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Titania−Silica Materials from the Molecular Precursor $Ti[OSi(O^tBu)_3]_4$: Selective Epoxidation Catalysts

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The tris(*tert*-butoxy)siloxy complex $Ti[OSi(O^tBu)_3]_4$ (**1**) was pyrolytically converted at low temperatures to the theoretical yield of homogeneous $TiO_2{\cdot}4SiO_2$ materials. **1** also serves as a soluble model for isolated, tetrahedral titanium atoms in a silica matrix. The solid-state transformation of **1** to $TiO_2{\cdot}4SiO_2$ affords a low-surface-area material (**2a**, 22 $m^2\ g^{-1}$ for samples heated to 500 °C) consisting of roughly spherical particles with an average diameter of ca. 25 nm (by transmission electron microscopy). The solution-phase thermolysis of **1** affords a xerogel (**2b**) consisting of smaller primary particles (≤ca. 5 nm) and possessing a much higher surface area (552 $m^2\ g^{-1}$ for samples heated to 500 °C). Acid catalysis of the pyrolytic conversion in solution affords a xerogel (**2c**) with a lower surface area (399 $m^2\ g^{-1}$ for samples heated to 500 °C). Supercritical drying of the "wet-gel" in CO_2 affords an aerogel (**2d**) with a morphology similar to that of the xerogel and a slightly higher surface area (677 $m^2\ g^{-1}$ for samples heated to 500 °C). The $TiO_2{\cdot}4SiO_2$ materials are amorphous as initially formed, and subsequent crystallizations of anatase (**2a**, **2b**), rutile, and cristobalite (**2a**) occur at relatively high temperatures. **1** is a homogeneous catalyst for the selective epoxidation of cyclohexene to cyclohexene oxide (64% yield; 20 turnovers after 2 h) using cumene hydroperoxide (CHP) as the limiting reagent. **2a**−**d** are heterogeneous catalysts that produce 6% (**2a**)−49% (**2d**) yields of cyclohexene oxide after 2 h (with 0.05 g of catalyst). Supporting **1** on silica affords a highly active epoxidation catalyst that provides yields of 94% cyclohexene oxide after 2 h (with a standard amount of 0.05 g of catalyst). The molecular route to homogeneous titania−silica materials described here represents an alternative to the sol−gel method, affording materials with surface areas comparable to those of related aerogels and moderate-to-excellent activities for the epoxidation of cyclohexene.

Introduction

There is considerable interest in the development of new synthetic routes to solid-state materials, because novel and superior properties are expected to result from strategies that permit fine control over formation of the structure.[1] A popular approach involves the use of building blocks derived from molecular precursors, which offer well-defined compositions and may provide low-temperature pathways to metastable structures.[2] In particular, the sol−gel method, based on the hydrolysis/condensation of alkoxide precursors, has received wide attention as a procedure for the synthesis of metal oxide materials.[3] However, certain inherent problems are associated with this method, including its limitation to fairly polar media (e.g., alcoholic or aqueous solutions) and the difficulties encountered in preparing homogeneous (atomically well-mixed) multicomponent oxides. The latter problem results from variations in the rates of hydrolysis for different metal precursors.[3,4]

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Research in our group on development of an alternative to the sol−gel technique for the synthesis of homogeneous, mixed-element oxide materials has focused on oxygen-rich precursors containing the $-OSi(O^tBu)_3$[5] or $-O_2P(O^tBu)_2$[6] ligand. The siloxide precursors provide metal−silica materials by the low-temperature (ca. 150−250 °C) thermal elimination of isobutylene and water, and the formation of zirconia−silica materials by this method (eq 1) has been the subject of a detailed study.[5a,b] The facile nature of this transformation allows the conversion to occur in solution, and this permits the use of combinations of different precursors in the generation of more complex stoichiometries.[5i] In addition, the hydrophobic nature of the precursors facilitate their use under nonhydrolytic conditions, and very high surface areas result from conversions in nonpolar solvents.

$$\mathrm{Zr[OSi(O^tBu)_3]_4} \xrightarrow[10^{-3}\ \mathrm{mmHg}]{190-200\ ^\circ\mathrm{C}} \mathrm{ZrO_2{\cdot}4SiO_2} + 12\ \mathrm{CH_2{=}CMe_2} + 6\mathrm{H_2O} \quad (1)$$

In this paper, we describe the preparation and characterization of $TiO_2{\cdot}4SiO_2$ materials from the molecular precursor $Ti[OSi(O^tBu)_3]_4$ (**1**), which was described in an earlier communication.[5a] **1** was also used to graft titanium species onto the surface of silica particles. We have examined these materials as catalysts in the selective oxidation of cyclohexene to cyclohexene oxide, as there has been considerable recent interest in the use of titania−silica materials for this purpose. In the 1970s, Shell developed a silica-supported titania epoxidation catalyst for the production of propylene oxide.[7] Many other titania−silica materials have been studied in this context, including the titanium-substituted molecular sieves TS1 and TS2,[8] the titanium-substituted zeolite Ti-β,[9] and Ti−MCM41 (where the titanium is incorporated into the walls of the mesoporous host[10] or grafted onto its surface[11]). The sol−gel process has been employed in the synthesis of amorphous titania−silica catalysts,[12] and considerable effort has focused on attempts to obtain homogeneous samples featuring a high concentration of Ti−O−Si heterolinkages. These efforts have concentrated on fine-tuning the hydrolysis rates for the titanium and silicon precursor alkoxides, by modifying the ligands of the titanium precursor[12a,c] or via prehydrolysis of the silicon precursor.[13] In addition, the diethoxysiloxane−ethyltitanate copolymer, $[SiO(EtO)_2TiO(EtO)_2]_x$, in which Ti−O−Si linkages preexist, has been used as a sol−gel precursor.[14]

Results and Discussion

Synthesis and Characterization of $Ti[OSi(O^tBu)_3]_4$ (1). The titanium complex **1** was prepared by refluxing 4 equiv of $HOSi(O^tBu)_3$[15] with $Ti(NEt_2)_4$[16] in toluene for 4 h (eq 2). The product was isolated from cold (−78 °C) pentane as colorless crystals that turn opaque under vacuum. **1** is monomeric in benzene solution (by the Signer method[17]), as is the analogous hafnium complex. In contrast, the zirconium analogue exists as a dimer in solution but as a monomer in the solid state.[5b] The room temperature ^1H and ^{13}C NMR spectra of **1** indicate a symmetrical structure with equivalent siloxide ligands.

$$\mathrm{Ti(NEt_2)_4} + 4\mathrm{HOSi(O^tBu)_3} \xrightarrow[\text{reflux, 4 h}]{\text{toluene}} \underset{(\mathbf{1})}{\mathrm{Ti[OSi(O^tBu)_3]_4}} + 4\mathrm{HNEt_2} \quad (2)$$

Given the “$Ti(OSiO_3)_4$” core of **1**, this compound serves as an excellent model for isolated, tetrahedral titanium centers in a silica matrix (vide infra). For example, considerable speculation has focused on the ^{29}Si NMR shifts expected for various tetrahedral $Si(OSi)_{4-n}(OTi)_n$ sites

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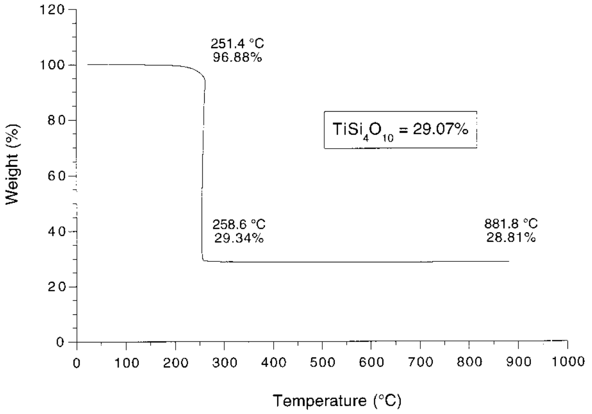

Figure 1. TGA of **1** under a flow of nitrogen (2 °C min^{-1} to 450 °C; 20 °C min^{-1} to 900 °C).

in titania–silica materials.[18] The observed ^{29}Si NMR resonance for **1** at −103.24 ppm is in the region expected for TiOSiO$_3$ sites. In general, infrared spectroscopy of titania–silica materials has been extensively used to identify Ti–O–Si heterolinkages, which give rise to a broad absorption band at 920–960 cm^{-1}.[8e,12b,c,f,i,19] For **1**, this band is seen as a strong, sharp absorption at 925 cm^{-1}, and this assignment is consistent with those for related Ti(OSiR$_3$)$_4$ complexes.[20]

Pyrolytic Conversion of 1 to TiO$_2$·4SiO$_2$ (2). The thermal gravimetric analysis (TGA) of **1** revealed a precipitous weight loss corresponding to the stoichiometric formation of TiO$_2$·4SiO$_2$ (Figure 1). The onset temperature for this decomposition (ca. 250 °C) is considerably higher than those observed for the corresponding zirconium and hafnium analogues (137 and 141 °C, respectively[5a,b]), possibly due to greater steric crowding in **1**, which may restrict the molecular motion required for decomposition. Another indication that the decomposition chemistry for **1** is different from that of the zirconium analogue comes from trapping of the volatiles eliminated in the solid-state thermolysis. For **1**, a 2:1 ratio of isobutylene to *tert*-butanol is observed, whereas predominantly isobutylene is observed in the decomposition of Zr[OSi(O^{t}Bu)$_3$]$_4$. The ceramic yield (29.34%) after heating a sample of **1** to ca. 260 °C under a flow of nitrogen corresponds to the quantitative formation of TiO$_2$·4SiO$_2$ (theoretical yield, 29.07%). Differential thermal analysis (DTA) revealed that the molecule-to-network formation is highly endothermic, and no melting of **1** prior to decomposition was observed. Bulk samples of the tan-colored, titania–silica material TiO$_2$·4SiO$_2$ (**2a**) were obtained by thermolysis of **1** in the solid state at 400 °C.

Given the relatively low temperature at which **1** decomposes to titania–silica materials, it is possible for this conversion to take place in hydrocarbon solution. With related oxygen-rich molecular precursors, we have shown that such conversions allow interesting alternatives to the sol–gel process, in that gels can be formed in nonpolar media and in the presence of other chemical components that are incorporated into the resulting material. In this way, homogeneous materials with very high surface areas have been obtained.[5]

Initial attempts to form TiO$_2$·4SiO$_2$ gels in solution gave inconsistent results, in that some samples of **1** in toluene were readily converted to TiO$_2$·4SiO$_2$ gels at 225 °C, whereas other samples gave solutions that did not convert to gels after prolonged heating (5 days) at 235 °C. This inconsistency may be due to traces of HNEt$_2$ that contaminate samples of **1** (see eq 2) and inhibit the pyrolytic transformation of **1** to TiO$_2$·4SiO$_2$. This hypothesis is supported by related work in which we have shown that the thermal decomposition of Zr[OSi(O^{t}Bu)$_3$]$_4$ is Brønsted acid-catalyzed and inhibited by proton-scavengers.[5b,21] Heating a solution of very pure **1** in toluene at 225 °C for 48 h resulted in formation of a gel, which was allowed to dry in air over 10 days to afford a white xerogel (**2b**).

More consistent results in the preparation of xerogels from **1** were obtained by the addition of acid catalysts to the solution. Thus, thermolysis of **1** in toluene in the presence of a small amount of concentrated HCl afforded a xerogel (**2c**) after heating for 24 h at 225 °C.

Baiker and co-workers have shown that titania–silica aerogels formed by the continuous extraction of solvent with supercritical CO$_2$ show superior catalytic performance in olefin epoxidation compared to that of large pore Ti-molecular sieves.[12d] We were therefore interested in investigating the structural and catalytic properties of aerogel materials generated from the single-source molecular precursor **1**. Extraction of the "wet" gel from the decomposition of **1** in toluene (without acid catalysis) by supercritical CO$_2$ afforded a titania–silica aerogel as a flocculent white material (**2d**).

Characterization of TiO$_2$·4SiO$_2$ Materials 2a–d. Elemental analyses of **2a–d** revealed that prior to calcination under oxygen the carbon content was typically ≤3%. This can be attributed to the incomplete loss of the butoxide groups or the retention of solvent or *tert*-butyl alcohol in the solid. After calcination under oxygen (2 h, 500 °C; heating rate, 10 °C min^{-1}), the carbon contents fell to <1%.

The crystallization behavior of the TiO$_2$·4SiO$_2$ materials **2a** and **2b** at high temperatures was examined. As initially isolated, **2a** was amorphous by powder X-ray diffraction (PXRD), but heating to 1100 °C for 2 h under a flow of oxygen (heating rate of 10 °C min^{-1}) induced the crystallization of anatase, with an average crystallite diameter of 5 nm, as approximated by the Scherrer equation.[22] Further heating of this sample to 1400 °C under an argon flow yielded a mixture of anatase, rutile, and cristobalite, with average crystallite diameters of 35, 26, and 24 nm, respectively (Table 1). **2b** was also amorphous as isolated, and crystallization was not

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Table 1. Surface Area Measurements (BET method) and X-ray Powder Diffraction Data for $TiO_2{\cdot}4SiO_2$ 2a and 2b[a]

	2a		2b	
temp (°C)	surf. area ($m^2\ g^{-1}$)	crystallinity	surf. area ($m^2\ g^{-1}$)	crystallinity
300	20	amorphous	555	amorphous
500	22	amorphous	552	amorphous
700	16	amorphous	482	amorphous
900	17	amorphous	349	amorphous
1100		anatase (5 nm)	78	anatase (7 nm)
1200[b]		anatase (12 nm)		
1300			<1	anatase (22 nm)
1400[b]		anatase (35 nm)	[c]	[c]
1400[b]		rutile (26 nm)	[c]	[c]
1400[b]		cristobalite (24 nm)	[c]	[c]

[a] The surface area measurements and PXRD powder diffraction patterns were recorded on samples that had been heated to the temperature indicated under oxygen and then cooled to room temperature [b] Heated at a rate of 10 °C min^{-1} to 1400 °C under a flow of argon. [c] Not measured.

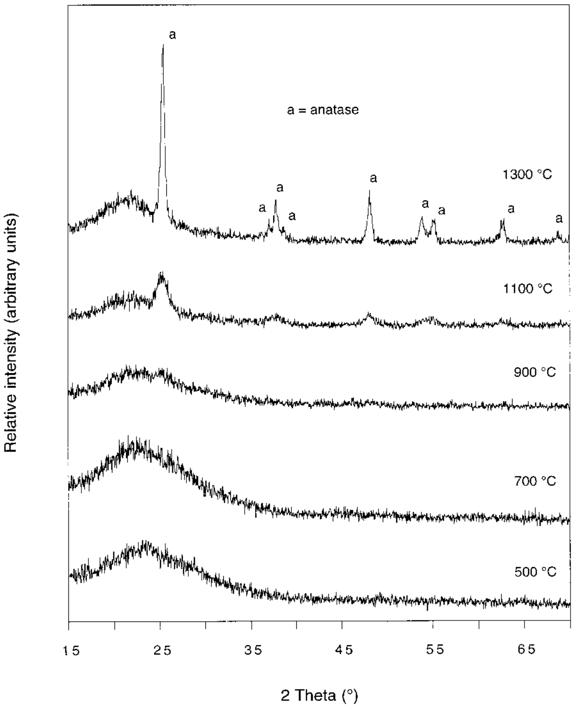

Figure 2. Room temperature PXRD powder patterns of **2b**. Each sample was calcined for 2 h under a flow of oxygen at the temperature indicated.

observed until the sample was heated to 1100 °C for 2 h under a flow of oxygen, where anatase (with an average crystallite size of 7 nm) was detected (Figure 2). After the sample was heated to 1300 °C under oxygen, the anatase crystallites increased in size to an average of 22 nm (Table 1). No rutile or cristobalite was observed under these conditions.

As mentioned previously, infrared spectroscopy has been used extensively to characterize titanium-containing silica materials. Infrared bands at ca. 450, 800, 1100, and 1200 cm^{-1} are assigned to Si−O−Si vibrations.[19c] The absorption band at 920−960 cm^{-1}, attributed to Ti−O−Si heterolinkages involving tetrahedrally coordinated titanium atoms,[8e,12b,c,f,i,19] has been used for the semiquantitative determination of Ti−O−Si connectivities. Recent work, however, has suggested that this peak is a combination of Ti−O−Si and Si−O$^-$ vibrational modes for materials calcined at low temperatures.[23]

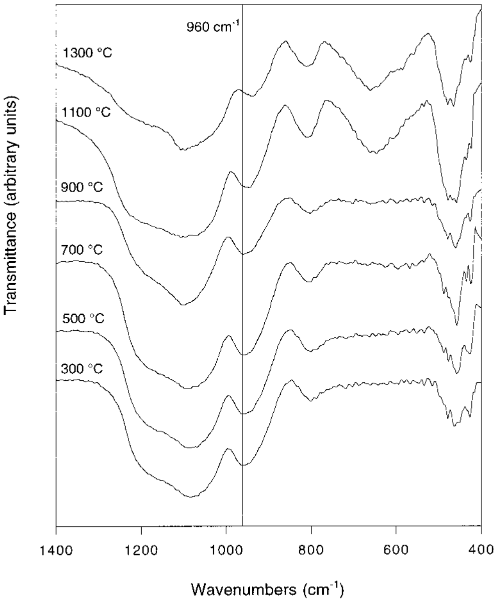

Figure 3. Room temperature IR spectra of **2b**. Each sample was calcined for 2 h under a flow of oxygen at the given temperature.

Infrared spectra were recorded for samples of **2b** that had been heated to various temperatures under a flow of oxygen for 2 h (Figure 3). Absorptions corresponding to Si−O−Si vibrations were observed at the predicted wavenumbers. As the sample was calcined to higher temperatures, these signals (particularly those at ca. 450 and 800 cm^{-1}) increased in intensity. As expected, the Ti−O−Si absorption at ca. 960 cm^{-1} decreased in intensity and shifted slightly to lower wavenumbers as the samples were heated to higher temperatures. These observations are consistent with the PXRD data, which also describe how the heating of **2b** results in sintering and phase separation with the crystallization of titania and silica.

UV−vis spectroscopy has also been employed in the characterization of titania−silica materials.[10c,12i,13a,19a,b,12f,24] The electronic absorption of interest has been attributed to charge transfer between the oxide ions of the lattice and an empty d-orbital of Ti(IV), and positions of this band have been estimated at 45 000−48 000 cm^{-1} for tetrahedral Ti(IV) and at ca. 42 000 cm^{-1} for octahedral Ti(IV) sites.[25] Diffuse reflectance UV−vis (DRUV) spectra were recorded at room temperature on samples of **1** and **2a**−**d** that had been calcined for 2 h at 500 °C under a flow of oxygen. The observed maximum for **1** (44 000 cm^{-1}) is somewhat characteristic for isolated tetrahedral Ti(IV) species in a silica matrix (e.g., a value of 45 000 cm^{-1} for samples of amorphous titania−silica with varying Ti/Si ratios has been attributed to such sites[24c]). Presumably, this reflects the tetrahedral geometry at the metal center of **1** and the "silica-like" nature of the siloxide ligands.

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(24) (a) Beghi, M.; Chiurlo, P.; Costa, L.; Palladino, M.; Pirini, M. F. *J. Non-Cryst. Solids* **1992**, *145*, 175. (b) Fernandez, A.; Leyrer, J.; González-Elipe, A. R.; Munuera, G.; Knözinger, H. *J. Catal* **1988**, *112*, 489. (c) Klein, S.; Weckhuysen, B. M.; Martens, J. A.; Maier, W. F.; Jacobs, P. A. *J. Catal.* **1996**, *163*, 489. (d) Corma, A.; Camblor, M. A.; Esteve, P.; Martinéz, A.; Pérez-Pariente, J. *J. Catal.* **1994**, *145*, 151.

(25) Boccuti, M. R.; Rao, K. M.; Zecchina, A.; Leofanti, G.; Petrini, G. *Stud. Surf. Sci. Catal.* **1989**, *48*, 133.

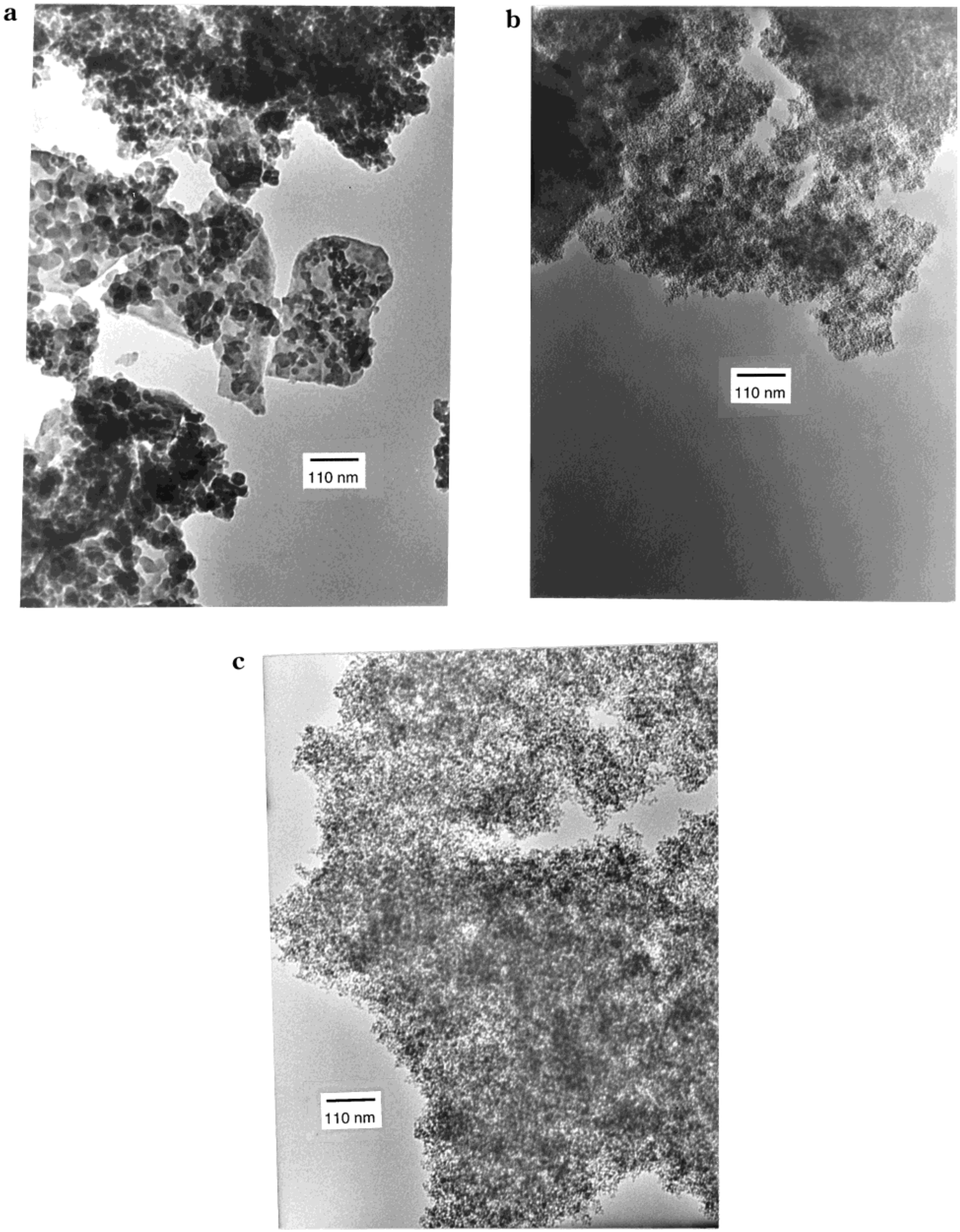

Figure 4. TEM micrographs of $TiO_2 \cdot 4SiO_2$ materials calcined to 500 °C for 2 h in a flow of oxygen (1 cm = 110 nm): (a) **2a** (solid-state conversion), (b) **2b** (xerogel, noncatalyzed), and (c) **2d** (aerogel).

The absorbance maxima for the titanium-containing materials are all broadened and shifted to lower wavenumbers with respect to **1** (**2a**, 43 500 cm^{-1}; **2b,** 39 000 cm^{-1}; **2c**, 37 000 cm^{-1}; **2d,** 40 000 cm^{-1}), which is consistent with the presence of some octahedral titanium sites. Such sites may arise from the coordination of residual organic material or hydration, but attempts to confirm this by dehydrating a sample of **2b** in situ had no effect on the observed absorbance maximum at 39 000 cm^{-1}.[26] In fact, some octahedral sites within the silica matrix are to be expected from the titanium content of **2b** (20 mol % titania), because it has been shown that octahedral titanium sites exist in titania–silica samples with titania contents greater than ca. 8

mol %.[12i,18d] An alternative explanation is the presence of nanodomains of titania (<5 nm; not observed by PXRD), which should cause a shift in the absorption edge toward that of bulk anatase (30 000 cm^{-1}).[12i]

The surface areas and porosities of the TiO_2·$4SiO_2$ materials **2a**−**d** (calcined at 500 °C under oxygen) differ according to the synthetic procedures used to prepare each sample. As expected, the sample obtained by the solid transformation of **1** (**2a**) has a low surface area (22 m^2 g^{-1}; determined by the BET (Brunauer−Emmett−Teller) method) and a low total pore volume of 0.29 cm^3 g^{-1}. The thermolysis of **1** in toluene results in a material (**2b**) with a much higher surface area and pore volume (552 cm^2 g^{-1} and 1.84 cm^3 g^{-1}, respectively). These properties, which approach those associated with aerogels, presumably result from use of nonpolar solvents, which due to their low surface tension minimize collapse of the network pore structure during solvent evaporation.[3a] For comparison, aerogel **2d**, prepared by exchange of the toluene solvent with supercritical CO_2, possesses a surface area of 677 m^2 g^{-1} and a total pore volume of 2.53 cm^3 g^{-1}. For **2c**, which was obtained by an acid-catalyzed route, the surface area was 399 m^2 g^{-1} and the total pore volume was 1.766 cm^3 g^{-1}.

Figure 4 shows TEM micrographs of **2a**, **2b**, and **2d** (calcined at 500 °C for 2 h under a flow of oxygen). **2a** consists of densely packed, roughly spherical particles with diameters of 20−30 nm and a large dispersity in size. In contrast, the xerogel and aerogel materials are made up of much smaller particles (<ca. 5 nm) that are of uniform size and resemble titania−silica aerogel materials synthesized by the sol−gel method.[12h] The aerogel (Figure 4c) is less densely packed than the xerogel material, as might be expected.

Epoxidation Catalysis. Samples of **1**, **2a**−**d**, and **1** supported on silica were investigated as catalysts in the epoxidation of cyclohexene to cyclohexene oxide. Initial experiments at 65 °C using 0.05 g of **2b** (calcined to 500 °C under oxygen) and aqueous hydrogen peroxide (30 wt %) failed to yield any cyclohexene oxide product (after 2 h), as determined by GC. Under these conditions, the solid catalyst underwent an immediate color change from white to yellow upon addition of the peroxide, indicating formation of surface titanium-peroxo species.[12d] The observed lack of catalysis is attributed to the presence of water, which is known to severely inhibit the epoxidation reaction.[27] Accordingly, further experiments employed organic hydroperoxides (*tert*-butyl hydroperoxide, TBHP, and cumene hydroperoxide, CHP) as oxidants for the epoxidation of cyclohexene.

It was found that the molecular precursor **1** (0.172 g) in toluene (5 mL) at 65 °C is an active homogeneous catalyst for the epoxidation of cyclohexene with CHP as the stoichiometric oxidant. After 2 h at 65 °C, a 63.8% yield of cyclohexene oxide (relative to the initial amount of the limiting reagent, CHP) was observed. This conversion corresponds to 20 turnovers.

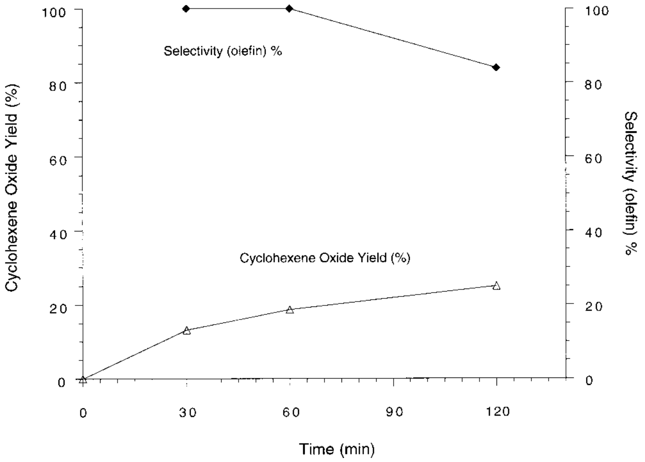

Figure 5. Yield of cyclohexene oxide (Δ) relative to initial cumene hydrogen peroxide as a function of time during the epoxidation of cyclohexene with **2c** (0.05 g). Selectivity (◆) of the reaction to olefin as a function of time.

Samples of **2a**−**d** (calcined to 500 °C under oxygen) were found to exhibit activity as catalysts for the epoxidation of cyclohexene with CHP or TBHP as the oxidant, in toluene at 65 °C. To compare activities for the heterogeneous catalysts, results were standardized with respect to the mass of catalyst used (0.05 g). In control experiments with **2c** and no hydroperoxide, or with CHP and no catalyst, no cyclohexene oxide product was observed by GC analysis after 2 h. To determine whether the active species leached into solution during a typical catalytic run, a sample of **2c** and CHP in toluene (5.0 mL) was heated to 65 °C for 3 h with rapid stirring. The mixture was then filtered via cannula while still hot, and the filtrate was treated with cyclohexene at 65 °C. Samples of this reaction mixture taken after 10, 30, 60, and 120 min contained no cyclohexene oxide product (by GC analysis), indicating that leaching of a catalytically active titanium species into solution had not occurred. At this time, we cannot rule out the possibility that catalytically inactive species have leached into solution.

Xerogel **2b** is an active catalyst with both TBHP and CHP as the oxidant at 65 °C in toluene solvent (5.0 mL), yielding 16.2% (TBHP) and 37.8% (CHP) of cyclohexene oxide after 2 h (relative to initial peroxide). In general, the initial cyclohexene oxide production is rapid (over the first 30 min of the reaction), and a reduced rate is observed during the remaining 90 min. This is attributed to retardation of the catalysis caused by increasing quantities of the alcohol coproduct in the reaction mixture, hindering formation of the active titanium−hydroperoxide complex and its subsequent reaction with cyclohexene.[28]

To investigate the selectivity of the epoxidation (defined in eq 3), a representative experiment was performed using cyclohexene (1 mL), xerogel **2c** (0.05 g), and CHP (0.92 mL) in toluene (5 mL). The results are presented in Figure 5, which illustrates the yield of cyclohexene oxide and the selectivity for olefin as a function of time. The catalyst was found to be 100% selective over the first 1 h of the reaction. However, the

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(26) A sample of **2b** (0.05 g) was suspended in H_2O (3 mL) and stirred at ambient temperature for 2 h. The material was dried in air for 24 h, and the DRUV−vis spectrum recorded at room temperature exhibited a peak maximum at 39 000 cm^{-1}. The sample was heated to 450 °C in the spectrometer under a flow of dry air and held at that temperature for 3 h. Upon cooling to room temperature, the DRUV−vis spectrum was again recorded, and it showed no shift in the absorbance maximum.

(27) Sheldon, R. A. *J. Mol. Catal.* **1980**, *7*, 107.

(28) A similar effect has been studied in the homogeneous epoxidation of olefins with organic hydroperoxides: Sheldon, R. A.; van Doorn, J. A. *J. Catal.* **1973**, *31*, 427.

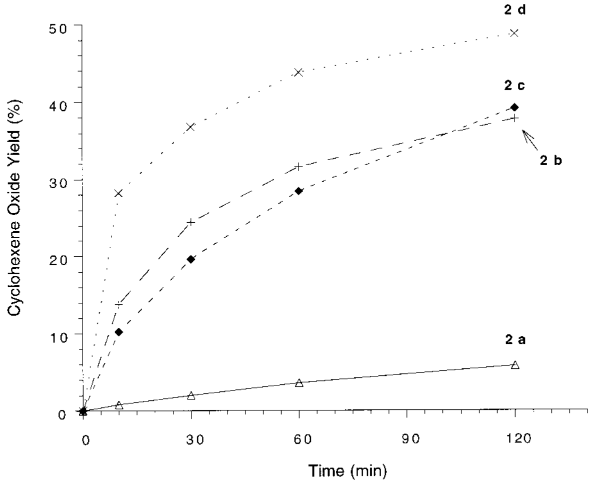

Figure 6. Yield of cyclohexene oxide relative to initial cumene hydrogen peroxide as a function of time during the epoxidation of cyclohexene with 0.05 g of **2a** (△), **2b** (+), **2c** (◆), and **2d** (×).

selectivity drops to 84% after the second hour, consistent with further reactivity of the epoxide to give a mixture of products.[29]

$$S_{\mathrm{olefin}}\ (\%) = 100 \times [\mathrm{epoxide}]_f/[\mathrm{olefin}]_i - [\mathrm{olefin}]_f \quad (3)$$

A graph comparing the activities of **2a**–**d** as catalysts (on a per gram basis) in the epoxidation of cyclohexene with CHP under identical reaction conditions is presented in Figure 6. Generally, the titania–silica materials with higher surface areas and greater pore volumes exhibit a higher activity for the production of cyclohexene oxide. This is presumably a consequence of the increased number of active titanium sites accessible for reaction. After 1 h, this trend is less evident, and after 2 h, the activities have leveled off to comparable rates. Notably, however, the production of cyclohexene oxide is greater for **2c** than for **2b**, despite the surface area of **2c** being ca. 150 m^2 g^{-1} less. This may be due to a higher concentration of site-isolated titanium in **2c**, which is consistent with the UV–vis data suggesting the presence of smaller titanium domains for **2c** (vide supra).

It is of interest to note that Baiker et al. report that their uncalcined titania–silica aerogels have a greater activity toward the epoxidation of cyclohexene (using CHP), than that of samples calcined to temperatures between 400 and 800 °C.[12d] The enhanced activity was attributed to the presence of organic residues in the material, but the mechanism responsible is unknown. The influence of calcination on the epoxidation activity of $TiO_2{\cdot}4SiO_2$ was therefore investigated, using samples of **2c** and **2d**. Under identical reaction conditions, the percent yield of cyclohexene oxide after 2 h at 65 °C is considerably higher for materials that have been calcined at 500 °C under a flow of oxygen (**2c**, 37.8%; **2d**, 48.8%) relative to the uncalcined materials (**2c**, 17.4%; **2d**, 14.4%). At this point, the exact cause of the increased activity is not known; it is possible that a structural change occurs during the calcination process or that the difference in activities is due to removal of the residual organic material, exposing or activating the titanium atoms in the catalyst.

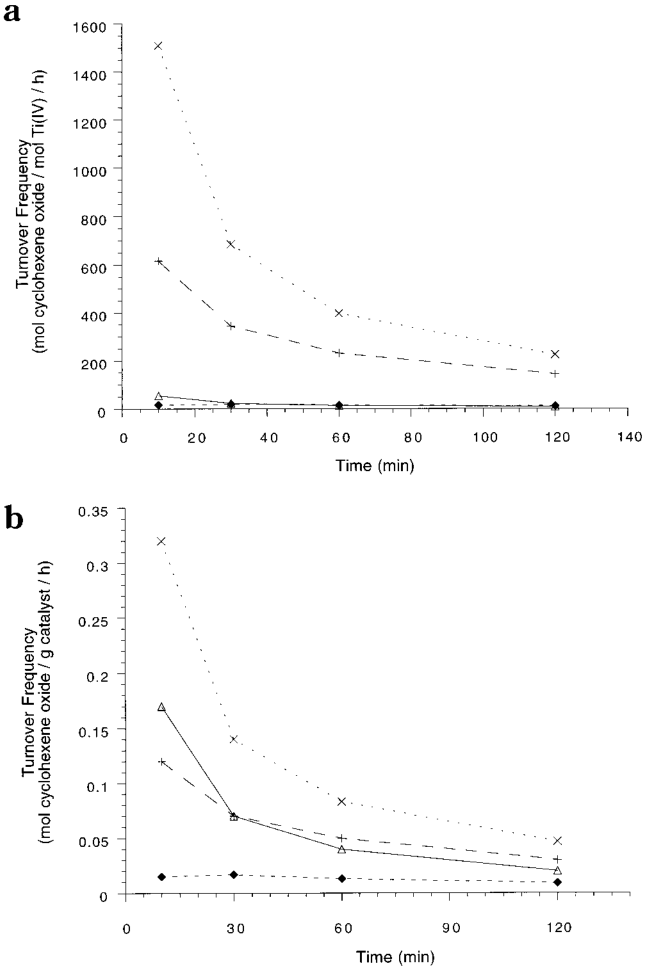

Figure 7. Turnover frequencies (TOFs) as a function of time during the epoxidation of cyclohexene with **1** (◆, 0.17 g), **2d** (△, 0.05 g), the Shell catalyst (+, 0.05 g), and **1** supported on silica (×, 0.05 g). (a) TOF = moles cyclohexene oxide per moles Ti(IV) per hour. (b) TOF = moles cyclohexene oxide per gram catalyst per hour.

To investigate the use of the titanium siloxide precursor $Ti[OSi(O^tBu)_3]_4$ in grafting titanium sites onto a silica substrate,[30] a sample of hydrated silica (Degussa Aerosil 200; surface area, 203 m^2 g^{-1}; pore volume, 0.17 cm^3 g^{-1}) was treated with **1**. After calcination (300 °C under nitrogen for 1 h, 600 °C under dry air for 4 h), the resultant material (surface area, 199 m^2 g^{-1}; pore volume, 0.20 cm^3 g^{-1}) was found to be extremely active in the epoxidation of cyclohexene with CHP as oxidant, producing a 94.4% yield of cyclohexene oxide after 2 h at 65 °C in toluene (5.0 mL).

To make comparisons between the different systems investigated in this study, the catalyst activity in

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[29] GC/MS analysis of an aliquot of a typical catalytic experiment taken after 2 h indicated the presence of small amounts of multiple oxidation products, including 2-cyclohexen-1-ol, 7-oxabicyclo[4.1.0]-heptan-2-ol, and 1,2-cyclohexanediol.

[30] (a) Fraile, J. M.; García, J. I.; Mayoral, J. A.; de Mènorval, L. C.; Rachdi, F. *J. Chem. Soc., Chem. Commun.* **1995**, 539. (b) Cativiela, C.; Fraile, J. M.; García, J. I.; Mayoral, J. A. *J. Mol. Catal. A* **1996**, *112*, 259. (c) Jorda, E.; Tuel, A.; Teissier, R.; Kervennal, J. *J. Chem. Soc., Chem. Commun.* **1995**, 1775. (d) Jorda, E.; Tuel, A.; Teissier, R.; Kervennal, J. *J. Catal.* **1998**, *175*, 93. (e) Oldroyd, R. D.; Thomas, J. M.; Maschmeyer, T.; MacFaul, P. A.; Snelgrove, D. W.; Ingold, K. U.; Wayner, D. D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2787. (f) Chen, L. Y.; Chuah, G. K.; Jaenicke, S. *Catal. Lett.* **1998**, *50*, 107.

Table 2. Comparison of Initial Rates in the Epoxidation of Cyclohexene Calculated over the First 10 min of the Reaction

sample	initial rate (mmol/min/g cat)
1	0.25
2a	0.08
2b	1.38
2c	1.02
2d	2.82
titania supported on silica (Shell catalyst)	2.08
1 supported on silica	5.28
5 wt % $TiO_{2\ aerogel}$[a]	2.95
10 wt % $TiO_{2\ aerogel}$[a]	6.01

[a] Initial rate measured over 5 min; see Hutter et al.[12d]

Table 3. Comparison between the Composition, Surface Area, and Pore Volume of Titania−Silica Materials Prepared Using Different Procedures

sample	comp.[a]	surf. area; temp[b]	pore vol[c]	ref
2a (solid-state conversion)	25	22; 500	0.3	this work
2b (xerogel)	25	552; 500	1.8	this work
xerogel (sol−gel hydrolysis)	10	683; 400	1.7	12c
xerogel (sol−gel, prehydrolysis[d])	10	533; 400	1.2	12c
xerogel (sol−gel hydrolysis)	5.2	236; 540	[e]	35
2d (aerogel; CO_2 extraction)	25	677; 500	2.5	this work
aerogel (sol−gel hydrolysis; CO_2 extraction)	20	674; 400	1.5	12c
aerogel (sol−gel hydrolysis; ^{i}PrOH extraction)	10	598; 400	3.6	12c
titanium silicalite-1 (TS-1 zeolite)	2.4	348; 540	[e]	35
Ti−MCM41	2.3[e]	936; 540	0.5	10a

[a] Composition in weight percent of TiO_2. [b] Surface area in square meters per gram and calcination temperature in degrees Celsius. [c] In cubic centimeters per gram. [d] Prehydrolysis of tetramethoxysilicon(IV) with acidified H_2O. [e] Value not reported.

turnover frequencies (TOFs), defined as moles of epoxide produced per mole of Ti(IV) per hour were determined and compared with a standard catalyst prepared by introduction of titanium sites onto silica using $Ti(O^iPr)_4$ (the "Shell catalyst"; surface area, 172 m^2 g^{-1}; pore volume, 0.22 cm^3 g^{-1}).[7,12d] The results are illustrated in Figure 7a, which compares the catalyst efficiencies for **1**, the most active TiO_2·$4SiO_2$ material (**2d**), and the titanium-supported catalysts. This comparison can be misleading, however, as it assumes that all of the titanium in the catalysts are equally accessible for reaction with the substrates. This is clearly not the case; for the homogeneous (**1**) and titanium-supported catalysts, it is reasonable to assume that all of the titanium centers are available for reaction, whereas for TiO_2·$4SiO_2$ materials **2a**−**d**, the titanium is located throughout the bulk of the material in addition to that at the surface, and therefore much of it is inaccessible. When comparing the different catalyst systems, it is therefore convenient to calculate the TOF's in terms of the *mass* of catalyst (i.e., moles of epoxide produced per *gram* of catalyst per hour; see Figure 7b). In these comparisons, we see that the aerogel **2d** is comparable to the Shell catalyst, and supported **1** is a superior epoxidation catalyst for this reaction.

The initial rates of the epoxidation of cyclohexene for the different catalysts were calculated and compared with values of highly active titania−silica aerogels prepared by the sol−gel method (Table 2).[12d] We observe that the values for **2a**−**c** are significantly lower than those for the aerogels described by Baiker. Catalyst **2d** exhibits a slightly better initial rate than that of the 5 wt % aerogel, whereas the rate for material obtained by grafting **1** onto silica approaches that reported for the best aerogel catalyst reported.

Concluding Remarks

The $Ti(OSiO_3)_4$ core of $Ti[OSi(O^tBu)_3]_4$ makes this compound an interesting model for isolated titanium atoms on silica. Here, we have shown that the spectroscopy of **1** and its chemistry are consistent with what is expected for isolated titanium sites in silica. Related molecular models based on titanium silsesquioxane structures have been investigated, but these compounds possess Si−C bonds.[31]

In this study, we have shown that the molecular species **1** is a versatile reagent for both the preparation of bulk TiO_2·$4SiO_2$ materials and grafting titanium species onto the surface of silica. As for other tris(alkoxy)siloxy derivatives,[5] **1** undergoes a clean pyrolytic conversion to the stoichiometric amount of the metal oxide−silica material. The chemistry involved in network formation appears to involve the Brønsted acid-catalyzed elimination of isobutylene from $-O^tBu$ groups to produce Si−OH functionalities, which then condense with one another (to produce water) or with an $Si-O^tBu$ group (to produce *tert*-butanol). The present study with **1** emphasizes the importance of reaction conditions in determining properties for the final TiO_2·$4SiO_2$ material and the benefits of employing pure, isolated molecular precursors in obtaining clean conversions and useful properties. A recent communication by Neumann and co-workers described the reaction of $TiCl_4$ with $HOSi(O^tBu)_3$ in solution in the presence of NEt_3, followed by removal of solvent and calcination. The resulting material possessed a low surface area (25 ± 5 m^2 g^{-1}) and exhibited a low activity toward the epoxidation of cyclooctene.[32]

The use of **1** as a precursor to titania−silica materials can provide distinct advantages, derived from the solubility properties of this compound. In particular, the thermolysis can be carried out under nonhydrolytic conditions, and with nonpolar hydrocarbon solvents, very high surface areas are obtained. As shown in Table 3, **2b** and **2d** exhibit surface areas and pore volumes that are comparable to those reported for titania−silica xerogels and aerogels prepared under optimized sol−gel conditions. Note that **2b** and **2d** have a compara-

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(31) (a) Feher, F. J.; Gonzales, S. L.; Ziller, J. W. *Inorg. Chem.* **1988**, *27*, 3440. (b) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1990**, *29*, 1604. (c) Abbenhuis, H. C. L.; Krijnen, S.; van Santen, R. A. *Chem. Commun.* **1997**, 331. (d) Maschmeyer, T.; Klunduk, M. C.; Martin, C. M.; Shephard, D. S.; Thomas, J. M.; Johnson, B. F. G. *Chem. Commun.* **1997**, 1847. (e) Crocker, M.; Herold, R. H. M.; Orpen, A. G. *Chem. Commun.* **1997**, 2411.

(32) Juwiler, D.; Blum, J.; Neumann, R. *Chem. Commun.* **1998**, 1123.

tively high titanium loading (25 wt % TiO_2), and it is widely assumed that surface areas for titania−silica materials decrease markedly with titanium content.[12c,13,19b] In this study, we have also demonstrated the utility of acid catalysis in initiating thermolytic condensation and giving more consistent results. Variations in the drying method afford materials with different physical and catalytic properties. For example, extraction of toluene from the wet gel with supercritical CO_2 affords an aerogel (**2d**) with a greater surface area and enhanced catalytic activity.

For many applications in catalysis, a high dispersion of titanium in a silica matrix (and a high concentration of Si−O−Ti heterolinkages) is desired.[12] With respect to catalytic epoxidation, isolated titanium sites are thought to be most active, and large domains of titania are known to catalytically decompose the peroxide oxidant.[12d] The relatively high catalytic activities for **2b**−**d** suggest a high degree of dispersion of the titanium throughout the silica matrix. This is further supported by PXRD data, which indicate that the crystallization of anatase and rutile require heating to high temperatures, because the delayed crystallization of titania in titania−silica samples seems to be correlated with homogeneity in the starting material.[13,18d] This crystallization behavior is consistent with the observed decrease in intensity and shift of the IR stretch at 960 cm^{-1} (associated with Ti−O−Si linkages) as **2b** is heated to high temperatures. The UV−vis data may suggest the presence of titania nanodomains (too small to be detected by PXRD; ≤ca. 5 nm) in samples heated to 500 °C, but infrared spectra indicate that significant quantities of Ti−O−Si linkages remain in these samples (Figure 3).

For the first time, we have shown that a tris(*tert*-butoxy)siloxide precursor such as **1** is effective for the introduction of catalytically active sites on an oxide surface. The catalyst derived from supporting **1** onto the surface of silica particles is surprisingly active and significantly more active than the Shell catalyst generated by reaction of $Ti(O^iPr)_4$ with silica particles. This suggests that the $-OSi(O^tBu)_3$ ligand provides an important and beneficial effect on the structure of the supported catalytic site. In particular, the trialkoxy(siloxy) ligand set probably serves to produce isolated $-O-Ti(-O-Si)_3$ sites on the catalyst surface. Future work will address optimization of this approach in the preparation of new catalysts. In particular, grafting **1** onto supports of very high surface area (e.g., silica aerogels[33] and MCM materials[34]) should lead to highly active catalysts.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen or argon using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Dry oxygen-free solvents were used throughout. NMR spectra were recorded on a GE QE−300 (at 300 (^1H) or 75.5 (^{13}C) MHz), or a Bruker DRX 500 (at 99.4 (^{29}Si) MHz). Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. Thermolyses were performed using a Lindberg 1700 °C or a Lindberg 1200 °C three-zone tube furnace. Thermal analysis were performed on a Du Pont model 2000 thermal analysis system. Surface areas were measured using the BET method on a QuantaChrome Autosorb 6 surface area analyzer. Powder X-ray diffraction was performed on a Phillips PW1720 or a Siemens D5000 diffractometer. DRUV−vis spectra were recorded on a Varian Cary 4 UV−vis spectrometer modified for in situ heating under a flow of gas, using MgO as a reference. GC analyses were performed with a Hewlett Packard HP 6890 series GC system, using a methyl siloxane capillary (50.0 m × 320 μm × 1.05 μm nominal), and integration was performed relative to an internal standard (dodecane). The TEM micrographs were obtained on a JEOL 200CX microscope at 160 kV. The samples were prepared by depositing a pentane suspension of the finely ground powders onto “type A” carbon-coated copper grids from Ted Pella, Inc. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Desert Analytics, and the College of Chemistry Microanalytical Facility. $LiNEt_2$ was freshly prepared from $HNEt_2$ and ^nBuLi. $Ti(NEt_2)_4$ was synthesized according to the literature procedure.[16] Cyclohexene (distilled), dodecane, hydrogen peroxide (30 wt % solution in water), cumene hydroperoxide (80% tech.), and *tert*-butyl hydroperoxide (5.0−6.0 M solution in decane) were purchased from Aldrich and used as received unless otherwise stated.

$Ti[OSi(O^tBu)_3]_4$ (1). A toluene solution (50 mL) of $HOSi(O^tBu)_3$ (5.067 g, 19.16 mmol) was added to a stirring toluene solution (50 mL) of $Ti(NEt_2)_4$ (1.755 g, 4.78 mmol). The mixture was refluxed for 4 h, the toluene was removed in vacuo, and the solid was extracted with pentane (75 mL). Concentration and cooling to −78 °C afforded 4.104 g of **1** as white crystals in 78% yield. Molecular weight (benzene): 1360. Calcd for monomer: 1102. Anal. Calcd for $C_{48}H_{108}O_{16}Si_4Ti$: C, 52.3; H, 9.88. Found: C, 52.5; H, 9.94. IR (Nujol, CsI, cm^{-1}): 1386 m, 1364 m, 1240 m, 1215 wsh, 1190 s, 1065 vs, 1027 wsh, 980 vw, 925 vs, 830 m, 805 vw, 700 m, 665 vw, 491 wsh, 470 w, 425 w, 375 w, 320 w. ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 1.54 (108H). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ 32.31 (CMe_3), 72.91 (CMe_3). ^{29}Si NMR (99.4 MHz, benzene-d_6, 22 °C): δ −103.24.

Preparation of Shell Epoxidation Catalyst.[7,12d] A 20.0 g sample of Aerosil 200 (Degussa) was placed in a 1 L flask. Deionized water (150 mL) was added, and the resulting mixture was agitated until all of the silica was wet. After standing for 3 h, the excess water was removed under vacuum, and the resultant solid was heated to 77 °C under vacuum, lightly ground, and sieved (the material passing through a 1 mm sieve but not a 0.355 mm sieve was kept). The resulting solid was heated to 200 °C under a nitrogen atmosphere for 6 h. A 5.0 g sample was suspended in anhydrous 2-propanol (25 mL). A 2-propanol solution (4.5 mL) of $Ti(O^iPr)_4$ (0.473 g, 1.66 mmol) and acacH (0.333 g, 3.33 mmol) was prepared and allowed to stand for 40 min before being added to the silica suspension. The aerosil immediately turned yellow. This mixture was refluxed for 22 h. The solid was collected on a frit and washed with 50 mL of 2-propanol. The catalyst was then heated further in a tube furnace, initially to 300 °C under nitrogen for 1 h, and then 600 °C under dry air for 4 h. Anal. Found: Ti, 0.97%.

Supporting 1 on Silica. 1.83 g (1.66 mmol) of **1** was supported on 5.0 g of hydrated silica (prepared as above) using a method similar to that described for the preparation of the Shell catalyst. No acacH was added to the solution of $Ti[OSi(O^tBu)_3]_4$ solution prior to addition to the silica slurry, and no color change was observed on mixing of the two components. After 22 h of reflux, the solid was collected on a frit and dried as described above. Anal. Found: Ti, 1.01%.

Formation of 2a. A sample of **1** (0.500 g) was weighed in a quartz boat in an inert atmosphere glovebox. The sample was removed and heated under an oxygen flow at a rate of 10 °C min^{-1} to 400 °C (2 h at 400 °C). The sample was allowed to

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cool to room temperature, affording 0.147 g of a white solid (29.4%). This material (carbon content, 0.34%) was subsequently calcined to various temperatures. After calcination at 500 °C under oxygen, the carbon content was 0.14% (hydrogen was not detected).

Formation of Xerogel 2b. 1 (1.50 g) was dissolved in a mixture of dry toluene (10.0 mL) and nondistilled wet toluene (1.0 mL) in a 100 mL Pyrex ampule. The solution was frozen, and the vessel was evacuated. The ampule was heated at a rate of 10 °C min^{-1} to 225 °C and was maintained at this temperature for 48 h. This afforded a solid wet "gel" that was removed and allowed to dry in air for 10 days to form the xerogel. The hard xerogel was ground to a fine powder and heated under a nitrogen flow at a rate of 0.1 °C min^{-1} to 50 °C (12 h at 50 °C) and then further heated at a rate of 0.1 °C min^{-1} to 100 °C (12 h at 100 °C) to afford a light brown solid. This material (carbon content, 2.77%) was subsequently calcined to various temperatures. After calcination at 500 °C under oxygen, the carbon content was 0.15% (hydrogen was not detected).

Formation of Xerogel 2c. This material was prepared in a manner similar to that described for **2b**, using 1.50 g of **1**, 10 mL of toluene, and 2 drops of concentrated HCl. The thermolysis and drying were carried out under conditions identical to those for **2b**, to give an off-white solid. This material (carbon content, 1.23%; chlorine content, 0.38%) was subsequently calcined to various temperatures. After calcination at 500 °C under oxygen, the carbon content was 0.95% (hydrogen was not detected).

Formation of Aerogel 2d. A sample of the transparent, wet gel, prepared as described for **2b** above, was dried using supercritical carbon dioxide in a 300 mL Polaron Critical Point Dryer. The majority of the toluene was replaced by flowing liquid CO_2 (5 °C, 850 psi) over a 3 h period. During this process, the gel changed from colorless and transparent to opaque and white. The system was maintained under these conditions overnight to ensure complete diffusion of the toluene from within the gel. After an additional 1 h of liquid CO_2 purging, the CO_2 inlet was closed, and the temperature of the vessel was raised to 45 °C. The CO_2 was vented to maintain a pressure of 1350−1450 psi. After maintaining these conditions for 1 h, the system was vented to ambient pressure over 45 min to afford the aerogel as an off-white solid. This material (carbon content, 1.89%) was subsequently calcined to various temperatures. After calcination at 500 °C under oxygen, the carbon content was 0.19% (hydrogen was not detected).

Catalysis Procedure. A sample of catalyst (0.05 g) was added to a 50 mL round-bottom flask that had previously been evacuated and filled with nitrogen three times. Toluene (5.00 mL), cyclohexene (2.50 mL, 24.7 mmol), and dodecane (0.25 mL) were added by syringe through a septum under a flow of nitrogen. The mixture was allowed to equilibrate at the reaction temperature of 65 °C for 10 min. Cumene hydroperoxide (0.92 mL) or *tert*-butyl hydroperoxide (1.00 mL) was added by syringe to the rapidly stirring solution. Aliquots (ca. 0.25 mL) were removed from the reaction mixture by syringe after 10, 30, 60, and 120 min and filtered. The filtrate was analyzed by GC, and assignments were made by comparison with authentic samples analyzed under the same conditions.

For the catalysis using **1**, the aliquots (ca. 0.5 mL) were removed and immediately quenched with distilled water (0.25 mL). Vigorous agitation resulted in the formation of a white solid, presumed to be $TiO_x(OH)_y$. This was filtered twice to remove all traces of the solid, and GC was performed as described above.

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