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Silica-Supported, Single-Site Titanium Catalysts for Olefin Epoxidation. A Molecular Precursor Strategy for Control of Catalyst Structure

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Abstract: A molecular precursor approach involving simple grafting procedures was used to produce site-isolated titanium-supported epoxidation catalysts of high activity and selectivity. The tris(*tert*-butoxy)siloxy titanium complexes Ti[OSi(O^{t}Bu)$_3$]$_4$ (**TiSi4**), (^{i}PrO)Ti[OSi(O^{t}Bu)$_3$]$_3$ (**TiSi3**), and (^{t}BuO)$_3$TiOSi(O^{t}Bu)$_3$ (**TiSi**) react with the hydroxyl groups of amorphous Aerosil, mesoporous MCM-41, and SBA-15 via loss of HO^{t}Bu and/or HOSi(O^{t}Bu)$_3$ and introduction of titanium species onto the silica surface. Powder X-ray diffraction, nitrogen adsorption/desorption, infrared, and diffuse reflectance ultraviolet spectroscopies were used to investigate the structures and chemical natures of the surface-bound titanium species. The titanium species exist mainly in isolated, tetrahedral coordination environments. Increasing the number of siloxide ligands in the molecular precursor decreases the amount of titanium that can be introduced this way, but also enhances the catalytic activity and selectivity for the epoxidation of cyclohexene with cumene hydroperoxide as oxidant. In addition, the high surface area mesoporous silicas (MCM-41 and SBA-15) are more effective than amorphous silica as supports for these catalysts. Supporting **TiSi3** on the SBA-15 affords highly active cyclohexene epoxidation catalysts (0.25−1.77 wt % Ti loading) that provide turnover frequencies (TOFs) of 500−1500 h^{-1} after 1 h (TOFs are reduced by about half after calcination). These results demonstrate that oxygen-rich siloxide complexes of titanium are useful as precursors to supported epoxidation catalysts.

Introduction

Catalytic oxidation processes play an important role in the industrial production of fine chemicals.[1] Among the newer oxidation catalysts attracting interest are titanium-substituted zeolites (e.g., TS-1, TS-2, Ti-β, and Ti−ZSM), which have been shown to be active for selective oxidations of a variety of organic compounds in the presence of hydrogen peroxide.[2−7] However, large organic molecules cannot access the active sites that are located inside the relatively small cavities and channels of the zeolites. A solution to this problem was reported in 1992, with the introduction of mesoporous molecular sieves (M41S) which can be synthesized with pore sizes from 15 to 100 Å.[8,9] The earliest application of these materials in producing supported titanium oxidation catalysts was described by Corma et al., who reported the synthesis of Ti-containing MCM-41.[10,11] Subsequently, Thomas and co-workers have conducted in-depth studies into the synthesis and characterization of epoxidation catalysts derived from MCM-41 mesoporous silica. In these investigations, Ti(IV) ions were grafted onto MCM-41 with titanocene as a molecular precursor.[12] Such surface-grafted Ti↑MCM-41 catalysts appear to be substantially more active than framework-embedded Ti→MCM-41 materials in terms of activity per titanium center, because of the greater accessibility of the grafted metal centers to the reactants.[13,14]

Investigations of titanium-supported epoxidation catalysts support the general consensus that the most active and selective sites are isolated, mononuclear, 4-coordinate Ti(IV) centers.[15−19] More generally, it is now recognized that a number of the most

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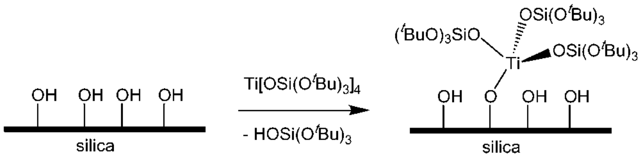
promising oxidation catalysts are characterized by well-defined active sites containing one or only a few metal centers on the surface of an oxide support.[20−23] Typically, these active sites are associated with a specific inorganic structure that gives rise to the desired catalytic properties. Thus, an important challenge in catalysis research is the development of synthetic methods that allow the chemical modification of oxide surfaces with introduction of inorganic surface species with a precise structure and composition.[24] Unfortunately, there is a current lack of reliable, general synthetic methods that allow such fine control over solid-state structures. Most attempts to produce single-site, catalytic structures of this type have involved aqueous impregnation techniques. However, aqueous conditions often promote the agglomeration of metal oxide species on the support.[25]

We have been investigating the use of oxygen-rich molecular precursors for the controlled synthesis of well-dispersed, mixed-element oxides with specific microstructures.[24−42] Potential advantages to this approach derive from the molecular-level control that may be exerted over the structure of a catalytic site. For example, metal complexes containing the tris(*tert*-butoxy)siloxide [$-OSi(O^tBu)_3$] ligand are convenient precursors to homogeneous (well-dispersed) metal oxide−silica materials containing isolated $M(OSiO_3)_n$ structures. The generation of homogeneously dispersed structures of this type appears to be promoted by the facile, low-temperature elimination of isobutene and water from the precursors under mild conditions. The titanium siloxide precursor $Ti[OSi(O^tBu)_3]_4$ (**TiSi4**) serves as an efficient precursor to dispersed $TiO_2{\cdot}4SiO_2$ materials which behave as active epoxidation catalysts.[37] The observed catalytic properties of these materials presumably reflect the high concentration of isolated, tetrahedral titanium sites that result from the preparative route involving a molecular precursor, with a preformed tetrahedral $Ti(OSiO_3)_4$ core, and the nonaqueous synthetic conditions.

The results obtained with the **TiSi4** system suggested that a similar approach might be used to introduce single, tetrahedral titanium sites onto a silica surface, by way of a grafting procedure involving reaction of the precursor with hydroxy groups on the surface (Scheme 1). In initial investigations along these lines, we observed that treatment of amorphous silica with **TiSi4** produced catalysts that were highly active (on a per site basis) for the selective epoxidation of cyclohexene with cumene hydroperoxide as the oxidant. These catalysts were more active than the Shell catalyst derived from treatment of silica with $Ti(O^iPr)_4$.[37]

Scheme 1



The synthetic approach outlined in Scheme 1 represents a potentially general route to isolated, surface-bound species of a particular structure and composition. This will require that the intially grafted, molecular species undergo facile thermolytic eliminations of isobutene and water to give a stable inorganic "single site". Given this possibility, we have initiated a detailed investigation into the use of this approach for preparing epoxidation catalysts based on titanium. In this endeavor, we have targeted materials with a high surface area, to provide the highest concentration of active sites per unit volume of catalyst, and with the highest loading of site-isolated titanium centers.

The high surface area supports employed in these studies are the mesoporous silicas MCM-41 and SBA-15. SBA-15 is a newly discovered mesoporous silica molecular sieve with uniform hexagonal channels ranging from 50 to 300 Å and thick framework walls (31−64 Å). This is a promising new catalyst support material, especially given its thick walls, which provide a hydrothermal stability that exceeds that for the thinner-walled MCM-41 materials.[43,44] The incorporation of titanium into mesoporous SBA-15 has been reported;[45−47] however, only one recent report describes the catalytic behavior of these materials in the selective oxidation of an alkene.[48]

In search of the most effective molecular precursor for grafting titanium siloxide species onto a silica surface, we examined three complexes with varying Ti:Si ratios: $Ti[OSi(O^tBu)_3]_4$ (**TiSi4**), $(^iPrO)Ti[OSi(O^tBu)_3]_3$[49] (**TiSi3**), and $(^tBuO)_3TiOSi(O^tBu)_3$[50] (**TiSi**). As described below, the grafting of these titanium siloxides onto the inner walls of mesoporous silica provides catalysts with a large concentration of accessible, isolated, and structurally well-defined active sites for the epoxidation of cyclohexene.

Results and Discussion

Synthesis of the Molecular Precursors. The titanium complex $Ti[OSi(O^tBu)_3]_4$ (**TiSi4**), with a Ti/Si ratio of 1:4, was

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prepared from $Ti(NEt_2)_4$ and $HOSi(O^tBu)_3$ according to the previously reported procedure.[26,37] A precursor with a 1:3 Ti/Si ratio, $(^iPrO)Ti[OSi(O^tBu)_3]_3$ (**TiSi3**), was prepared by a modification of the method reported by Abe and co-workers,[49] involving the reaction of 3 equivs of $HOSi(O^tBu)_3$ with $Ti(O^iPr)_4$ in refluxing benzene for 1 h. The product was isolated from cold (−30 °C) hexane as colorless crystals. Colorless crystals of the complex $(^tBuO)_3TiOSi(O^tBu)_3$[50] (**TiSi**), synthesized from $Ti(O^tBu)_4$ and 1 equiv of $HOSi(O^tBu)_3$ in hexane, was purified by sublimation followed by recrystallization from pentane at −30 °C.

Infrared spectroscopy of titania−silica materials has been extensively used to identify Ti−O−Si heterolinkages, which give rise to an absorption band at 920−960 cm^{-1}.[51−53] The titanium compounds **TiSi4**, **TiSi3**, and **TiSi** display strong, sharp absorption bands at 925, 935, and 945 cm^{-1}, respectively. These assignments are consistent with those reported in the literature for **TiSi4**[37] and **TiSi**.[50]

Thermal gravimetric analyses (TGAs) of **TiSi4**, **TiSi3**, and **TiSi** in flowing nitrogen revealed a precipitous weight loss corresponding to the stoichiometric formation of $TiO_2{\cdot}4SiO_2$, $TiO_2{\cdot}3SiO_2$, and $TiO_2{\cdot}SiO_2$, respectively, and confirmed the Ti/Si molar ratio expected in each case. The observed and calculated ceramic yields for **TiSi4**, **TiSi3**, and **TiSi** were 29.25% (29.07%), 29.03% (28.99%), and 26.94% (26.36%), respectively (calculated values are given in parentheses). The onset temperatures for the decompositions, **TiSi4** (250 °C), **TiSi3** (180 °C), and **TiSi** (190 °C), appear to be somewhat related to the number of siloxide ligands in the complex. The higher decomposition temperature for **TiSi4** is possibly due to its greater steric crowding, which may restrict the molecular motion required for decomposition. Differential thermal analyses (DTAs) revealed that the molecule-to-network formation is highly endothermic. No melting of **TiSi4** occurred prior to decomposition, while **TiSi3** and **TiSi** melt at ca. 120 and 100 °C, respectively.

According to molecular mechanics calculations, all three complexes exhibit a pseudotetrahedral coordination environment at the titanium center. The compound **TiSi4** fills an approximately spherical space with a van der Waals radius of 8 Å (diameter of 16 Å). The space-filling structures for **TiSi3** and **TiSi** are distorted from spherical, due to the inequivalent sizes of the ligands. For **TiSi3**, the shortest van der Waals distance across the molecule is 11 Å and the longest is 15 Å. The complex **TiSi** occupies a space of about 8 × 11 Å.

Grafting of the Molecular Precursors. The mesoporous silica materials MCM-41[8,9,54] and SBA-15[43,44] were prepared according to literature procedures. These support materials were dehydrated at 200 °C under a dynamic vacuum for 24 h and handled under a nitrogen atmosphere thereafter. The OH site densities on the surfaces of these support materials were determined by monitoring reactions of the materials with $(THF)_2Mg(CH_2Ph)_2$ by ^1H NMR spectroscopy.[41] By this method, the OH coverages on MCM-41 and SBA-15 were determined to be 1.7(1) and 1.0(1) OH/nm^2, respectively. The OH coverage on the MCM-41 material is within the range of previously reported values, 1−3 OH/nm^2.[18,55] To our knowledge, the OH coverage on SBA-15 has not been reported previously.

Table 1. Preparation and Physicochemical Properties of Various Ti-Grafted Samples and Silica Supports

sample[a]	Ti-loading (wt %)	Ti/nm²	BET surface area (m^2g^{-1})	pore vol[b] (cm^3g^{-1})	pore diameter[b] (Å)
SBA-15			800	0.75	65.4
TiSi4−SBA15-(0.25)	0.25	0.040	530	0.60	65.4
TiSi4−SBA15-(0.25)C	0.25	0.040	830	0.88	65.2
TiSi3−SBA15-(0.25)	0.25	0.040	580	0.63	65.4
TiSi3−SBA15-(0.25)C	0.25	0.040	580	0.61	65.4
TiSi3−SBA15-(0.48)	0.48	0.076	580	0.69	65.4
TiSi3−SBA15-(0.50)C	0.50	0.079	650	0.68	65.4
TiSi3−SBA15-(0.94)	0.94	0.15	490	0.55	65.8
TiSi3−SBA15-(1.00)C	1.00	0.16	610	0.65	65.0
TiSi3−SBA15-(1.34)	1.34	0.21	360	0.38	56.4
TiSi3−SBA15-(1.41)C	1.41	0.23	560	0.73	65.5
TiSi3−SBA15-(1.64)	1.64	0.26	450	0.48	56.0
TiSi3−SBA15-(1.77)C	1.77	0.28	590	0.59	65.2
TiSi−SBA15-(1.37)	1.37	0.22	620	0.75	56.1
TiSi−SBA15-(1.47)C	1.47	0.24	730	0.89	56.2
TiSi−SBA15-(1.77)	1.77	0.28	450	0.52	66.2
TiSi−SBA15-(1.89)C	1.89	0.30	590	0.72	65.2
TiSi−SBA15-(3.97)	3.97	0.65	360	0.42	65.4
TiSi−SBA15-(4.39)C	4.39	0.72	670	0.84	65.4
$Ti(O^iPr)_4$−SBA15-(1.48)	1.48	0.24	540	0.74	56.4
$Ti(O^iPr)_4$−SBA15-(1.58)C	1.58	0.25	660	0.84	56.5
MCM-41			1030	0.78	27.2
TiSi3−MCM41-(1.32)	1.32	0.16	920	0.32	20.1
TiSi3−MCM41-(1.42)C	1.42	0.17	1230	0.68	24.4
Aerosil			150	0.53	
TiSi3−Aerosil-(1.30)	1.30	1.09	140	0.78	
TiSi3−Aerosil-(1.40)C	1.40	1.18	190	0.91	

[a] **TiSi*x***−support-(*y*) represents titanium precursors grafted onto the silica support (SBA-15, MCM-41, or Aerosil), where **TiSi4**, **TiSi3**, and **TiSi** are $Ti[OSi(O^tBu)_3]_4$, $^iPrOTi[OSi(O^tBu)_3]_3$, and $(^tBuO)_3TiOSi(O^tBu)_3$, respectively, and *y* is the wt % of Ti loading. C denotes the samples that were calcined at 300 °C in a flow of O_2 for 3 h. [b] Determined from BJH adsorption.

The titanium siloxide precursors were grafted onto the silica supports by stirring a suspension of the support in a hexane solution of the precursor for 22 h at ambient temperature. In this way, various grafted titanium epoxidation catalysts were obtained (Table 1). Additional catalysts were prepared by calcination of the initially grafted materials at 300 °C under flowing oxygen (Table 1). The Ti content in the resulting materials is in close agreement with the composition in the synthetic mixtures.

The maximum titanium loading (obtained by employing a large excess of the precursor and determined by elemental analysis) was observed to vary according to the size of the titanium precursor. This is perhaps expected for MCM-41, since the estimated diameter of **TiSi4** (ca. 16 Å) is roughly half the diameter of the MCM-41 channel (ca. 33 Å). Therefore, it may be that initial chemisorption of precursor molecules in the channels of MCM-41 inhibits subsequent molecules from entering the channel, leading to a low level of surface derivatization. This may help explain the low maximum loading of titanium onto MCM-41 (0.05 wt %; 0.006 Ti/nm^2) with **TiSi4**. Consistent with this, a higher loading on MCM-41 was achieved with the smaller molecular precursor **TiSi3** (1.42 wt % or 0.178 Ti/nm^2).

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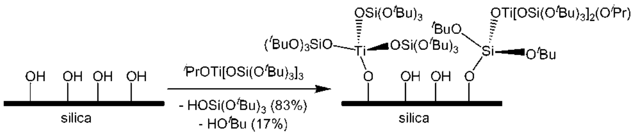
Scheme 2



The average pore diameter for the SBA-15 sample used in this study (ca. 65 Å) is much larger than the molecular diameter of **TiSi4**; however, the maximum Ti loading on SBA-15 was still quite low (0.25 wt % or 0.040 Ti/nm^2). This result suggests that the low maximum loadings observed for **TiSi4** may result from the shrouding effect of the $-OSi(O^tBu)_3$ groups surrounding the titanium center of this precursor. Indeed, the less bulky precursors **TiSi3** and **TiSi** could be supported onto the SBA-15 with much higher Ti loadings of 1.77 (0.28 Ti/nm^2) and 4.39 wt % (0.72 Ti/nm^2), respectively. In addition, the least sterically hindered precursor examined in this study, $Ti(O^iPr)_4$, is much more reactive toward the silica supports, such that complete coverage (6.76 wt %; 1.1 Ti/nm^2) on the SBA-15 was observed. Moreover, supporting **TiSi4** onto aerosil silica, which has no pore structural restriction, yielded a maximum loading of only 0.10 wt % (0.066 Ti/nm^2).

To gain insight into the chemistry of the grafting process, the chemisorption of molecular species onto SBA-15 was monitored by ^1H NMR spectroscopy. In principle, the reaction of a surface-bound $-OH$ group with the precursor should result in elimination of silanol and/or alcohol, depending on the precursor employed.[24,56,57] The products from the grafting reactions of **TiSi4**, **TiSi3**, and **TiSi** in benzene-d_6 were identified by ^1H NMR spectroscopy as $HOSi(O^tBu)_3$ and HO^tBu, and integration of the NMR spectra provided silanol/alcohol ratios of 6, 5, and 7, respectively. The greater amounts of $HOSi(O^tBu)_3$ relative to HO^tBu indicate that the Ti−OSi bond is more readily cleaved relative to the Ti−OC and Si−OC bonds. Interestingly, there was no HO^iPr detected (by ^1H NMR spectroscopy) after the grafting reaction of **TiSi3** onto SBA-15. Thus, this precursor appears to bind to the surface exclusively via reactions of the siloxide ligand (Scheme 2).

Properties for the catalysts prepared for this study (Table 1) indicate that the regular structures of the mesoporous supports remain intact after the grafting procedures. For example, the low-angle XRD patterns of the Ti-grafted MCM-41 and SBA-15 materials are similar to those of siliceous MCM-41 and SBA-15, respectively, and can be indexed to a hexagonal lattice. The **TiSi*x***-MCM41 samples have a well-resolved pattern with a diffraction peak at 2.2° (2θ; corresponding to a d_{100} spacing of about 39 Å), which is in agreement with the literature.[8,9] A well-resolved pattern with a prominent peak at 0.95° and two weak peaks at 1.6 and 1.8° 2θ observed in the **TiSi*x***−SBA15 samples are consistent with the pattern reported for SBA-15.[43] Calcination does not affect the XRD patterns except to increase the signal intensities.

For all the titanium-containing materials, N_2 adsorption−desorption measurements confirmed the expected mesoporous structures. The **TiSi3**−MCM41 materials exhibit the typical type IV isotherm without a hysteresis loop. At a relative pressure P/P_o between 0.30 and 0.40, the isotherm exhibits a sharp inflection characteristic of capillary condensation within the mesopores.[58,59] The **TiSi*x***−SBA15 samples all display an irreversible type IV isotherm with a H1 hysteresis loop and a sharp inflection in the P/P_o range from 0.6 to 0.80, which is higher than that for MCM-41 materials, suggesting larger pore sizes. As the titanium loading increases, the inflections in the isotherms show reduced sharpness and shift toward lower P/P_o values over a larger P/P_o range. Both the surface areas and pore diameters of grafted materials decrease with increasing titanium content (Table 1), indicating some modification of the tubular channels of the support, as expected. Calcination under flowing oxygen at 300 °C for 3 h removed the organic components [typically <10 wt %] of the materials. The surface areas of the grafted samples typically increase upon calcination, and this is consistent with grafting of the precursors into the pores of the mesoporous supports. The calcination also results in pore diameters and total pore volumes that are very similar to those of the original supports (Table 1).

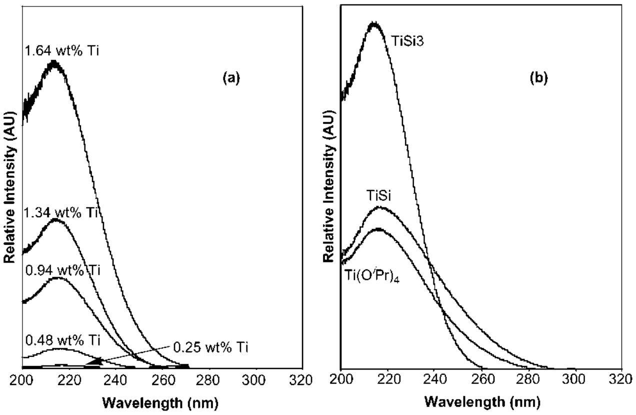


Figure 1. DRUV−vis spectra of uncalcined samples: (a) **TiSi3** supported onto SBA-15 at various Ti loadings and (b) **TiSi3** (1.34 wt % Ti), **TiSi** (1.37 wt % Ti), and $Ti(O^iPr)_4$ (1.48 wt % Ti) supported onto SBA-15.

Characterization of the Titanium Sites of the Catalysts. After confirming that the bulk structure of the support is maintained upon the introduction of titanium, DRUV−vis spectroscopy was used to probe the local environment of the titanium centers. Figure 1a presents spectra for a series of uncalcined **TiSi3**−SBA15 materials. No complicating absorptions due to silica are expected,[46] and all samples feature an intense and narrow UV absorption band at around 215 nm. This type of spectrum indicates that the titanium exists mainly in an isolated, tetrahedral environment, as it is well-known that bands with a maximum at about 200−220 nm and an absorption onset at about 290 nm arise from oxygen to tetrahedral titanium(IV) charge transfer (LMCT).[60−63] For increasing Ti loading, the absorption maximum remains at the same wavelength but increases in intensity. Note that the characteristic band for titania particles (anatase) exhibits a maximum at about 330 nm.[61]

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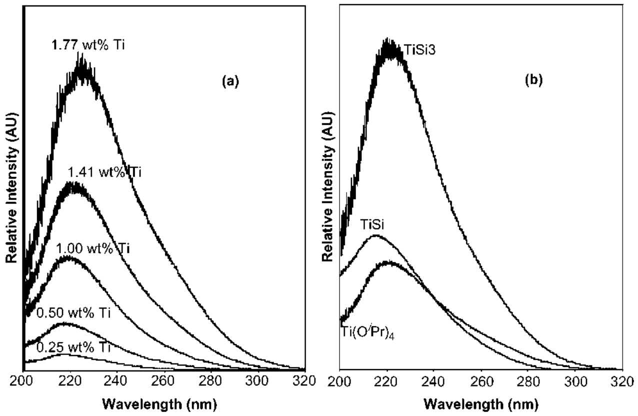

Figure 2. DRUV−vis spectra of calcined samples: (a) **TiSi3** supported onto SBA-15 at various Ti loadings and (b) **TiSi3** (1.41 wt % Ti), **TiSi** (1.47 wt % Ti), and Ti(O^{i}Pr)$_4$ (1.58 wt % Ti) supported onto SBA-15.

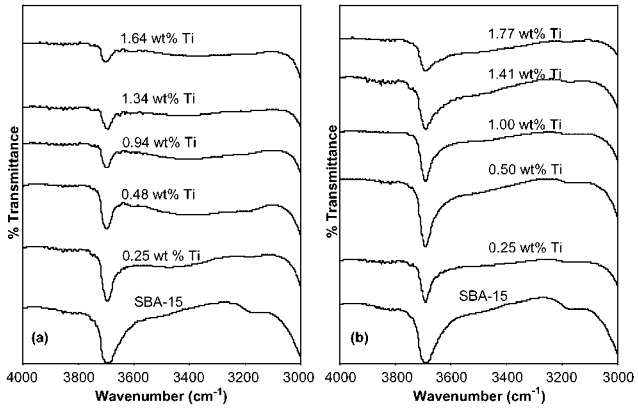

Figure 3. IR spectra of (a) uncalcined and (b) calcined samples of **TiSi3** supported onto SBA-15 at various Ti loadings.

Apparently, the exclusion of water in the synthetic procedure prevents formation of titania on the silica surface, as demonstrated by the absence of a UV absorption band above 300 nm. The spectra for **TiSi**−SBA15 and Ti(O^{i}Pr)$_4$−SBA15 exhibit an absorption at ca. 215 nm that is of lower intensity, and a broad shoulder in the range of 250−280 nm (Figure 1b). This suggests that these samples may contain a decreased amount of isolated, tetrahedral Ti(IV), and perhaps a small amount of oligomerized Ti(IV) species.[63]

Calcination of the samples at 300 °C under flowing O$_2$ for 3 h changes the local environment of the titanium centers. DRUV−vis spectra of calcined **TiSi3**−SBA15 samples exhibit a shoulder in the 250−300 nm region (more apparent with Ti loadings >1 wt %), and the λ_{max} values increase with increasing titanium content (Figure 2a). Given that the major absorptions for these samples occur at wavelengths <230 nm, it appears that most of the titanium is still present as isolated, tetrahedral Ti(IV). The small shift in the λ_{max} values upon calcination (ca. 2−10 nm) is consistent with small changes in the coordination environment of the tetrahedral Ti species (e.g., Ti(OH)(OSi)$_3$ vs Ti(OSi)$_4$).[64] The significant contribution of species absorbing at wavelengths above 250 nm suggests the presence of oligomers and/or TiO$_2$-like nanoclusters.[61,62] The relative amounts of such species, compared to the isolated tetrahedral ones, cannot be estimated by means of DRUV−vis spectroscopy, because the molar absorption coefficients for the various surface complexes are not known. It may be noted, however, that the bands are broader than for the uncalcined samples, implying a somewhat broader distribution of Ti environments. The uncalcined and calcined (Figure 2b) samples derived from **TiSi** and Ti(O^{i}Pr)$_4$ display more similar DRUV−vis spectra, suggesting only slight changes in the Ti coordination environment upon calcination.

Figure 3 compares the FTIR spectra of the **TiSi3**−SBA15 samples with that of SBA-15. The SBA-15 has a narrow band at 3700 cm^{-1} that overlaps with a weak and very broad band in the range of 3700−3200 cm^{-1}. The first band may be assigned to an O−H stretch for isolated surface silanols, and the second to silanols interacting by H bonds.[46,63] In all spectra of the **TiSi3**−SBA15 materials, a sharp band at 3700 cm^{-1} may be attributed to the OH stretching vibration of isolated silanol groups that are located mainly at the surface of the internal walls of the SBA-15 channels. The intensity of the hydroxyl band associated with the silica surface is considerably attenuated upon the introduction of Ti, indicating their participation in the grafting reactions. The OH stretch is completely diminished upon grafting the SBA-15 with an excess of Ti(O^{i}Pr)$_4$, which results in a loading of 6.76 wt % (or 1.06 Ti/nm^2). In the calcined **TiSi3**−SBA15 samples, besides free silanols (at ca. 3700 cm^{-1}) and H-bonded hydroxyls, a shoulder at ca. 3650 cm^{-1} is also present (Figure 3b). This band may be attributed to Brønsted OH groups close to Ti Lewis acid sites and/or to Ti−OH groups.[17,63] The IR absorption at 950 cm^{-1}, which is generally attributed to the presence of Ti−O−Si linkages,[63,65] is found in all samples. However, this absorption is more intense in the **TiSi3**−MCM41 samples due to the thinner walls of the MCM-41 support.

Catalytic Epoxidation of Cyclohexene. Initial experiments at 65 °C with 0.025 g of **TiSi3**−SBA15-(1.64) (**TiSi3** supported on SBA-15, at 1.64 wt % Ti loading) or **TiSi3**−SBA15-(1.77)C (**TiSi3** supported on SBA-15, at 1.77 wt % Ti loading, calcined at 300 °C/O$_2$/3 h) and aqueous hydrogen peroxide (30 wt %) in acetonitrile resulted in a very low yield of cyclohexene oxide product (<5% after 2 h), as determined by gas chromatography. The observed lack of catalytic activity is attributed to the presence of water, which is known to severely inhibit the epoxidation reaction.[66] However, experiments employing organic hydroperoxides (*tert*-butyl hydroperoxide, TBHP, and cumene hydroperoxide, CHP) as oxidants revealed significant activities for the production of cyclohexene oxide.

In metal-catalyzed epoxidations, the structure of the hydroperoxide can play an important role in determining the product selectivities and the rates of the epoxidation process. For example, electron-withdrawing substituents in the hydroperoxide were shown to increase the rate of epoxidation by enhancing the electrophilic nature of the Ti−hydroperoxide complex.[67,68] The sample **TiSi3**−SBA15-(1.64) was found to exhibit activity as a catalyst for the epoxidation of cyclohexene, with either TBHP or CHP as the oxidant, in toluene at 65 °C, yielding 61% (TBHP) and 98% (CHP) of cyclohexene oxide after 2 h (relative to initial peroxide). Thus, the epoxidation is significantly more efficient with CHP as the oxygen-transfer reagent. In contrast,

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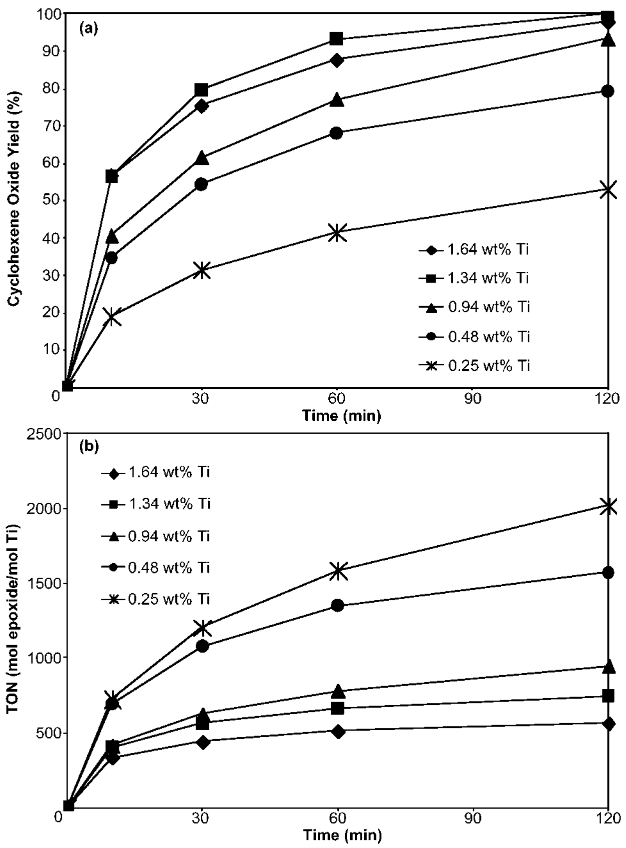

Figure 4. (a) Yield of cyclohexene oxide and (b) turnover numbers (TONs) as a function of time during the epoxidation of cyclohexene with 0.025 g of uncalcined **TiSi3**−SBA15-(*y*), where *y* = 1.64 (◆), 1.34 (■), 0.94 (▲), 0.48 (●), and 0.25 (∗) wt % Ti.

Table 2. Comparison of Initial Rates in the Epoxidation of Cyclohexene with **TiSi3**−SBA15 Calculated Over the First 10 min of the Reaction

Ti loading (wt %)	initial rate	
	mmol epoxide/g cat/min	mol epoxide/mol Ti/min
0.25	3.8	73
0.48	6.9	66
0.94	8.1	41
1.34	11.3	40
1.64	11.3	33

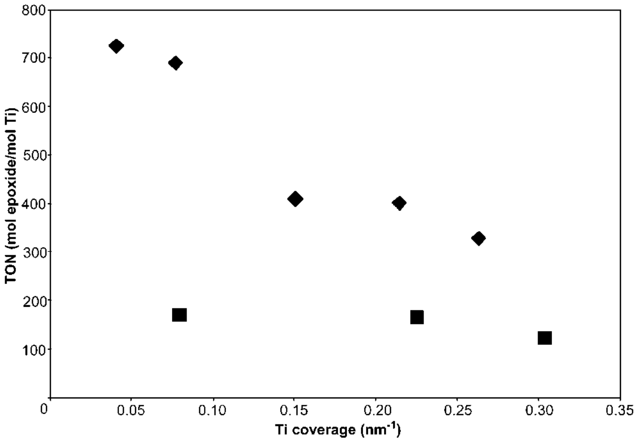

Figure 5. Initial turnover numbers (TONs) at the first 10 min of reaction as a function of Ti coverage in the epoxidation of cyclohexene with 0.025 g of uncalcined (◆) and calcined (■) **TiSi3**−SBA15.

a study by Oldroyd et al. on the epoxidation of cyclohexene with catalysts obtained by grafting Ti onto MCM-41[14] concluded that TBHP was superior to CHP as the organic hydroperoxide. Thus, the procedure described here represents an attractive alternative, given the much lower cost of CHP compared to that of TBHP.

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 by increasing quantities of the alcohol coproducts in the reaction mixture, hindering formation of the active titanium−hydroperoxide complex and its subsequent reaction with cyclohexene.[66] To determine whether the active species leached into solution during a typical catalytic run, a sample of **TiSi3**−SBA15-(1.64) and CHP in toluene 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, indicating that leaching of a catalytically active titanium species into solution was negligible.

The activities of various uncalcined catalysts **TiSi3**−SBA15-(*y*), where *y* is the wt % of Ti, in the epoxidation of cyclohexene with CHP under identical reaction conditions are compared in Figure 4. Generally, the higher the Ti content, the more active the catalyst (Figure 4a). However, catalytic activities expressed as turnover numbers (TONs; defined as moles of epoxide produced per mole of Ti) reveal that the activities decrease as the Ti content increases (Figure 4b). Thus, the more isolated sites appear to be more active, as has been observed for other titanium-supported silica catalysts.[12,13,18,53,63,69,70] These catalysts were found to be 90−100% selective for epoxidation of the olefin after a reaction time of 2 h (% selectivity = 100 ($[\text{epoxide}]_t/[\text{olefin}]_i - [\text{olefin}]_t$), where *t* is the reaction time).

Activities for the various catalysts may also be described by initial rates for the epoxidation of cyclohexene. Initial rates, as calculated for the first 10 min of the reactions, indicate that as the Ti loading increases, the catalyst activities (on a per gram basis) also increase. However, the initial rates calculated for individual Ti sites decrease as the Ti loading increases (Table 2). Again, these results indicate that the more isolated Ti sites are most active. The activities of the samples derived from supporting **TiSi3** onto SBA-15 (on a per-site basis) decrease as the Ti coverage increases (Figure 5). If the titanium sites were identical in all samples, one would expect the TONs to be independent of the Ti loading. However, the results in Figure 5 suggest that catalysts with low loadings of titanium possess the highest proportion of the most active sites.

To compare results obtained for three silica supports, SBA-15, MCM-41, and Aerosil, we examined materials obtained by supporting similar amounts (weight percentages) of **TiSi3** onto the surface of each. As shown in Figure 6, with a similar Ti loading the **TiSi3**−SBA15 and **TiSi3**−MCM41 catalysts exhibit a higher activity than **TiSi3**−Aerosil (on a per Ti basis). Oldroyd et al. reported a comparison between titanium centers grafted onto MCM-41 and Aerosil supports, and found similar results.[14] These differences likely arise from the higher surface area of

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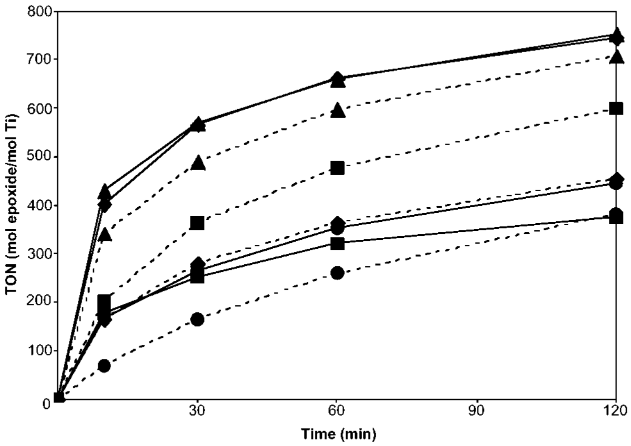

Figure 6. Turnover numbers (TONs) as a function of time during the epoxidation of cyclohexene with uncalcined (solid line) and calcined (dotted line) catalysts: **TiSi3**−SBA15 (◆), **TiSi3**−MCM41 (▲), **TiSi3**−Aerosil (●), and $\mathrm{Ti(O^{i}Pr)_4}$−SBA15 (■).

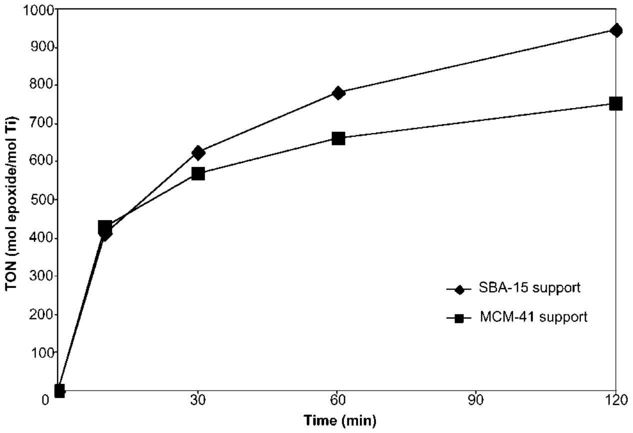

Figure 7. Turnover numbers (TONs) as a function of time during the epoxidation of cyclohexene with uncalcined **TiSi3**−SBA15-(0.94) (◆) and **TiSi3**-MCM41-(1.32) (■) with ca. 0.16 Ti/nm^2.

SBA-15 and MCM-41, which allows for a greater dispersion of the Ti centers and therefore a higher concentration of the more active, site-isolated Ti species. In contrast, Fraile et al. reported that MCM-41 does not show clear advantages over silica as a support in epoxidation reactions of cyclohexene with either TBHP or H_2O_2.[71]

With similar Ti coverages (ca. 0.15−0.16 Ti/nm^2), SBA-15 is superior to MCM-41 as a support. In the epoxidation of cyclohexene with CHP, the TONs of **TiSi3** supported on SBA-15 are higher than those of **TiSi3** supported on MCM-41, especially after the first 30 min of the reaction (Figure 7). The superiority of the SBA-15 support is presumed to derive from its greater thermal stability.[43,44]

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) compared to samples calcined to temperatures between 400 and 800 °C.[72] This enhanced activity was attributed to the presence of organic residues in the material, but the mechanism responsible for this effect is unknown. The influence of calcination on the epoxidation activity of **TiSi3**−SBA15, **TiSi3**−MCM41, and **TiSi3**−Aerosil was investigated. Samples were calcined at 300 °C for 3 h under a flow of oxygen. Under identical reaction conditions, the percent yield of cyclohexene oxide after 2 h at 65 °C was considerably higher for materials that had not been calcined (Figure 6). These results presumably reflect differences in the titanium coordination environments for the calcined and uncalcined catalysts, as indicated by DRUV−vis and IR spectroscopic results. Even though the tetrahedral Ti sites are present in both types of samples, it may be reasonably proposed, on the basis of better catalytic performance in the epoxidation reaction, that the uncalcined catalysts have more isolated tetrahedral Ti active sites. During the calcination, the mobility of bi- and monopodally anchored Ti species could lead to oligomerization.[17] Also, calcination may result in migration of the titanium centers into the support framework. This process could be facilitated by the siloxide ligands of the precursor, which are converted to new silica centers on the surface. This "new silica" may remain closely associated with the titanium centers and render them less accessible and more like framework Ti centers. Note that this cannot occur when $\mathrm{Ti(O^{i}Pr)_4}$ is used as a precursor. In fact, the calcined samples derived from supporting $\mathrm{Ti(O^{i}Pr)_4}$ onto SBA-15 out-performed the uncalcined ones in the production of cyclohexene oxide (Figure 6).

Thomas and co-workers have reported that grafting $\mathrm{Ti(OSiPh_3)_4}$ onto the internal surface of MCM-41 (without further calcination) produces an epoxidation catalyst of high activity and selectivity. For this catalyst, it was proposed that the presence of the phenyl groups stabilizes the catalytic Ti centers toward attack from atmospheric moisture.[73] Similarly, the $\mathrm{-OSi(O^{t}Bu)_3}$ groups in our uncalcined catalysts may enhance the stability of the titanium centers with respect to reaction with the alcohol coproducts and/or moisture.

The uncalcined catalyst derived from supporting $\mathrm{Ti(OSiPh_3)_4}$ onto MCM-41, with Si/Ti = 72, was reported to be active toward the epoxidation of cyclohexene with TBHP at 50 °C in decane. Its TON for the conversion of TBHP to cyclohexene oxide per mole of Ti was approximately 38 mmol^{-1} after 10 min of reaction.[73] In comparison, the uncalcined **TiSi3**−MCM41-(1.32) (Si/Ti = 47.4) exhibits an activity for the production of cyclohexene oxide at 65 °C in toluene with TONs of 24.3 and 430 after 10 min with TBHP and CHP, respectively, and the uncalcined **TiSi3**−SBA15-(0.94) (Si/Ti = 72.1) exhibits a TON of 412 with CHP after 10 min. These comparisons emphasize the high activities observed for cyclohexene epoxidation catalysts obtained from grafted (alkoxy)siloxide titanium species, in particular when CHP is used as the oxidant. Presumably, the presence of the $\mathrm{-OSi(O^{t}Bu)_3}$ ligands enhances the Lewis acidity of the active Ti sites, leading to higher inherent activity for these uncalcined catalysts.[16,74]

To further investigate the influence of the $\mathrm{-OSi(O^{t}Bu)_3}$ ligand of the precursor on the performance of epoxidation catalysts, we compared results obtained from the four precursors **TiSi4**, **TiSi3**, **TiSi**, and $\mathrm{Ti(O^{i}Pr)_4}$. At Ti loadings greater than 1 wt %, **TiSi3** is superior to **TiSi** and $\mathrm{Ti(O^{i}Pr)_4}$ as a catalytic precursor, and **TiSi** is better than $\mathrm{Ti(O^{i}Pr)_4}$ (Figure 8). The latter comparison is consistent with the fact that catalysts derived from $\mathrm{Ti(O^{i}Pr)_4}$ have a tendency to form oligomeric titano−oxo species

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Table 3. Comparison of Turnover Frequencies (TOFs) for the Epoxidation of Cyclohexene Calculated Over the First Hour of the Reaction

precursor	support	Ti loading (wt %)	Si/Ti ratio	oxidant	reaction temp (°C)	TOF^a	ref
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	SBA-15	1.64	39.3	CHP	65	510	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	SBA-15	1.64	39.3	TBHP	65	257	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	SBA-15	1.77^b	39.7	CHP	65	285	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	SBA-15	1.34	47.6	CHP	65	643	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	SBA-15	1.41^b	48.5	CHP	65	384	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	SBA-15	1.41^b	48.5	CHP	40	175	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	MCM-41	1.32	47.4	CHP	65	651	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	MCM-41	1.42^b	49.1	CHP	65	634	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	MCM-41	1.42^b	49.1	TBHP	65	63.2	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	Aerosil	1.30	46.8	CHP	65	326	this work
$(^iPrO)Ti[OSi(O^tBu)_3]_3$	Aerosil	1.40^b	48.8	CHP	65	259	this work
$(^tBuO)_3TiOSi(O^tBu)_3$	SBA-15	3.97	14.7	CHP	65	200	this work
Cp_2TiCl_2	MCM-41	6.76	10	TBHP	40	121	12
Cp_2TiCl_2	MCM-41		24.4	TBHP	25	16.4	13
Cp_2TiCl_2	MCM-41		44.7	TBHP	30	33.8	14
Cp_2TiCl_2	MCM-41		44.7	CHP	30	31.2	14
$Ti(O^iPr)_4$	MCM-41	5.99		TBHP	25	14.0	71

^{a} Turnover frequency (mol epoxide/mol Ti/h). ^{b} These catalysts were calcined at 300 °C under a flow of O_2 for 3 h before used.

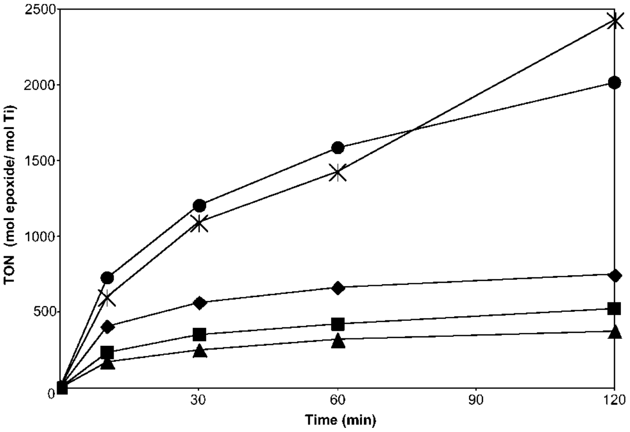

Figure 8. Turnover numbers (TONs) as a function of time during the epoxidation of cyclohexene with uncalcined **TiSi4**−SBA15-(0.25) (∗), **TiSi3**−SBA15-(0.25) (●), **TiSi3**−SBA15-(1.34) (◆), **TiSi**-SBA15-(1.37) (■), and $Ti(O^iPr)_4$−SBA15-(1.48) (▲).

and/or some anatase byproducts during grafting procedures.[12,56] In addition, Maschmeyer et al. reported that Ti-grafted MCM-41 derived from Cp_2TiCl_2 is composed of isolated, tetrahedral titanium sites that result from stabilization of the Ti centers by the relatively stable cyclopentadienyl ligands.[12] We propose that the bulky siloxide ligands of our precursors provide the same benefit, in stabilizing site-isolated titanium on the silica surface. The siloxide ligands are probably bulky enough to prevent dimerization or oligomerization of the titanium species during the grafting process. At low Ti loadings, the possibility of dimerization/oligomerization is relatively low, therefore catalysts derived from **TiSi3** and **TiSi4** have a very similar activity (Figure 8).

In this study, **TiSi3**−SBA15-(1.64) gave the best performance as a catalyst for the epoxidation of cyclohexene with CHP in toluene at 65 °C. To make comparisons between the systems investigated in this study and those reported in the literature, the catalyst activity, expressed as turnover frequencies (TOFs) averaged over the first hour, was determined and compared (Table 3). Other precursors used to introduce Ti onto silica surfaces are Cp_2TiCl_2[12−14] and $Ti(O^iPr)_4$.[71] Our catalysts appear to be more active than those reported toward the production of cyclohexene oxide. For example, **TiSi3**−MCM41-1.42C (Si/Ti = 49.1) was far more active in the epoxidation of cyclohexene with either CHP or TBHP than the catalyst derived from supporting Cp_2TiCl_2 onto MCM-41 (Si/Ti = 44.7).

Concluding Remarks

We describe here a facile method for grafting the molecular precursors $Ti[OSi(O^tBu)_3]_4$, $^iPrOTi[OSi(O^tBu)_3]_3$, and $(^tBuO)_3TiOSi(O^tBu)_3$ onto silica supports (SBA-15, MCM-41, and Aerosil-200). These precursors appear to be useful for the efficient introduction of isolated, tetrahedral TiO_4 species onto a silica surface. Thus, oxygen-rich precursors of this type, which have previously been shown to provide facile routes to well-dispersed, mixed-element oxides,[24−42] also appear to provide facile routes to single-site catalytic species supported on an oxide surface.[37] We attribute both behaviors to the preexisting TiO_4 and SiO_4 environments for the molecular precursors.

The epoxidation catalysts derived from the (alkoxy)siloxide precursors exhibit activities and selectivities that are comparable to or better than previously described high-performance titanium-containing catalysts. The characterization data currently available indicate that the best catalysts possess the highest coverage of isolated, tetrahedral Ti centers. It is therefore somewhat interesting that the epoxidation catalysts described here are highly selective and active with CHP as the oxidant, whereas related catalysts derived from titanocene dichloride as the molecular precursor perform better with TBHP as the oxidant.[14]

Examination of the influence of the Ti:Si ratio of the (alkoxy)siloxide precursor on catalyst performance revealed two important trends. First, the presence of fewer $-OSi(O^tBu)_3$ ligands in the precursor facilitates the grafting procedure, such that it is easier to obtain higher Ti loadings. This is attributed mainly to the steric bulk of the siloxide ligand, which retards the grafting reaction in the most sterically encumbered cases (i.e., $Ti[OSi(O^tBu)_3]_4$). Second, however, maximization of the number of siloxide ligands in the precursor optimizes the catalytic properties (for both calcined and uncalcined samples). The latter observation probably reflects a higher degree of site isolation for the most sterically protected Ti centers.

In a comparison of three silica supports we observed that high surface area mesoporous silicas (MCM-41 and SBA-15) are more effective, as demonstrated by the higher activities observed for these supports. Additionally, with a similar Ti coverage, SBA-15 is somewhat superior to MCM-41 as a support (as indicated by TONs).

Experimental Section

All manipulations were performed under an atmosphere of nitrogen with standard Schlenk techniques and/or in a Vacuum Atmospheres drybox. Dry oxygen-free solvents were used throughout. Calcinations were performed with a Lindberg 1200 °C three-zone tube furnace. NMR spectra were recorded on a Bruker AMX300 spectrometer (at 300 MHz). Infrared spectra were acquired as Nujol mulls with CsI cells on a Perkin-Elmer 1330 spectrometer. Surface area and pore volume analyses were measured by using the B.E.T. method on a Quanta-Chrome Autosorb 6 surface area analyzer with all samples heated at 120 °C, under vacuum, for a minimum of 2 h immediately prior to data collection. Powder X-ray diffraction was performed on a Siemens D5000 diffractometer with Cu α radiation of wavelength 1.54056 Å. DRUV−vis spectra were recorded on a Varian Cary 4 UV−vis spectrometer with MgO as a reference. GC analyses were performed with a Hewlet 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). Elemental analyses were performed by Mikroanalytisches Labor Pascher. The titanium complexes $\mathrm{Ti[OSi(O^tBu)_3]_4}$[26,37] (**TiSi4**), $\mathrm{(^iPrO)Ti[OSi(O^tBu)_3]_3}$[49] (**TiSi3**), and $\mathrm{(^tBuO)_3TiOSi(O^tBu)_3}$[50] (**TiSi**) were synthesized according to the literature procedures. All reagents were purchased from Aldrich and used as received, unless stated otherwise.

Synthesis of SBA-15. A synthesis for mesoporous silica SBA-15 has been reported.[43,44] In our typical synthesis, 4.0 g of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide), $\mathrm{EO_{20}PO_{70}EO_{20}}$ (BASF, Pluronic P123), was dissolved in 30 g of deionized water and 120 g of 2 M HCl solution with stirring at 35 °C. Then 8.50 g of tetraethyl orthosilicate was added into that solution with stirring at 35 °C for 24 h. The mixture was aged at 80 °C overnight without stirring. The solid product was recovered by filtration, washed with deionized water, and air dried at room temperature. The as-synthesized sample was calcined at 550 °C for 24 h under a flow of dry air.

Synthesis of MCM-41. As reported previously,[8,9,54] a typical synthesis involves dissolving 4.39 g (0.012 mol) of cetyltrimethylammonium bromide in 200 g of deionized water containing 1.10 g (0.0275 mol) of NaOH with heating to 30 °C. To this solution was added 14.75 mL (0.10 mol) of tetramethyl orthosilicate. The mixture was vigorously stirred at room temperature for 24 h and then heated to 90 °C for 24 h without stirring. The product was isolated by vacuum filtration and washed with deionized water and methanol until the pH of the washings was neutral. The resulting white powder was dried in air at ambient temperature. The surfactant was removed by acid/solvent extraction, using a solution of 500 mL of methanol and 7.0 g of aqueous HCl (37.5%) per 6 g of sample. This mixture was refluxed for 1 day, then filtered and washed with methanol until pH was neutral. The product was allowed to air dry before calcination at 550 °C for 24 h under a flow of dry air.

Catalyst Preparation. To remove any physisorbed water before the grafting procedure, the silica support (SBA-15, MCM-41, or Degussa Aerosil-200) was dehydrated at 200 °C for 24 h under a dynamic vacuum. A 0.5 g sample of the support was suspended in hexane (25 mL). A hexane solution (25 mL) of the titanium precursor was prepared, the concentration of which depended on the desired Ti loading. The precursor solution was then added to the SBA-15 suspension. The resulting mixture was stirred at room temperature for 22 h and then filtered and washed with hexane (3 × 25 mL). The grafted material was dried at room temperature under reduced pressure. Calcination of the sample was performed in a tube furnace under flowing oxygen. The temperature was ramped at a rate of 2 °C $\mathrm{min^{-1}}$ to 300 °C, and this temperature was maintained for 3 h. These samples are designated as **TiSi*x***−support-(*y*), where **TiSi4**, **TiSi3**, and **TiSi** are $\mathrm{Ti[OSi(O^tBu)_3]_4}$, $\mathrm{^iPrOTi[OSi(O^tBu)_3]_3}$, and $\mathrm{(^tBuO)_3TiOSi(O^tBu)_3}$, respectively, the support is SBA-15, MCM-41, or Aerosil, and *y* is the wt % of Ti loading. C denotes the samples that were calcined at 300 °C in a flow of oxygen for 3 h.

Catalysis Procedure. A sample of catalyst (0.025 g) was added to a 50 mL round-bottom flask. Toluene (5.00 mL) and distilled cyclohexene (1.00 mL, 9.88 mmol) were added by syringe through a septum under a flow of nitrogen. Dodecane (0.250 mL) was added as an internal standard via micropipet. The mixture was allowed to equilibrate at the reaction temperature of 65 °C for 10 min. Cumene hydroperoxide (0.92 mL, 4.98 mmol) or *tert*-butyl hydroperoxide (1.00 mL, 5.00 mmol) was added by syringe to the rapidly stirred solution. Aliquots (ca. 0.15 mL) were removed from the reaction mixture by syringe after 10, 30, 60, and 120 min and then filtered. The filtrate was analyzed by GC, and assignments were made by comparison with authentic samples analyzed under the same conditions.

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