-200	3.92	0.84	0.98
	3.94	0.85	0.99
	3.86	0.82	0.95
average	3.91 ± 0.04	0.84 ± 0.02	0.97 ± 0.02
silica-500	3.90	0.81	2.02
	3.84	0.80	2.00
	3.86	0.79	1.98
average	3.87 ± 0.03	0.80 ± 0.01	2.00 ± 0.02

[a] The appended numbers refer to the temperature, in °C, at which the silica was partially dehydroxylated prior to the chemisorption reaction. [b] Normalized per gram of solid. [c] Calculated on the basis of the number of surface hydroxyl groups on silica pretreated in vacuo at each temperature: 0.40 (500 °C) and 0.86 mmol/g (200 °C).

experiment, Ti analysis was performed (vide supra), and the ratio HNEt$_2$/Ti was calculated.

In experiments in which propene and 2-propanol were generated together, the yields were determined by GC/MS. The gases were condensed into a small glass bulb of known volume (ca. 15 mL) using liquid N$_2$. The products were then analyzed on a HP 6890 GC/MS equipped with a J&W Scientific DB1 capillary column (30 m × 0.252 mm × 0.25 μm). Injections were performed in split mode (50:1) at 250 °C. The column flow rate was set at 0.5 mL of He/min, isothermal at 50 °C. Two hundred microliters of the gas mixture was injected, resulting in two well-separated peaks at 2.02 (propene) and 2.24 min (2-propanol). The total ion intensity for each peak was obtained by integration, and the pressure of each gas was calculated by comparing the integrated ion intensity to calibration curves prepared for each pure substance under the same experimental conditions. At the end of the experiment, Ti analysis was performed, and the ratios 2-propanol/Ti and propene/Ti were calculated.

Reactions of Silica-Supported Titanium Complexes. All alcohols, including D-labeled alcohols (Aldrich), and cyclohexene were vacuum-distilled and stored over activated molecular sieves. *tert*-Butylhydroperoxide (99%, anhydrous in decane, Aldrich) was dried over powdered molecular sieves. All reagents were stored in glass bulbs under vacuum and degassed by three freeze−pump−thaw cycles before use. They were introduced into the reactors via vapor phase transfer through a high-vacuum manifold equipped with a Hg diffusion pump, capable of maintaining a pressure of <10^{-4} Torr.

Volatile products (^{i}PrOH, C$_3$H$_6$, HNEt$_2$) arising from reactions of silica-supported titanium complexes were separated and quantified by GC/MS, following the procedures described above.

Results

Reaction of Ti(O^{i}Pr)$_4$ with Silica. When Ti(O^{i}Pr)$_4$ vapor reacts with silica at room temperature in a closed reactor with an initial pressure of 10^{-4} Torr, an irreversible chemisorption takes place over a period of 1 h. In an in situ IR experiment, the initially transparent silica disk becomes opaque, and volatile organic products are liberated into the gas phase. This experiment was performed using silicas which had been partially dehydroxylated at two different temperatures. Silica-200, treated at 200 °C, contains 0.86 mmol of OH/g, while silica-500 contains 0.40 mmol of OH/g.[37] After approximately 1 h of desorption of unreacted Ti(O^{i}Pr)$_4$ to a liquid N$_2$ trap, the amount of chemisorbed Ti was measured to be 3.91 ± 0.04 and 3.87 ± 0.03 wt % on silica-200 and -500, respectively. These values are reproducible (Table 1). However, the similarity of these results was unexpected, given that the number of surface hydroxyl groups on silica-200 is slightly more than double that on the same quantity of silica-500. The amount of chemisorbed Ti corresponds to 1.0 Ti/≡SiOH on silica-200 and 2.0
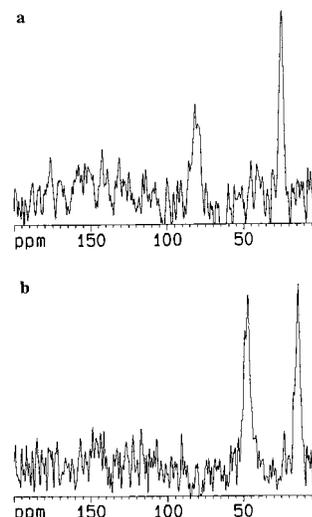
Figure 1. ^{13}C CP/MAS spectra of silica-500 treated with (a) Ti(O^{i}Pr)$_4$ to give **2** or (b) Ti(NEt$_2$)$_4$ to give **4**, followed by desorption of unreacted starting material and evacuation of volatile products. Spin rate, 4 kHz.

Ti/≡SiOH on silica-500, where ≡SiOH represents a surface hydroxyl group. In both cases, the surface coverage is 2.5 Ti/nm^2.

The solid-state ^{13}C CP/MAS spectra of both chemisorbed surface complexes derived from Ti(O^{i}Pr)$_4$ consist of two resonances at 25 and 78 ppm (Figure 1a), similar to a reported spectrum.[7] These signals are assigned to the methyl and methine carbons of chemisorbed isopropyl groups by comparison to the spectrum of Ti(O^{i}Pr)$_4$.[38] In situ infrared spectroscopy confirms that the intense ν(SiO−H) mode of silica at 3747 cm^{-1} disappears from each type of silica during the reaction, from which we infer the complete reaction of the surface hydroxyl groups. At the same time, new bands appear in the C−H stretching (3000−2800 cm^{-1}) and deformation (1500−1300 cm^{-1}) regions, assigned to 2-propoxide ligand vibrations (Figure 2a).[39−41]

The low-frequency vibrations on each type of silica include bands at 1005 (ν(C−O)), 630 (ν(Ti−OC)),[39,40,42] 951, and 857 cm^{-1} (Figure 2b). The assignment of the IR band at 951 cm^{-1} is of particular interest, since the intensity of a band in this region often correlates with catalytic activity. Therefore, reaction of Ti(O^{i}Pr)$_4$ with a silica in which the surface hydroxyl groups were labeled with ^{18}O (ca. 80% enrichment) was undertaken. The resulting spectrum contained the same band, essentially unshifted from the spectrum of Ti-modified unlabeled silica. On this basis, and since isopropyl groups are also reported to have a skeletal vibration at ca. 950 cm^{-1},[43] we assign the observed vibration to a ligand mode.

Volatile products were identified by GC and GC/MS as a mixture of 2-propanol and propene on each type of silica.[44] Absolute quantities are shown in Table 2. The 2-propanol and

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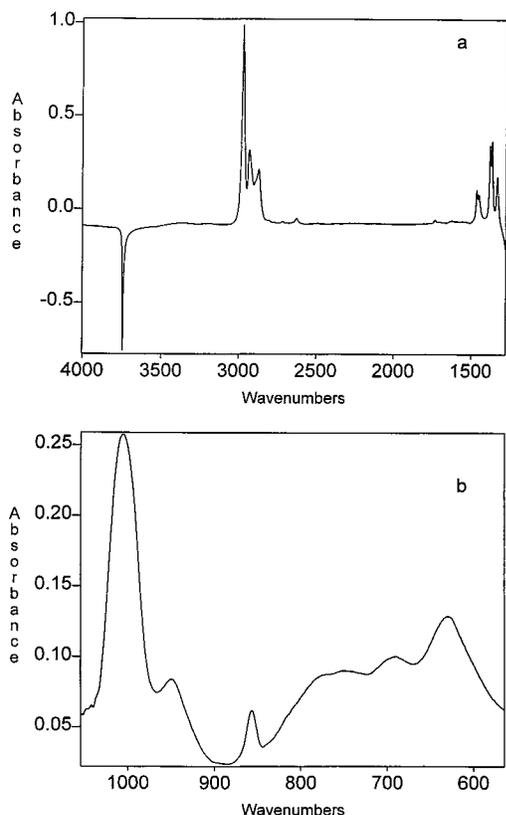
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(41) IR difference spectrum (spectrum of silica background subtracted): 2959, 2945, 2872, 2628, 1465, 1452, 1380, 1367, 1332, 1005, 951, 857, 747, 690, 630 cm^{-1}. The spectra of the supported Ti complexes on silica-200 and silica-500 are qualitatively very similar, although the ligand vibrations on silica-500 are slightly more intense.

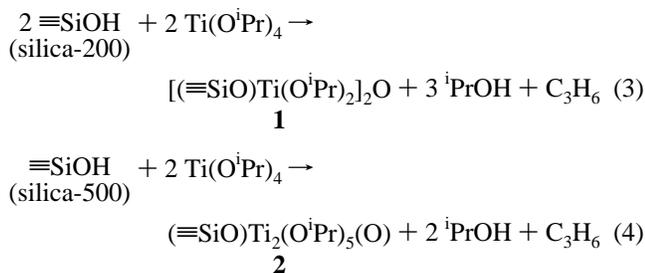(42) Kriegsmann, H.; Licht, K. *Ze. Elektrochem.* **1958**, *62*, 1163−1174.

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Figure 2. In situ IR difference spectra of a self-supporting disk of silica-500 treated with $Ti(O^iPr)_4$ to give **2**, followed by desorption of unreacted starting material and evacuation of volatile products, in two frequency regions of partial transparency of the silica disk. The reference spectrum of silica-500 has been subtracted such that negative peaks correspond to vibrations which are no longer present on the silica surface after reaction.

propene are liberated in reproducible and stoichiometric amounts, regardless of Ti loading in the range 2.28−3.87 wt % (where the highest value corresponds to maximum Ti loading).[45] Thus, regardless of the extent of reaction of the surface hydroxyls, grafting of $Ti(O^iPr)_4$ occurs according to the reactions shown in eqs 3 and 4 for silica-200 and silica-500, respectively:

$$2 \equiv SiOH + 2 Ti(O^iPr)_4 \rightarrow$$
(silica-200)
$$[(\equiv SiO)Ti(O^iPr)_2]_2O + 3\ ^iPrOH + C_3H_6 \quad (3)$$
$$\mathbf{1}$$

$$\equiv SiOH + 2 Ti(O^iPr)_4 \rightarrow$$
(silica-500)
$$(\equiv SiO)Ti_2(O^iPr)_5(O) + 2\ ^iPrOH + C_3H_6 \quad (4)$$
$$\mathbf{2}$$

Calcination of **1** and **2** in 300-Torr O_2 at 750 °C completely removes the surface hydrocarbon fragments. The amount of CO_2 liberated corresponds to 6.1 and 7.6 CO_2/Ti, respectively (Table 3), consistent with the empirical formulas of **1** and **2** given in eqs 3 and 4.

Reaction of $Ti(NEt_2)_4$ with Silica. The gas−solid reactions of yellow $Ti(NEt_2)_4$ with silica-200 or -500 at room-temperature

(44) A blank experiment showed that 2-propanol is not chemisorbed on the surface hydroxyl groups of silica at room temperature, nor is it dehydrated to propene in the presence of silica under these conditions.

(45) Less than maximum loading of Ti is achieved by terminating the grafting reaction before all of the surface hydroxyls have reacted.

Table 2. Quantification of Ligand-Derived Volatiles during Grafting of $Ti(O^iPr)_4$ on Modified and Unmodified Silicas

grafting reaction	wt % Ti	mmol of Ti[a]	mmol of ^iPrOH[a]	mmol of C_3H_6[a]	^iPrOH/Ti	C_3H_6/Ti
silica-500 + $Ti(O^iPr)_4$	3.87	0.81	0.86	0.38	1.06	0.47
	3.14	0.65	0.68	0.31	1.04	0.48
	2.28	0.48	0.51	0.23	1.07	0.47
silica-200 + $Ti(O^iPr)_4$	2.62	0.55	0.83	0.27	1.51	0.49
$(\equiv SiO)Ti(O^iPr)_3 + Ti(O^iPr)_4$	3.42[b]	0.71	0.37	0.35	0.51	0.49

[a] Normalized per gram of solid. [b] Titanium analysis was performed after the second grafting reaction.

Table 3. Quantification of Hydrocarbons in Supported Ti Complexes by Calcination

surface complex	wt % Ti	mmol of Ti[a]	mmol of CO_2[a]	CO_2/Ti obsd	CO_2/Ti expected
$[(\equiv SiO)Ti(O^iPr)_2]_2O$ (**1**)	3.92	0.82	5.00	6.1	6.0
$(\equiv SiO)Ti_2(O^iPr)_5(O)$ (**2**)[b]	3.86	0.80	6.10	7.6	7.5
$(\equiv SiO)Ti_2(O^iPr)_5(O)$ (**2**)[c]	3.85	0.80	6.00	7.5	7.5
$(\equiv SiO)Ti(O^tBu)_3$ (**6**)	1.98	0.41	5.21	12.7	12.0[d]
$(\equiv SiO)Ti(O^iPr)_2$ (**8**)	1.94	0.40	4.24	10.6	9.0[d]
$(\equiv SiO)Ti(OO^tBu)_3$ (**10**)	1.98	0.41	4.76	11.6	12.0
$(\equiv SiO)TiOTi(OO^tBu)_5$ (**12**)	3.90	0.82	15.60	9.5	10.0

[a] Normalized per gram of solid. [b] Prepared by direct grafting of $Ti(O^iPr)_4$ on silica, as in eq 4. [c] Prepared by grafting of $Ti(O^iPr)_4$ on **8**, as in eq 12. [d] Observed values are slightly higher than expected due to retention of residual amine and alcohol on the Ti sites (see text).

proceed with a color change of the solids from colorless to yellow. After 1 h of reaction, $HNEt_2$ is the exclusive gas-phase product detected by IR spectroscopy and GC. The ^{13}C CP/MAS spectra of the solid products are qualitatively similar on silica-200 and -500 and consist of two resonances at 13.7 and 47.0 ppm (Figure 1b), assigned to the methyl and methylene carbons of diethylamido ligands, respectively, by comparison to the NMR spectrum of $Ti(NEt_2)_4$.[46] In the IR spectrum, complete disappearance of the IR vibration at 3747 cm^{-1} due to surface hydroxyl groups was observed on both types of silica. Bands characteristic of the diethylamide ligands[47] are clearly visible (Figure 3a), as well as a new band at 957 cm^{-1} (Figure 3b).[48] The vibrations at 992 and 616 cm^{-1} are assigned to $\nu_s(NC_2)$ and $\nu(Ti-N)$ on the basis of literature assignments for $Ti(NEt_2)_4$.[47] Reaction of $Ti(NEt_2)_4$ with ^{18}O-labeled surface hydroxyl groups[35] (Figure 4a,b) resulted in a shift of the 957-cm^{-1} band to 936 cm^{-1} (Figure 4c,d). On this basis, and by comparison to shifts of similar magnitude in the IR spectra of silica-supported, ^{18}O-labeled vanadium[49] and molybdenum[50] complexes, the vibration is assigned as $\nu(Si-OTi)$.

On silica-200, the amount of chemisorbed titanium after complete reaction of the surface hydroxyl groups with $Ti(NEt_2)_4$ is 2.0 ± 0.1 wt %, which corresponds to 1.3 Ti/nm^2, or 0.47 Ti/$\equiv$SiOH (Table 4). Also, 1.9 ± 0.1 equiv of $HNEt_2$ is liberated per chemisorbed Ti, consistent with the stoichiometry shown in eq 5:

(46) $^{13}C\{^1H\}$ in CDCl$_3$: 13.3 and 45.0 ppm.

(47) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. (A)* **1969**, 980−984.

(48) IR difference spectrum (silica background subtracted): 2973, 2937, 2880, 2848, 1464, 1448, 1373, 1353, 992, 957, 910, 882, 616 cm^{-1}. The spectra of the supported Ti complexes on silica-200 and silica-500 are qualitatively very similar, although the ligand vibrations on silica-500 are slightly more intense.

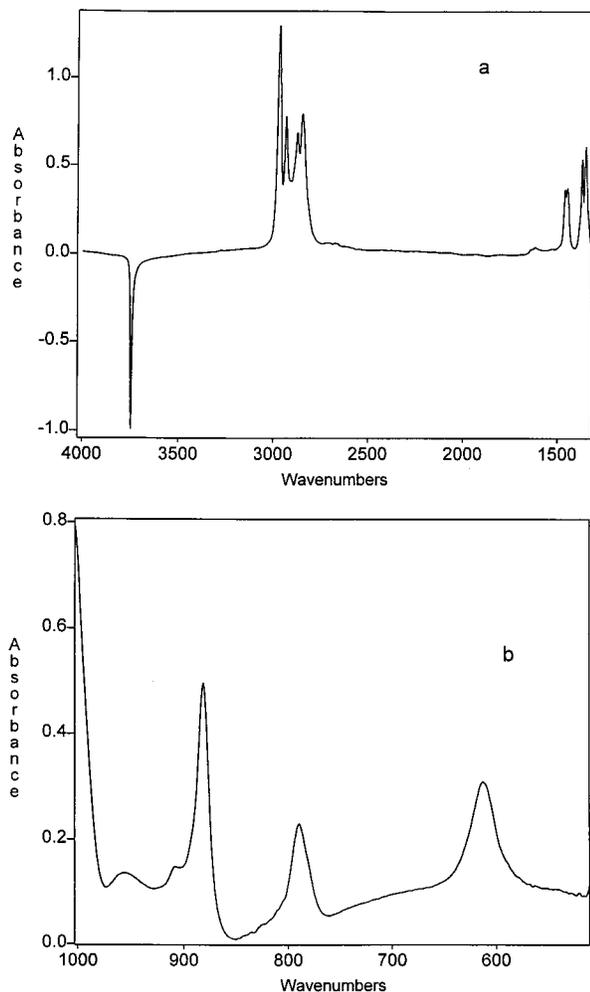(49) Rice, G. L.; Scott, S. L. *J. Mol. Catal. A: Chem.* **1997**, *125*, 73−79.

(50) Cornac, M.; Janin, A.; Lavalley, J. C. *Polyhedron* **1986**, *5*, 183−186.

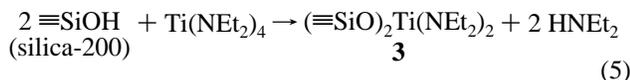**Table 4.** Mass Balance for Materials Prepared by the Room-Temperature Chemisorption of Ti(NEt$_2$)$_4$ on Silica

silica support[a]	wt % of Ti	mmol of Ti[b]	Ti/≡SiOH[c]	mmol of HNEt$_2$[b]	HNEt$_2$/Ti
silica-200	1.94	0.40	0.47	0.73	1.83
	1.86	0.39	0.45	0.80	2.05
	1.97	0.41	0.48	0.75	1.84
	2.00	0.42	0.49	0.85	2.03
average	1.94 ± 0.06	0.41 ± 0.01	0.47 ± 0.02	0.78 ± 0.05	1.94 ± 0.12
silica-500	2.14	0.45	1.12	0.44	0.98
	1.98	0.41	1.03	0.42	1.02
	1.96	0.41	1.02	0.40	0.98
	2.00	0.41	1.04	0.41	1.00
average	2.02 ± 0.08	0.42 ± 0.02	1.05 ± 0.05	0.42 ± 0.02	0.99 ± 0.02

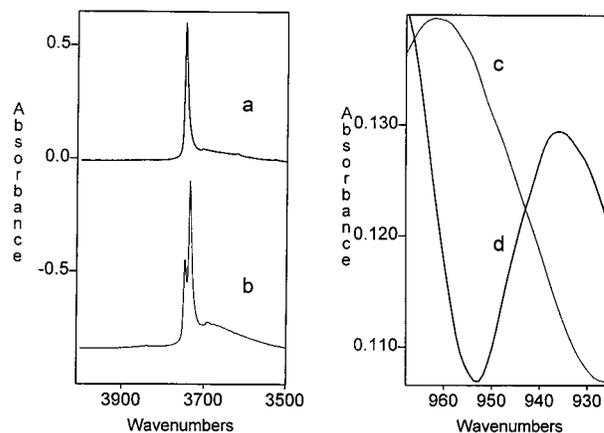[a] The appended numbers refer to the temperature, in °C, at which the silica was partially dehydroxylated prior to the chemisorption reaction. [b] Normalized per gram of solid. [c] Calculated on the basis of the number of surface hydroxyl groups on silica pretreated in vacuo at each temperature: 0.40 (500 °C) and 0.86 mmol/g (200 °C).

Figure 4. In situ IR difference spectra of self-supporting disks of silica-500 (a) unmodified, showing $\nu(\mathrm{Si^{16}O-H})$; (b) after exchange with $\mathrm{H_2^{18}O}$, showing an additional band for $\nu(\mathrm{Si^{18}O-H})$; (c and d) after reaction of unmodified and partially exchanged silicas, respectively, with Ti(NEt$_2$)$_4$ to give **4**, showing the displacement of $\nu(\mathrm{TiO-Si})$ from 957 to 936 cm^{-1} upon ^{18}O substitution.

surface reaction is shown in eq 6:

$$\underset{\text{(silica-500)}}{\equiv\!\mathrm{SiOH}} + \mathrm{Ti(NEt_2)_4} \rightarrow \equiv\!\mathrm{SiOTi(NEt_2)_3} + \mathrm{HNEt_2} \quad (6)$$
$$\mathbf{4}$$

Note that, on both types of silica, the amount of chemisorbed Ti after grafting Ti(NEt$_2$)$_4$ is one-half the amount obtained by the reaction of Ti(O^{i}Pr)$_4$ with each silica (see above). In view of this finding, and in contrast to the dinuclear formulations of **1** and **2**, the supported amido complexes **3** and **4** shown in eqs 5 and 6 are formulated as mononuclear.

Reactions of (≡SiO)$_n$Ti(NEt$_2$)$_{4-n}$ with Alcohols. The reactions of either **3** or **4** with excess *tert*-butyl alcohol vapor cause an immediate color change from yellow to white and nearly complete (ca. 90%) displacement of the amido ligands as HNEt$_2$, eqs 7 and 8:

$$(\equiv\!\mathrm{SiO})_2\mathrm{Ti(NEt_2)_2} + 2\,{}^t\mathrm{BuOH} \rightarrow$$
$$\mathbf{3}$$
$$(\equiv\!\mathrm{SiO})_2\mathrm{Ti(O^tBu)_2} + 2\,\mathrm{HNEt_2} \quad (7)$$
$$\mathbf{5}$$

$$(\equiv\!\mathrm{SiO})\mathrm{Ti(NEt_2)_3} + 3\,{}^t\mathrm{BuOH} \rightarrow$$
$$\mathbf{4}$$
$$(\equiv\!\mathrm{SiO})\mathrm{Ti(O^tBu)_3} + 3\,\mathrm{HNEt_2} \quad (8)$$
$$\mathbf{6}$$

The amount of HNEt$_2$ liberated was quantified by gas-phase

Figure 3. In situ IR difference spectra of a self-supporting disk of silica-500 treated with Ti(NEt$_2$)$_4$ to give **4**, followed by desorption of unreacted starting material and evacuation of volatile products, in two frequency regions of partial transparency of the silica disk. The reference spectrum of silica-500 has been subtracted such that negative peaks correspond to vibrations which are no longer present on the silica surface after reaction.

$$\underset{\text{(silica-200)}}{2\equiv\!\mathrm{SiOH}} + \mathrm{Ti(NEt_2)_4} \rightarrow (\equiv\!\mathrm{SiO})_2\mathrm{Ti(NEt_2)_2} + 2\,\mathrm{HNEt_2}$$
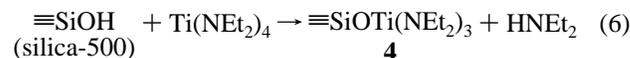$$\mathbf{3}$$
$$(5)$$

On silica-500, the amount of chemisorbed titanium which corresponds to complete reaction of surface hydroxyl groups is 2.0 ± 0.1 wt %, and corresponds to 1.05 Ti/≡SiOH (Table 4). At the same time, 1.0 equiv of HNEt$_2$ is evolved per chemisorbed Ti during the grafting reaction. The stoichiometry of this
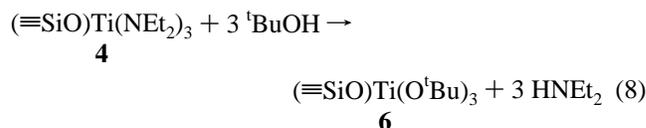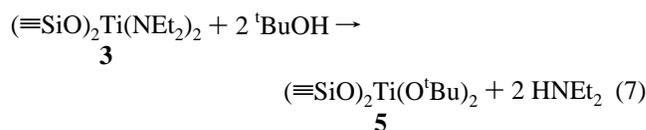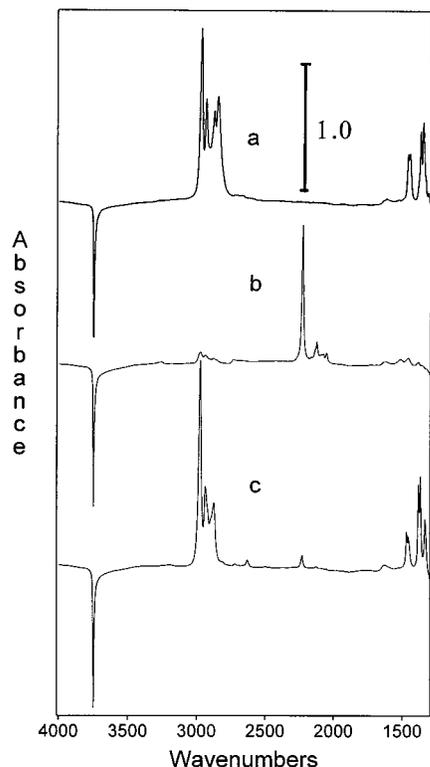
Figure 5. In situ IR difference spectra of a self-supporting disk of silica-500 treated with (a) Ti(NEt$_2$)$_4$ to give **4**, followed by (b) (CD$_3$)$_3$-COD to give **6**, followed by (c) Ti(O^{i}Pr)$_4$ to give **2**. The reference spectrum of silica-500 has been subtracted. At each stage of the experiment, unreacted reagents and volatile products were removed by evacuation before recording the spectrum and adding the next reagent.
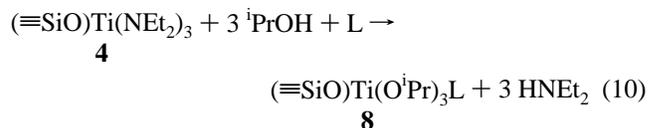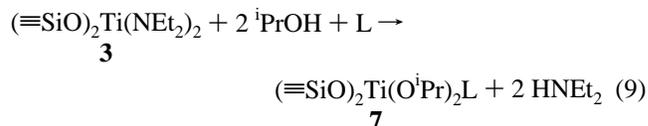
IR spectroscopy as 2.0/Ti for **3** (eq 7) and 2.8/Ti for **4** (eq 8). In the IR spectrum of **4** treated with (CD$_3$)$_3$COD, the ν(C–H) vibrations of the diethylamido ligands decreased in intensity by 96% upon evacuation, while new bands were observed at 2235, 2135, 2076, and 2054 cm^{-1}, assigned to the ν(C–D) vibrations of perdeuterio-*tert*-butyl groups which are strongly chemisorbed (Figure 5a,b). The ^{13}C CP/MAS NMR spectra of both **5** and **6** consist of a major peak at 30.6 ppm, corresponding to the methyl carbons of the *tert*-butyl groups, and a minor, variable intensity peak at 12.8 ppm, assigned to the methylene carbon of a small amount of residual, strongly adsorbed diethylamine (Figure 6a). The quaternary carbon of the *tert*-butoxo ligand was not observed. Calcination of **6** in O$_2$ at 750 °C released 12.7 CO$_2$/Ti (Table 3), in agreement with the proposed formula for **6** in eq 8 and a small amount of chemisorbed HNEt$_2$ (<1 amine per Ti).

Similar color changes were observed when **3** or **4** was exposed to excess 2-propanol, and diethylamine was again observed in the gas phase. When the reaction of **4** was performed with (CD$_3$)$_2$CDOD, the appearance of ν(C–D) modes in the IR spectrum was accompanied by an approximately 80% decrease in intensity of the ν(C–H) vibrations, due to displacement of the amido ligands. The ^{13}C CP/MAS NMR spectra on silica-200 and −500 are qualitatively similar and consist of five peaks at 11.7, 23.8, 43.0, 66.3, and ca. 80 ppm, even after prolonged evacuation of volatiles (Figure 6b). The signals at 23.8 and ca. 80 ppm are assigned to the methyl and methine carbons of coordinated 2-propoxide ligands, as for **1** and **2** (Figure 1a). The peaks at 11.7 and 43.0 ppm are slightly shifted from those of **3** and **4** (see above) and are assigned to the methyl and methylene carbons of coordinated diethylamine. Finally, the peak at 66.3 ppm is assigned to the methine carbon of
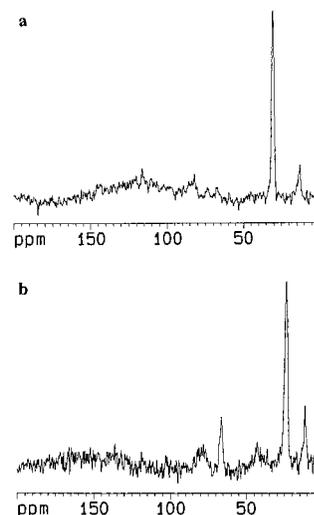
Figure 6. ^{13}C CP/MAS spectra of silica-500 modified with Ti(NEt$_2$)$_4$ to give **4**, followed by (a) *tert*-butyl alcohol to give **6** or (b) 2-propanol to give **8**. In each case, unreacted reagents and volatile products were removed by evacuation before the spectrum was recorded. Spin rate, 4 kHz.

coordinated 2-propanol.[51] The exchange reactions are shown in eqs 9 and 10:

$$(\equiv\mathrm{SiO})_2\mathrm{Ti(NEt_2)_2} + 2\ ^i\mathrm{PrOH} + \mathrm{L} \rightarrow$$
$$\mathbf{3}$$
$$(\equiv\mathrm{SiO})_2\mathrm{Ti(O^iPr)_2L} + 2\ \mathrm{HNEt_2}\quad(9)$$
$$\mathbf{7}$$

$$(\equiv\mathrm{SiO})\mathrm{Ti(NEt_2)_3} + 3\ ^i\mathrm{PrOH} + \mathrm{L} \rightarrow$$
$$\mathbf{4}$$
$$(\equiv\mathrm{SiO})\mathrm{Ti(O^iPr)_3L} + 3\ \mathrm{HNEt_2}\quad(10)$$
$$\mathbf{8}$$

where L is ^{i}PrOH, HNEt$_2$, or (in most cases) a siloxane oxygen from the silica surface. We have no direct evidence for the coordinated siloxane ligand, but its presence is likely in at least some of the surface complexes which bind neither free alcohol nor amine.

Calcination of **8** in dry O$_2$ at 750 °C liberated 10.6 CO$_2$/Ti (expected value, 9 CO$_2$/Ti for **8**, neglecting the contribution of the ligand L). Therefore, the amount of ^{i}PrOH and HNEt$_2$ strongly chemisorbed on the surface is less than 1 ligand per Ti. This result is also consistent with incomplete (ca. 80%) loss of the C–H vibrations due to HNEt$_2$ in the IR spectrum of **4** after reaction with (CD$_3$)$_2$CDOD.

Reactions of Mononuclear Surface Alkoxide Complexes with Ti(O^{i}Pr)$_4$. The modified silicas **5**−**8** all contain up to 2.0 wt % Ti. When maximum Ti loading is achieved, there are *no residual surface hydroxyl groups*. Even in the absence of hydroxyl grafting sites, each of these materials reacts irreversibly with additional Ti(O^{i}Pr)$_4$. The reactions are accompanied in each case by an effective doubling of the maximum Ti loading on silica from 2.0 to 3.9 wt % (Table 5), as well as liberation of 0.5 equiv each of 2-propanol and propene into the gas phase (last entry in Table 2).[52]

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(51) In free 2-propanol, this signal appears at 64.7 ppm. The methyl carbon signal of coordinated 2-propanol is presumed to be superimposed on the methyl signal of the 2-propoxide ligands at 23.8 ppm.
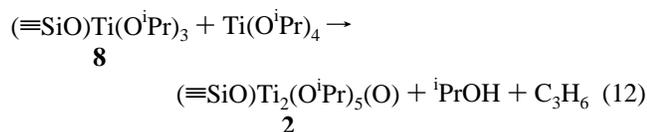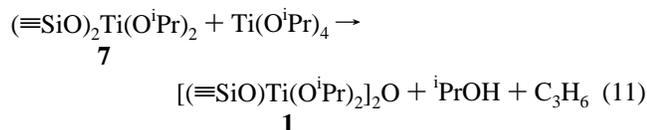
(52) A small amount of diethylamine was also detected in the gas phase by GC upon exposure of **5**−**8** to Ti(O^{i}Pr)$_4$ or ^{t}BuOOH, consistent with the retention of some coordinated HNEt$_2$ on the surface in reactions 7−10.

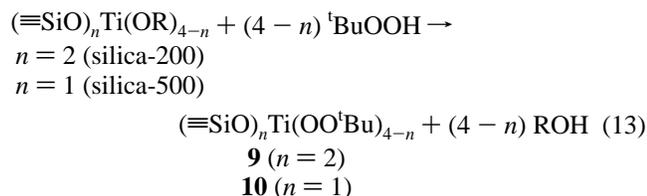**Table 5.** Titanium Content of Materials Prepared by Room-Temperature Chemisorption of Ti(O^{i}Pr)$_4$ on ($\equiv$SiO)$_n$Ti(O^{i}Pr)$_{4-n}$[a,b]

silica support[c]	wt % Ti	
	before reaction with ($\equiv$SiO)$_n$Ti(O^{i}Pr)$_{4-n}$	after reaction with ($\equiv$SiO)$_n$Ti(O^{i}Pr)$_{4-n}$
silica-500	1.98	3.96
	d	3.98
	d	3.94
	d	3.96
average		3.96 ± 0.02
silica-200	1.94	3.92
	d	4.00
	d	3.94
average		3.95 ± 0.04

[a] Prepared by the chemisorption of Ti(NEt$_2$)$_4$ on silica, followed by ligand metathesis with excess ^{i}PrOH. [b] On silica-500, $n = 1$; on silica-200, $n = 2$. [c] The appended numbers refer to the temperature, in °C, at which the silica was partially dehydroxylated prior to the *first* chemisorption reaction. [d] These are in situ IR experiments; therefore, the Ti loading resulting from the first grafting reaction was not measured. However, there are no remaining hydroxyl groups (as judged by the absence of ν(SiO$-$H)) at the time of second grafting reaction.

When deuterium-labeled **6** reacts with Ti(O^{i}Pr)$_4$, the ν(C$-$D) vibrations disappear almost completely from the IR spectrum, and new ν(C$-$H) vibrations, corresponding to unlabeled isopropyl groups, appear (Figure 5c). Calcination of the product of this reaction in O$_2$ liberated 7.5 CO$_2$/Ti, compared to 7.6 CO$_2$/Ti generated in the calcination of **2** (Table 3). The IR spectra of the products of the reactions of **5**$-$**8** with Ti(O^{i}Pr)$_4$ are superposable, both qualitatively and quantitatively, upon those of **1** and **2**. The ^{13}C CP/MAS spectra of these materials consist of two peaks at 25.0 and 78.0 ppm, assigned to the methyl and methine carbons of chemisorbed 2-propoxide ligands. The spectra are indistinguishable from those obtained by direct grafting of Ti(O^{i}Pr)$_4$ on the surface hydroxyl groups of silica (Figure 1). The net reactions are shown in eqs 11 and 12:

$$(\equiv\text{SiO})_2\text{Ti(O}^i\text{Pr)}_2 + \text{Ti(O}^i\text{Pr)}_4 \rightarrow$$
$$\textbf{7}$$
$$[(\equiv\text{SiO})\text{Ti(O}^i\text{Pr)}_2]_2\text{O} + {}^i\text{PrOH} + \text{C}_3\text{H}_6 \quad (11)$$
$$\textbf{1}$$

$$(\equiv\text{SiO})\text{Ti(O}^i\text{Pr)}_3 + \text{Ti(O}^i\text{Pr)}_4 \rightarrow$$
$$\textbf{8}$$
$$(\equiv\text{SiO})\text{Ti}_2(\text{O}^i\text{Pr)}_5(\text{O}) + {}^i\text{PrOH} + \text{C}_3\text{H}_6 \quad (12)$$
$$\textbf{2}$$

Reactions of Mono- and Dinuclear Surface Complexes with *tert*-Butylhydroperoxide and Cyclohexene. Displacement of alcohol (^{t}BuOH or ^{i}PrOH) from **5**$-$**8** by *tert*-butylhydroperoxide at room temperature was observed by IR and GC.[52] The exchange reactions are summarized in eq 13:

$$(\equiv\text{SiO})_n\text{Ti(OR)}_{4-n} + (4-n)\,{}^t\text{BuOOH} \rightarrow$$
$$n = 2 \text{ (silica-200)}$$
$$n = 1 \text{ (silica-500)}$$
$$(\equiv\text{SiO})_n\text{Ti(OO}^t\text{Bu)}_{4-n} + (4-n)\,\text{ROH} \quad (13)$$
$$\textbf{9}\ (n = 2)$$
$$\textbf{10}\ (n = 1)$$

When the reaction with ^{t}BuOOH was performed with deuterium-labeled **6**, a 97% decrease in the intensity of the ν(C$-$D) vibrations was observed by IR, while ν(C$-$H) vibrations
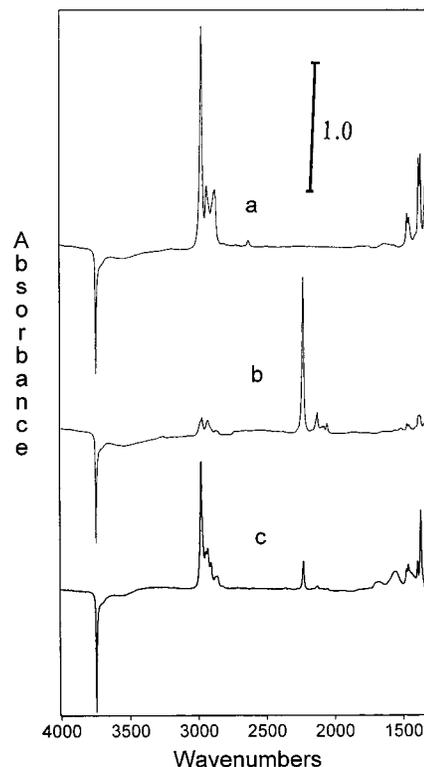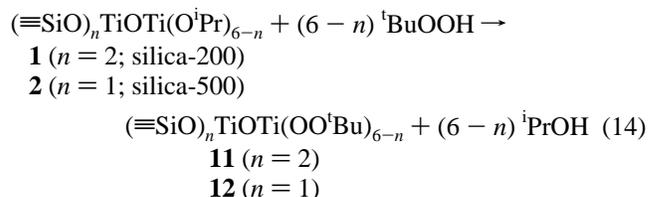

Figure 7. In situ IR difference spectra of a self-supporting disk of silica-500 (a) treated with Ti(O^{i}Pr)$_4$ to give **2**, followed by (b) (CD$_3$)$_2$-CDOD, followed by (c) (CH$_3$)$_3$COOH to give **12**. The reference spectrum of silica-500 has been subtracted. At each stage of the experiment, unreacted reagents and volatile products were removed by evacuation before recording the spectrum and adding the next reagent.

assigned to the *tert*-butylperoxo ligands appeared. No regeneration of silica hydroxyl groups was observed. A weak band at 888 cm^{-1} is assigned to the peroxo ν(O$-$O) vibration, by comparison to the spectrum of VO(C$_7$H$_3$O$_4$N)(OO^{t}Bu) with a band at 890 cm^{-1}.[53]

Calcination of **10** in O$_2$ at 750 °C resulted in the liberation of 11.6 equiv of CO$_2$/Ti, in reasonable agreement with the expected value (12). Both of the mononuclear alkylperoxo complexes **9** and **10** ($n = 2$ or 1) are stable in a vacuum and in the presence of cyclohexene vapor at room temperature; i.e., neither cyclohexene oxide nor any other oxidation product was detected by GC.

The dinuclear complexes **1** and **2**, obtained either by direct grafting of Ti(O^{i}Pr)$_4$ on silica or by grafting Ti(O^{i}Pr)$_4$ onto the mononuclear complexes **7** or **8**, also react with ^{t}BuOOH with liberation of ^{i}PrOH into the gas phase and formation of peroxo complexes ($\equiv$SiO)$_n$TiOTi(OO^{t}Bu)$_{6-n}$, eq 14:

$$(\equiv\text{SiO})_n\text{TiOTi(O}^i\text{Pr)}_{6-n} + (6-n)\,{}^t\text{BuOOH} \rightarrow$$
$$\textbf{1}\ (n = 2;\ \text{silica-200})$$
$$\textbf{2}\ (n = 1;\ \text{silica-500})$$
$$(\equiv\text{SiO})_n\text{TiOTi(OO}^t\text{Bu)}_{6-n} + (6-n)\,{}^i\text{PrOH} \quad (14)$$
$$\textbf{11}\ (n = 2)$$
$$\textbf{12}\ (n = 1)$$

The extent of the reaction in eq 14 is seen more clearly when the 2-propoxide ligands of **1** or **2** are first exchanged for perdeuterioalkoxide ligands. When the 2-propoxide ligands of **2** were exchanged for perdeuterio-*tert*-butoxide (Figure 7), the

(53) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467$-$475.

subsequent reaction with ^tBuOOH caused the loss of 87% of the $\nu(CD)$ vibrations, corresponding to essentially complete replacement of the ^tBuO ligands by ^tBuOO. No regeneration of surface hydroxyl groups was observed.

Calcination of **12** in O_2 at 750 °C led to the formation of 9.5 equiv of CO_2/Ti (Table 3), in reasonable agreement with the expected value (10). The ^{13}C CP/MAS NMR spectrum shows some retention of 2-propanol on the surface, with minor peaks appearing at 21 and 66 ppm assigned to coordinated 2-propanol (as for **7** and **8**, vide supra), as well as signals at 30 and 87 ppm, assigned to the methyl and quaternary carbons of the *tert*-butylperoxo ligands.

Following evacuation of excess ^tBuOOH, addition of cyclohexene vapor at room temperature caused the immediate appearance of cyclohexene oxide as the sole gaseous product detected by GC/MS.[54]

Discussion

Ambient temperature grafting reactions in which an organometallic or coordination complex becomes anchored on an oxide surface are generally assumed to yield supported species of the same nuclearity as the molecular precursor complex. In some cases, the surface species have been extensively characterized and their nuclearity demonstrated. For example, we have shown that the reaction of VOX_3 (where X is Cl or O^iPr) gives exclusively mononuclear $\equiv SiOVOX_2$ upon reaction with the surface hydroxyl groups of silica, regardless of the pretreatment temperature of the silica surface (and hence the density of the surface hydroxyl groups).[37] Previous studies[7,8,26,55] of the reactions of $Ti(OR)_4$ with silica have assumed the occurrence of simple grafting reactions which lead to mononuclear surface Ti complexes, eq 15.[56] Unlike for $VO(OR)_3$ reactions, multiple ligand substitutions on the surface are usually considered likely:

$$n \equiv SiOH + Ti(OR)_4 \rightarrow$$
$$(\equiv SiO)_n Ti(OR)_{4-n} + n\, ROH \qquad (n = 1 \text{ or } 2) \quad (15)$$
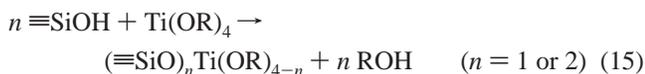
Our findings demonstrate that gas–solid reactions of $Ti(O^iPr)_4$ with silica, even with strict exclusion of water to preclude hydrolysis, are not as simple as previously supposed. The number of grafted Ti centers after complete reaction of the surface hydroxyl groups exceeds, on silica-500, the original number of surface hydroxyl groups by a factor of 2 (0.80 mmol of Ti/g present on silica which originally contained 0.40 mmol of OH/g), Table 1. To our knowledge, this is the first evidence for a single-step grafting procedure in which the number of chemisorbed molecular complexes ultimately exceeds the number of grafting sites.[57] In the more usual case, after complete reaction of the surface silanols, excess metal complex is weakly physisorbed and is readily removed by evacuation or washing with solvent.

On silica-200, 0.84 mmol of Ti/g is grafted on the silica surface which originally contained 0.86 mmol of OH/g. This

stoichiometry has been interpreted[25] as evidence for a 1:1 reaction with surface hydroxyls (i.e., $n = 1$ in eq 15). Such a reaction would generate isolated Ti surface complexes and ^iPrOH, formed exclusively by protonolysis of the 2-propoxide ligands by surface silanols. However, the average number of 2-propoxide ligands present on the surface, as measured by their total combustion to CO_2, is 2.0/Ti, which is not consistent with $n = 1$. In addition, the gaseous products contain unanticipated propene as well as the expected 2-propanol. Therefore, we conclude that, on both silica-200 and -500 surfaces, the grafting reaction is more complex than a simple ligand-exchange reaction on Ti.

Nevertheless, exchange between coordinated ligands and free alcohol is known to be facile in Ti alkoxide and mixed halide–alkoxide systems.[58] In the first step of grafting, we propose that an exchange occurs between the alkoxide ligands and the "silanols", eq 16, analogous to reactions suggested for $VO(O^iPr)_3$[37] and $Zr(O^tBu)_4$[59] with silica surfaces.

$$n \equiv SiOH + Ti(O^iPr)_4 \rightarrow \underset{\textbf{7, 8}}{(\equiv SiO)_n Ti(O^iPr)_{4-n}} + n\, HO^iPr$$
$$(16)$$

The propensity of Ti to coordinate additional ligands increases as electron-donating alkoxide ligands are progressively substituted by electron-withdrawing ligands (such as halides).[60] Substitution of an alkoxide ligand by a siloxide ligand derived from the silica surface will cause the Lewis acidity of Ti to increase due to the strongly electron-withdrawing character of the silica "siloxide" ligand.[37] The initially formed mononuclear chemisorbed complexes **7** and **8** are therefore stronger Lewis acids than $Ti(O^iPr)_4$, and indeed when they are generated under conditions in which they are stable (eqs 9 and 10), they do coordinate additional ligands L (L is ^iPrOH, $HNEt_2$ or silica oxygens). The next step in the mechanism of direct grafting of $Ti(O^iPr)_4$ is therefore suggested to be coordination of additional $Ti(O^iPr)_4$, eq 17:[61]

$$\underset{\textbf{7, 8}}{(\equiv SiO)_n Ti(O^iPr)_{4-n}} + Ti(O^iPr)_4 \rightarrow \underset{\textbf{Ia,b}}{\{(\equiv SiO)_n Ti_2(O^iPr)_{8-n}\}}$$
$$(17)$$

The structures of the intermediate dinuclear alkoxo–siloxo complexes **I** may resemble structurally characterized bimetallic molecular complexes, such as dimeric $[TiCl_2(OEt)_2]_2$, in which the Ti achieves five-coordination through formation of two alkoxide bridges.[62] If sterically allowed, participation of surface oxygens in **I** may augment the Ti coordination number and even generate six-coordinate, edge-sharing octahedra linked via pairs of bridging alkoxides.[63,64] In solution chemistry, oxygen-containing donors/solvents such as THF and Et_2O are known to coordinate to mixed chloride–alkoxide complexes of Ti when there are not enough free ligands available to complete the coordination sphere of Ti.[65]

(54) Both mono- and dinuclear supported Ti complexes catalyze the conversion of cyclohexene to the epoxide when both *tert*-butylhydroperoxide and cyclohexene are present in excess. The possibility of Ti mobility and oligomerization of the mononuclear complexes under catalytic conditions is under investigation.
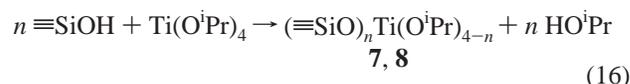
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(56) Hydrolysis–condensation reactions in aqueous sol–gel processes are, however, notorious for giving polynuclear TiOTi species.
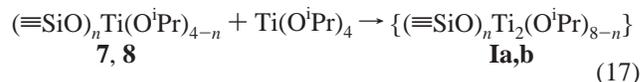
(57) The possibility of grafting $Ti(O^iPr)_4$ on siloxane sites, $\equiv SiOSi\equiv$, rather than silanols, is excluded by the low ratio of chemisorbed isopropyl groups per grafted Ti (observed, 2.5 $^iPr/Ti$ on silica-500). In a siloxane reaction, all four isopropyl groups would be retained on the surface: $\equiv SiOSi\equiv + Ti(O^iPr)_4 \rightarrow \equiv SiOTi(O^iPr)_3 + \equiv SiO^iPr$.

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The proposed intermediates **Ia** and **Ib** must undergo loss of coordinated 2-propoxide ligands in order to generate the stable surface complexes **1** and **2**. Metal alkoxides, including those of Ti,[66] undergo non-hydrolytic condensations to give polynuclear species containing μ-oxo bridges via elimination of dialkyl ether[67,68] or equal amounts of alcohol/alkene,[69] eq 18:

$$2 \text{ M(OR)}_n \rightarrow$$
$$(\text{RO})_{n-1}\text{M}-\text{O}-\text{M(OR)}_{n-1} + \text{R}_2\text{O or (ROH + R(-H)) (18)}$$
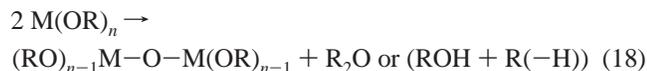
The silica surface may promote the formation of μ-oxo bridges in supported metal alkoxide complexes. We recently inferred a similar non-hydrolytic condensation in the reaction of silica-supported $\equiv$SiOVO(O^{i}Pr)$_2$ with Ti(O^{i}Pr)$_4$.[70] In addition, we note that the condensation step (eq 18) must be fast relative to the initial grafting step (eq 16) in order to generate the observed amounts of 2-propanol and propene products even when the grafting reaction is not allowed to proceed to completion (i.e., even when the surface loading of Ti is less than the maximum loading, as in the second and third entries in Table 2).

Although many molecular metal oxoalkoxide complexes are known,[71] there appears to be a strong tendency to isolate more stable, higher nuclearity clusters. Only one structurally characterized oxoalkoxide complex containing just two metal nuclei is known: Ta$_2$O(O^{i}Pr)$_8$(^{i}PrOH).[72] This complex consists of pairs of edge-sharing octahedra joined by one oxo and one 2-propoxo bridge. The surface complexes **1** and **2** may possess a similar oxo/alkoxo-bridged structural unit. We do not know, at this point, whether the coordination number of Ti is as high as 6 (which would require additional coordination of surface siloxane oxygens). Nor does the solid-state ^{13}C CP/MAS NMR spectrum (Figure 1) reveal whether bridging as well as terminal 2-propoxide ligands are present. Only one OCH signal was detected at 78 ppm. This chemical shift is consistent with terminal 2-propoxide ligands as in monomeric[73] Ti(O^{i}Pr)$_4$.[38] Although a bridging 2-propoxide methine signal is expected to have a different chemical shift,[63] fluxionality and/or the breadth of the solid-state signal may have precluded its detection in our study.

Oxide-supported Ti complexes, including TS-1, have an intense band at ca. 960 cm^{-1} which has been attributed by various authors to ν(Ti=O),[11] ν_{as}(SiOTi),[74,75] the localized ν(SiO) of an SiOTi unit,[76] ν(SiO) of defect sites,[77] and ν(Si$-$OH) associated with Ti sites.[78] In **1** and **2**, the band at 957 cm^{-1} is unlikely to be due to any of these. It is present

even in the complete absence of unreacted silanol groups, and its position is insensitive to ^{18}O-labeling of the surface oxygens. An intense band at 964 cm^{-1} is also present in the IR spectrum of Ti(O^{i}Pr)$_4$.[39,42] We therefore assign the vibration in the spectra of **1** and **2** to a skeletal vibration of the 2-propyl groups.[43] In contrast, the IR spectra of the supported diethylamido complexes **3** and **4** contain a band at 957 cm^{-1} which is not attributable to a ligand vibration. Because of the similarity of its position to the band assigned as ν_{as}(M$-$O$-$Si) in metal trialkylsiloxides[39] and its sensitivity to ^{18}O-labeling of the surface oxygens, we assign this band as ν(TiO$-$Si).[31] The vibration is best described as a mostly localized ν(Si$-$O) vibration of the SiOTi group, due to the mass difference between Ti and Si.[76] The assignment of this band is not consistent with a perturbed ν(Si$-$OH) mode,[78] since the ν(SiO$-$H) region of the IR spectrum shows no residual hydroxyl groups on the surface. However, there is certainly a possibility for overlap of ligand and Si$-$O vibrations in this spectral region, so our assignments are not necessarily exclusive.

The supported dialkylamido complexes **3** and **4** supply an indirect route to grafted mononuclear titanium alkoxides via ligand metathesis. The maximum loading of chemisorbed Ti using Ti(NEt$_2$)$_4$ as the molecular reagent does not exceed the number of surface hydroxyl groups, which react either individually (on silica-500) or in pairs (on silica-200). Thus, on silica-500, 0.42 mmol of Ti is grafted on a surface containing originally 0.40 mmol of OH/g, whereas on silica-200, 0.41 mmol of Ti is grafted on a surface containing originally 0.86 mmol of OH/g (Table 4). The reproducible but different stoichiometries of these reactions on each kind of silica resemble those of the reactions of the metal alkyls MR$_4$ (M is Zr,[79,80] Cr[81]) with silica surfaces.

Consistent with the greater acidity of alcohols relative to amines, the mononuclear amido surface complexes are readily transformed into mononuclear surface alkoxide complexes **5**$-$**8**. However, the amine is not quite quantitatively liberated from the surface: a small amount remains bound to the *tert*-butoxo surface complexes, and slightly more remains bound to the 2-propoxo surface complexes, which are presumably less sterically encumbered than the diethylamido surface complexes **3** and **4**. The ^{13}C NMR spectrum also shows evidence for coordination of some 2-propanol to mononuclear supported titanium 2-propoxide complexes (although not to dinuclear **1** or **2**). In agreement with a previous report,[7] but in contrast to another,[25] we find that alcohol does not cleave the SiO$-$Ti bond to any significant extent, since the ν(SiO$-$H) vibration never reappears in the IR spectrum.

The supported complexes **5**$-$**8** react with 1 equiv of Ti(O^{i}Pr)$_4$ to form the dinuclear surface complexes **1** and **2**, on silica-200 and -500 respectively, by a mechanism which likely resembles steps in the proposed grafting mechanism for Ti(O^{i}Pr)$_4$ on silica, eqs 17 and 18. The surface dinuclear complexes produced via grafting Ti(O^{i}Pr)$_4$ on **5**$-$**8** are identical, spectroscopically and analytically, to those produced by the direct grafting of Ti(O^{i}Pr)$_4$ on unmodified silica. Unfortunately, no low-frequency band appears upon reaction of **5**$-$**8** with Ti-(O^{i}Pr)$_4$ which can convincingly be assigned to a ν(Ti$-$O$-$Ti) mode. However, such bands are often difficult to detect.[71] The surface reactions are summarized in Schemes 1 and 2.
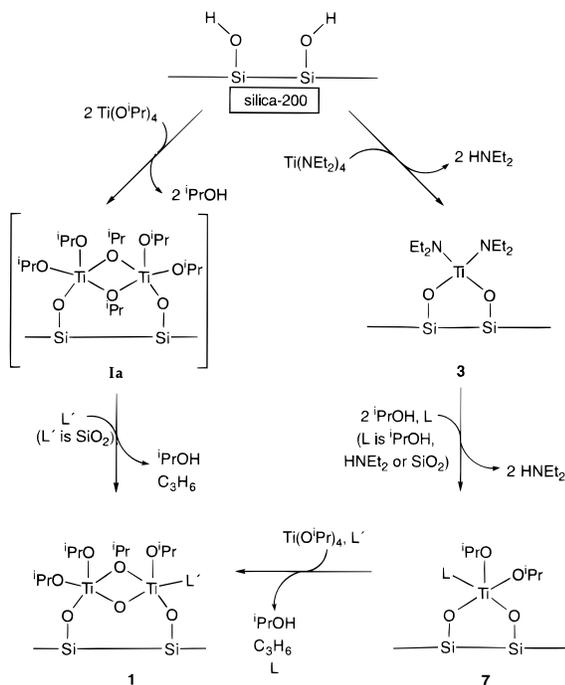
Both mononuclear and dinuclear surface alkoxide complexes react with *tert*-butylhydroperoxide. The greater acidity of

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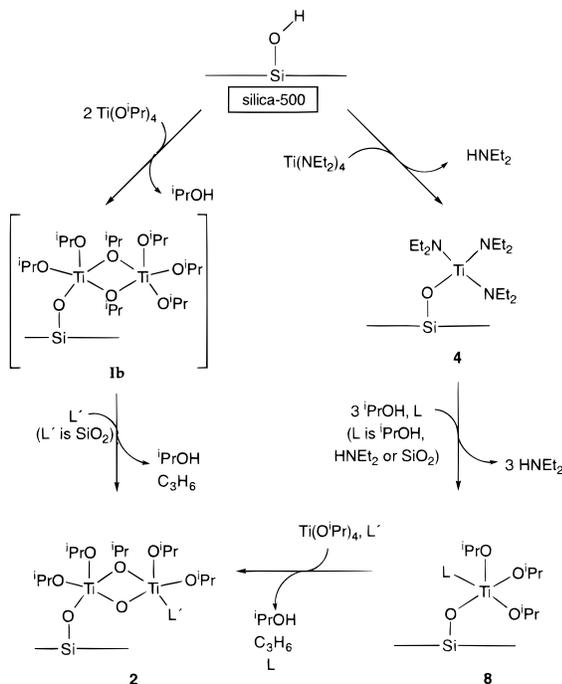
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Scheme 1

Scheme 2

is not cleaved by ^{t}BuOOH, in contrast to the reactivity of Ti silasesquioxanes.[83] On acidity grounds, the lack of reactivity of silica-supported complexes is as expected, since silica silanols are more acidic than alkylhydroperoxides. Alkylperoxo ligands may bind in an η^2 fashion to metal complexes, leading to an increase in coordination number at Ti.[33] Peroxo complexes of titanium are often seven-coordinate with pentagonal bipyramidal geometries, such as $[Ti(O_2)_3(H_2O)]^{2-}$,[84] and can be binuclear, such as $K_2[Ti(O_2)(C_7H_3O_4N)(H_2O)]_2O$, which contains a linear Ti–O–Ti bridge.[85] There are few structurally characterized alkylperoxo complexes of d^0 metals, and none have been isolated for Ti. However, $VO(OO^tBu)(C_7H_3O_4N)(H_2O)$ is a distorted pentagonal bipyramid with an η^2-OO^{t}Bu ligand.[53]

The reactivity of the dinuclear alkylperoxo complexes **11** and **12** toward cyclohexene resembles the stoichiometric epoxidation activity of Mo(VI) peroxo complexes such as $MoO(O_2)_2$-(HMPA) in organic solvents.[86] In contrast, mononuclear **9** and **10** show no reactivity toward cyclohexene at room temperature. Interestingly, the formation of a TiOTi species was observed by ^{17}O NMR in the reaction of $Ti(O^iPr)_4$ with cumene hydroperoxide.[87] The origin of the reactivity difference between mononuclear and dinuclear supported alkylperoxo complexes of titanium, the mechanism of epoxidation, and their activity under catalytic conditions are under investigation in our laboratory.

Conclusion

Two series of silica-supported Ti alkoxides have been synthesized and characterized. The direct reaction of $Ti(O^iPr)_4$ with silica gives only dinuclear surface complexes, in which pairs of Ti(IV) atoms are linked via an oxo bridge. Mononuclear alkoxide complexes must be prepared via an indirect route, involving the reaction of grafted Ti amido complexes with alcohols. The coordination numbers of the mono- and dinuclear surface alkoxide complexes are yet to be determined but may be augmented by additional surface oxygens. Both mono- and dinuclear surface alkoxide complexes react with *tert*-butyl-hydroperoxide; however, only the dinuclear alkylperoxo complexes react directly with cyclohexene. We suggest that high activity, in the absence of TiO_2 domain formation, in oxide-supported catalysts does not require that *all* Ti–O–Ti connectivity is absent in these systems.

Supporting Information Available: Figures S1−S3 and S5−S7 containing IR and ^{13}C CP/MAS NMR spectra analogous to those shown here, but on silica-200 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9829160

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alkylhydroperoxides relative to that of the alcohols[82] explains the virtually quantitative ligand exchange. The alkoxide ligands are almost completely displaced, as shown by a deuterium-labeling IR experiment (Figure 7). However, the siloxide linkage