

The Identity in Atomic Structure and Performance of Active Sites in Heterogeneous and Homogeneous, Titanium–Silica Epoxidation Catalysts

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The nature of the Ti(IV) active site in heterogeneous titano–silica epoxidation catalysts is shown to be same as that of a Ti(IV)-centered site bound to soluble homogeneous silsesquioxane catalysts. A range of techniques, encompassing pre- and near-edge X-ray absorption spectroscopy and molecular dynamics calculations, provides quantitative information pertaining to the four-coordinated site that is tripodally anchored to silica. The catalytic performance of a series of engineered active sites in $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Ti}(\text{OXPh}_3)]$, where X = Si, Ge, or Sn, shows that the order of enhancement is Ge > Sn > Si. This is compared with previously published⁷ performances of engineered active sites in solid titano–silicate catalysts. The key importance of accessibility to the four-coordinated Ti(IV) site is highlighted here.

Introduction

Titanium-based heterogeneous catalysts, involving silica supports, are employed in the production of epoxides using alkyl hydroperoxides (typically ethylbenzyl- or *tert*-butyl hydroperoxide) as oxidants.¹ High-performance, laboratory-scale variants of such catalysts, prepared from titanocene dichloride and mesoporous silica (MCM-41),^{2–5} have been shown by X-ray absorption spectroscopy and a range of other spectroscopic studies to possess active centers that are “single-site”, in the sense that such centers are isolated Ti(IV)–OH groups tripodally anchored, via covalent bonds to oxygen, to the silica support (see Figure 1a).

Recently, it has been shown^{5–7} that, when these single-site active centers are modified slightly so that the tripodal anchorage is no longer HOTi–(OSi)₃ but rather HOTi–(OSi)₂(OGe), there is a significant improvement in the catalytic activity. This result is a little surprising, in view of the fact that the general features of the chemistries of silicon and germanium are so very similar. In contrast, substitution of Sn in a like manner greatly depletes the activity. Modification, in a systematic fashion, of the immediate environment of the active site in heterogeneous Ti/SiO₂ epoxidation catalysts is not easy to accomplish. To study systematically the effect of varying the immediate environment of the titanium center on its catalytic activity, we have focused

our attention on a set of soluble model compounds based on the family of titanium(IV)-derivatized silsesquioxanes⁸ (with the general structure shown in Figure 1b). The great advantage of using these titanosilsesquioxanes (which have been extensively studied by Feher,^{9,10} Roesky,^{11,12} ourselves,^{13–15} and others^{16–23}) is that the immediate environment of the titanium (single-site) active center may be readily modified in a highly controlled fashion. The titanosilsesquioxanes are extremely soluble in solvents such as chloroform, enabling them to be used as homogeneous catalysts with catalytic activities comparable to those of heterogeneous catalysts such as the so-called Ti[†]MCM-41 and Ti–MCM-41 forms described elsewhere.^{3–7} These factors facilitate an analysis of the root-cause of the catalytic enhancement of the next-nearest atom sites on the titanium centers in titanosilicate catalysts²⁴ in general, as well as shedding further light on the influence of steric congestion^{14,15} on the catalytic epoxidizing performance of Ti(IV) active centers.

The studies described here entail the synthesis, characterization (by X-ray absorption spectroscopy), and catalytic testing of the following compounds: $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Ti}(\text{OXPh}_3)]$ where X is Si, Ge, or Sn (see Figure 1c) and comparison with the molecular precursor compounds Ti–(O–SiPh₃)₄ and Ti–(O–GePh₃)₄.^{25,26}

Experimental Section

Unless otherwise stated, all experiments were performed under an atmosphere of dry, oxygen-free nitrogen using conventional Schlenk techniques²⁷ and solvents that were freshly distilled before use. $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3]$ was synthesized following the method of Feher et al.²⁸ Ti–(O–SiPh₃)₄ (**4**) and Ti–(O–GePh₃)₄ (**5**) were synthesized using standard procedures,^{25,26} and these two materials not only serve as possible precursors to the catalyst preparations, but also serve as good model compounds for X-ray absorption studies, since we have

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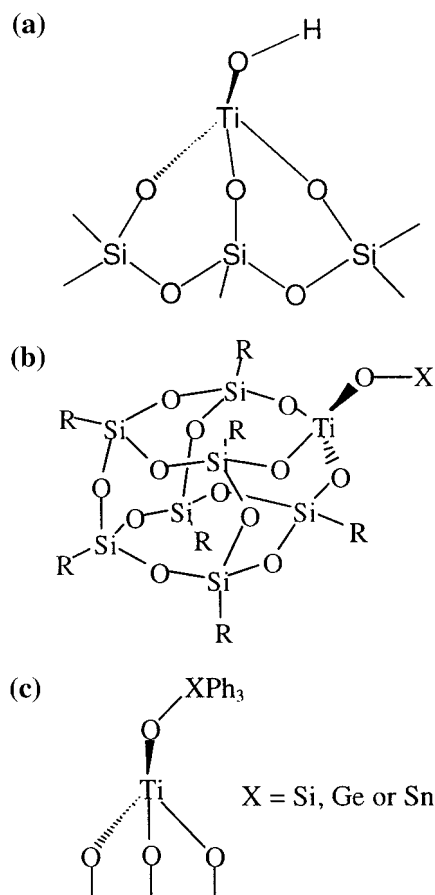


Figure 1. Schematic representation of the Ti(IV) centers (a) tripodally attached to silica, (b) within a titanosilsesquioxane $[R_7Si_7O_{12}Ti-OX]$, where R = cycloalkyl and X = Si, Ge, or Sn, and (c) anchored onto silica as $(\infty Si-O)_3-Ti-OXPh_3$.

solved their crystal structures, recently. All other reagents were used as obtained commercially.

Synthesis of $[(c-C_5H_9)_7Si_7O_{12}TiOSiPh_3]$ (1). In a procedure similar to that employed by Crocker et al. for the corresponding trimethyl derivative,¹⁶ $[(c-C_5H_9)_7Si_7O_9(OH)_3]$ (0.237 g, 0.271 mmol) and $Ti-(O-SiPh_3)_4$ (4) (0.374 g, 0.325 mmol) were added to 50 mL of THF, and the resulting mixture was refluxed for 4 days (the initial suspension of $Ti-(O-SiPh_3)_4$ dissolved to give a colorless solution after 24 h). On cooling to room temperature, the solution was filtered to remove excess $Ti-(O-SiPh_3)_4$, the solvent was removed in vacuo, and the crude product redissolved in CH_2Cl_2 (10 mL). After filtration and addition of MeCN, a white powder precipitated, which was filtered off, washed with pyridine, and then with acetone to finally yield (1) as a white powder (0.050 g, 15%).

Selected Spectroscopic Data for (1). 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62 (d, $^3J(H,H)$ = 10 Hz, 6H; $SiPh_3$), 7.43 (dd, $^3J(H,H)$ = 10 Hz, 7.5 Hz, 3H; $SiPh_3$), 7.39 (t, $^3J(H,H)$ = 7.5 Hz, 6H; $SiPh_3$), 1.73 (m, 20H; cyclopentyl-H), 1.52 (m, 36H; cyclopentyl-H), 0.98 (m, 7H; *ipso*-H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 135.00 (s, CH, $SiPh_3$), 130.14 (s, CH, $SiPh_3$), 127.88 (s, CH, $SiPh_3$), 29.72, 27.46, 27.39, 27.32, 27.18, 27.04, 26.97 (s, CH_2 , unassignable), 22.74, 22.23, 21.98 (s, 3:3:1, CH, *ipso*-H); m/z (FAB⁺): 988 ($M^+ - 3C_5H_9$), 918 ($M^+ - OSiPh_3$); Anal. Calcd for $C_{53}H_{78}O_{13}Si_8Ti$ (found): C, 53.3 (54.2), H 6.53 (6.91).

Synthesis of $[(c-C_5H_9)_7Si_7O_{12}TiOGePh_3]$ (2). To a solution of Ph_3GeOH (obtained from the reaction of Ph_3GeCl and water²⁹) (0.336 g, 1.05 mmol) in toluene (10 mL) was added

$Ti(OBu^i)_4$ (0.34 mL, 1.05 mmol), and the resulting solution was refluxed for 24 h. On cooling, the solvent was removed in vacuo to yield a colorless liquid. A solution of $[(c-C_5H_9)_7Si_7O_9(OH)_3]$ (0.765 g, 0.875 mmol) in THF (20 mL) was then added to this liquid, and the subsequent solution was refluxed for a further 48 h. On cooling, the solvent was removed in vacuo and the crude product was redissolved in CH_2Cl_2 (25 mL). After filtration and addition of MeCN, a white powder precipitated, which was filtered off, washed with pyridine, and then with acetone to finally yield (2) as a white powder (0.774 g, 71%).

Selected Spectroscopic Data for (2). 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.65 (d, $^3J(H,H)$ = 10 Hz, 6H; $GePh_3$), 7.41 (dd, $^3J(H,H)$ = 10 Hz, 7.5 Hz, 3H; $GePh_3$), 7.38 (t, $^3J(H,H)$ = 7.5 Hz, 6H; $GePh_3$), 1.73 (m, 20H; cyclopentyl-H), 1.52 (m, 36H; cyclopentyl-H), 0.98 (m, 7H; *ipso*-H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 134.08 (s, CH, $GePh_3$), 130.05 (s, CH, $GePh_3$), 128.35 (s, CH, $GePh_3$), 29.72, 27.52, 27.41, 27.32, 27.18, 27.06, 26.97 (s, CH_2 , unassignable), 22.33, 22.20, 21.98 (s, 3:3:1, CH, *ipso*-H); m/z (FAB⁺): 1032 ($M^+ - 3C_5H_9$), 918 ($M^+ - OGePh_3$); Anal. Calcd for $C_{53}H_{78}O_{13}Si_7GeTi$ (found): C, 51.3 (50.4), 6.30 (6.63).

Synthesis of $[(c-C_5H_9)_7Si_7O_{12}TiOSnPh_3]$ (3). To a solution of $[(c-C_5H_9)_7Si_7O_9(OH)_3]$ (0.664 g, 0.760 mmol) in toluene (40 mL) was added $TiCl_4$ (0.10 mL, 0.912 mmol), and the resulting pale yellow solution was stirred at 25 °C for 4 h. A solution of Ph_3SnOH (0.334 g, 0.912 mmol) in toluene (15 mL) was then added dropwise, and the resulting colorless solution was stirred at 25 °C for a further 24 h. After filtration, the solvent was removed in vacuo, and the crude product was redissolved in CH_2Cl_2 (10 mL). After filtration and addition of MeCN, a white powder precipitated, which was filtered off, washed with pyridine, and then with acetone to finally yield (3) as a white powder (0.210 g, 22%).

Selected Spectroscopic Data for (3). 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.66 (d, $^3J(H,H)$ = 10 Hz, 6H; $SnPh_3$), 7.48 (dd, $^3J(H,H)$ = 10 Hz, 7.5 Hz, 3H; $SnPh_3$), 7.45 (t, $^3J(H,H)$ = 7.5 Hz, 6H; $SnPh_3$), 1.73 (m, 20H; cyclopentyl-H), 1.52 (m, 36H; cyclopentyl-H), 0.98 (m, 7H; *ipso*-H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 135.77 (s, CH, $SnPh_3$), 130.24 (s, CH, $SnPh_3$), 128.51 (s, CH, $SnPh_3$), 29.72, 27.54, 27.42, 27.35, 27.18, 27.05, 27.01 (s, CH_2 , unassignable), 22.97, 22.65, 22.24 (s, 3:3:1, CH, *ipso*-H); m/z (FAB⁺): 1079 ($M^+ - 3C_5H_9$), 932 ($M^+ - SnPh_3$); Anal. Calcd for $C_{53}H_{78}O_{13}Si_7SnTi$ (found): C, 49.5 (47.9), 6.07 (5.65).

Catalysis. Tests were performed under argon using samples of catalyst that were predried at 80 °C, 10^{-4} Torr for 12 h and either (a) 1 equiv of catalyst to 70 equiv of cyclohexene, TBHP, and TMS (internal standard), in 0.5 mL of $CDCl_3$ at 45 °C or (b) 3 mg of catalyst, 0.03 mL of TBHP, 0.12 mL of cyclohexene, 0.05 mL of TMS (internal standard), and 0.42 mL of $CDCl_3$ at 30 °C for 1 h,⁷ in sealed vials that were magnetically stirred. Data quoted are derived from at least two runs. Conversions (based on TBHP consumed) and selectivities (based on the epoxide formed) were determined by 1H NMR spectroscopy.

X-ray Absorption Spectra. Room temperature Ti K-edge X-ray absorption data were collected at station 8.1 of Daresbury Laboratory, which operates at 2 GeV with a typical current in the range of 130 to 250 mA. This station is equipped with a Si(111) monochromator, ionization chambers for measuring incident and transmitted beam intensities, and a thirteen-element Canberra detector for measurements in fluorescence mode. The data were processed using the suite of programs available at the Daresbury Laboratory, namely EXCALIB (for converting the raw data to energy vs absorption coefficient), EXBROOK

TABLE 1: Catalytic Performance in Epoxidation at 45 °C of a Series of Soluble Silsesquioxanes with Well-Defined (single) Ti(IV) Active Sites^a

catalyst	TBHP conversion (%)		pre-edge intensity (arb. units)
	<i>t</i> = 30 min	<i>t</i> = 1 h	
[(<i>c</i> -C ₅ H ₉) ₇ Si ₇ O ₁₂ Ti(OSiPh ₃)] (1)	9.6	30	0.66
[(<i>c</i> -C ₅ H ₉) ₇ Si ₇ O ₁₂ Ti(OGepH ₃)] (2)	33	70	0.36
[(<i>c</i> -C ₅ H ₉) ₇ Si ₇ O ₁₂ Ti(OSnPh ₃)] (3)	15	28	0.57
Ti-(O-SiPh ₃) ₄ (4)	<1.0	<1.0	0.79
Ti-(O-GePh ₃) ₄ (5)	<1.0	<1.0	0.76

^a 1:70:70 of catalyst:TBHP:cyclohexene; 0.5 mL of CDCl₃; 45 °C. Selectivities > 98%.

TABLE 2: Comparison of the Performance of Insoluble Heterogeneous, Single-Site Ti(IV)/SiO₂ Epoxidation Catalysts⁷ with Their Homogeneous Soluble Molecular Analogues

homogeneous catalyst ^a	turnover frequency (h ⁻¹)	turnover frequency (h ⁻¹)	heterogeneous catalyst ^b
(1) [(<i>c</i> -C ₅ H ₉) ₇ Si ₇ O ₁₂ Ti(OSiPh ₃)]	18	26	Ti†SiO ₂ ^c
(2) [(<i>c</i> -C ₅ H ₉) ₇ Si ₇ O ₁₂ Ti(OGepH ₃)]	52	34	Ti†MCM-41
(3) [(<i>c</i> -C ₅ H ₉) ₇ Si ₇ O ₁₂ Ti(OSnPh ₃)]	33	12	Ti†Sn†MCM-41

^a 3 mg of catalyst:0.03 mL of TBHP:0.12 mL of cyclohexene; 0.42 mL of CDCl₃; 30 °C, 1 h. Selectivities > 98%. ^b Heterogeneous catalysts prepared as described in ref 7 (typical Si:Ti ratios of 1:44). 50 mg of catalyst:0.5 mL of TBHP:2 mL of cyclohexene:7 mL of MeCN; 30 °C, 1 h. Selectivities > 95%. ^c Degussa Aerosil 200 silica.

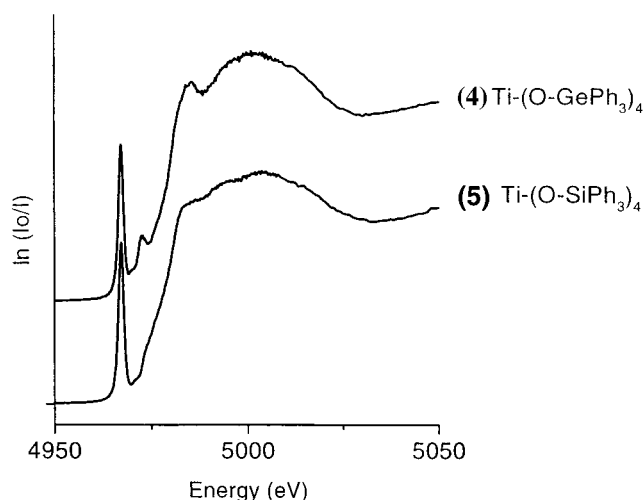
(for pre- and post-edge background subtraction), and EXCURV98 (for detailed analysis to extract the structural parameters).

Molecular Dynamics. The molecular dynamics runs were carried out using the Discover code (MSI, San Diego).³⁰ A 5 ps duration run, with a 1 fs time step, at 500 K was employed.

Results and Discussion

First, we present the catalytic performance of the titanasil-sesquioxane catalysts in the epoxidation of cyclohexene. Table 1 summarizes the results of the homogeneous catalysts; and Table 2 compares the performance, expressed in turnover frequency (i.e., per single Ti(IV) site), of a variety of homogeneous and heterogeneous⁷ catalysts. Clearly, the trend in activity of the homogeneous silicon (1) and germanium (2) silsesquioxane catalysts follows that found earlier for the corresponding heterogeneous catalysts. The reality of the enhancement of activity of a central Ti(IV) active site by a juxtaposed germanium (in place of silicon) is apparent. However, the activity of the tin-containing homogeneous analogue (3) lies between the silicon and the germanium forms, in conflict with the observations found for the heterogeneous catalysts. We believe that the reason the same order of catalytic activity of the homogeneous catalysts is not observed for the equivalent heterogeneous catalysts is because in the Ti†Sn†MCM-41 material it is only possible to form a mixture of active sites, such as those shown in Figure 1a, and inactive ones in which Ti(IV) is grafted onto particles of SnO₂.⁷ The inactive sites will lead to a reduction in the turnover frequency of the Ti†Sn†MCM-41 material.

In an attempt further to understand the catalytic performance of these materials, we probed their titanium centers using X-ray absorption near-edge spectroscopy (XANES) which is known to be sensitive to local coordination geometry, oxidation state, and electronic effects.^{31,32} In particular, the pre-edge peak is very sensitive to the local coordination geometry around the

**Figure 2.** Ti K-edge XANES spectra for the molecular compounds (4) and (5).

metal center under investigation, for example, titanium-containing MCM-41, zeolite β, and TS-1 all show an intense pre-edge peak in the dehydrated form³⁸ which decreases markedly upon hydration or interaction with coordinating molecules.^{2,33–36,38}

The Ti K-edge XANES of the two model compounds, Ti-(O-SiPh₃)₄ (4) and Ti-(O-GePh₃)₄ (5) (displayed in Figure 2) show almost identical pre-edge peak intensities, but exhibit some differences in their edge features. This suggests that the local coordination, in particular the oxygen environment in these two materials, is identical. Indeed the intense pre-edge peak representative of a tetrahedral coordination is consistent with their recently solved crystal structures.²⁵ Although these materials contain titanium in tetrahedral coordination, exposure to atmospheric moisture (note that Ti K-edge XAS experiments were performed in ambient conditions) or liquid reactants, used in a typical catalytic test, did not alter the pre-edge peak intensity, unlike the catalytically active Ti†MCM-41, Ti-zeolite β, or TS-1.³³ The molecular dynamics calculations (performed using the crystal structure information²⁵ concerning the isolated molecule as the starting point) allow us to understand why this is so. It is clear from Figure 3 that the twelve phenyl groups shroud the central, potentially catalytically active (and coordinatively unsaturated) Ti(IV) atom making access of reactants to the central Ti(IV) atom in the molecular Ti-(O-GePh₃)₄ very limited. This is consistent with the catalytic inactivity of the Ti-(O-GePh₃)₄ and Ti-(O-SiPh₃)₄ materials (see Table 1).

Comparison of the XANES of the catalytically active silicon (1) and germanium (2) titanasil-sesquioxane with model compounds (4) and (5) (see Figures 2 and 4 and Table 1) shows less intensity in the pre-edge peak (note that all the measurements were carried out ex situ, at ambient conditions). This behavior is similar to that exhibited by the other titanium-containing heterogeneous catalysts mentioned previously and indicates that substitution of three Ph₃XO- ligands by the silanol groups of the silsesquioxane now renders the central, unsaturated titanium(IV) accessible to interaction with water or other reactant molecules. This interpretation is confirmed by their observed catalytic activity and by the molecular simulation shown in Figure 3. It is apparent from Figure 3 that by anchoring the Ti centers tripodally and retaining one O-Ge-Ph₃ group, it is possible to create an accessible catalytically active species. Using a similar synthetic strategy, it is also possible to graft compound (4) onto the inner, silanol-rich surfaces of MCM-41 in the presence of a solvent which dissolves both compound (4) and

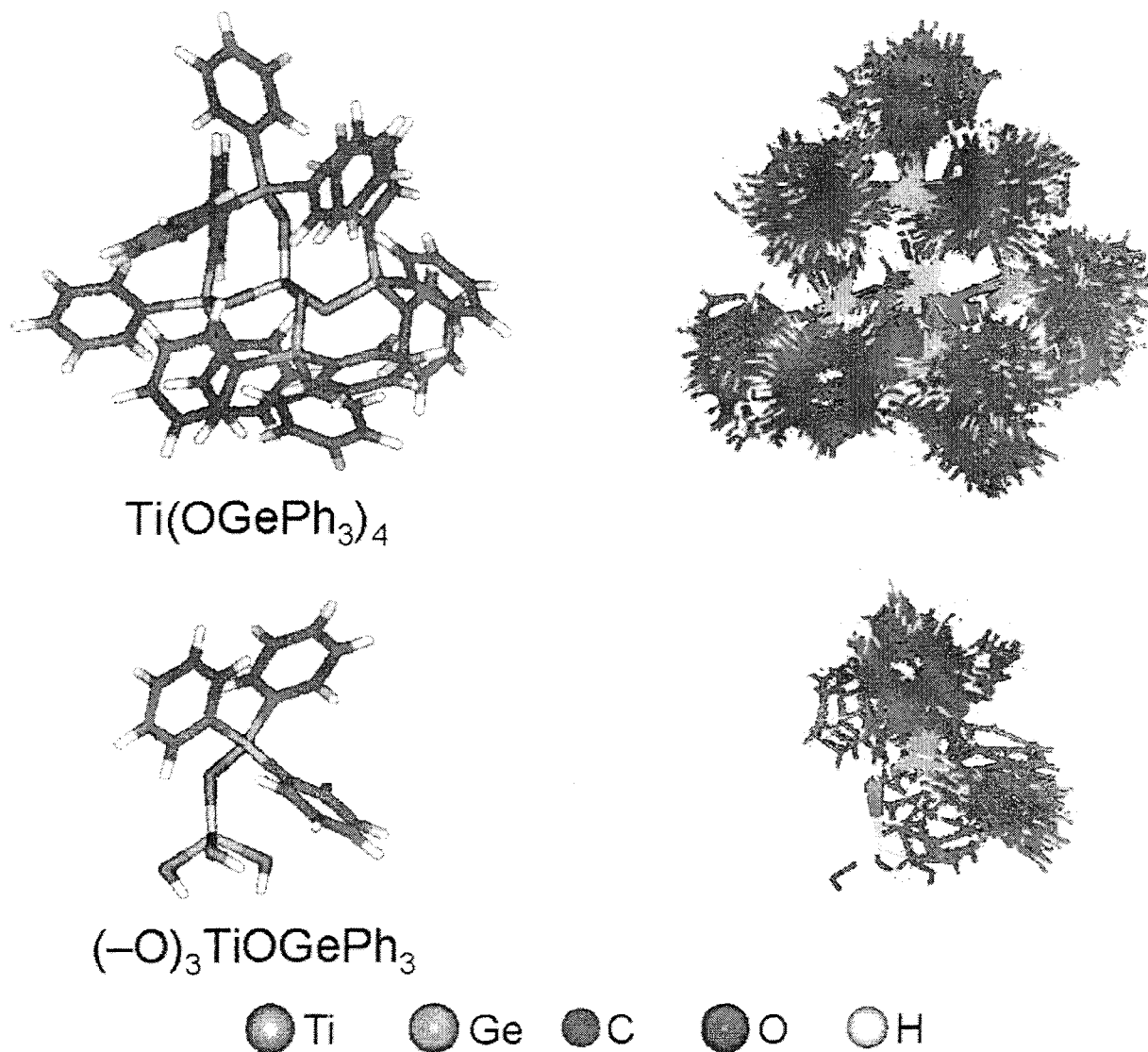


Figure 3. Results of molecular dynamics simulations for the isolated (top) and “anchored” (bottom) $\text{Ti}-(\text{O}-\text{GePh}_3)_4$ molecular clusters. For the anchored cluster, the Ti and the three pendant OH groups were kept fixed during simulation. These representations consist of superposition of frames from the simulation taken at 200 fs intervals, roughly the time scale for libration of the phenyl groups. Comparison of the top and bottom (right) views shows that access of reactants is far greater for the “anchored” than for the free Ti -centered entity. In the free state, the four triphenyl groups shroud the central, potentially catalytically active (and coordinatively unsaturated) $\text{Ti}(\text{IV})$ ion.

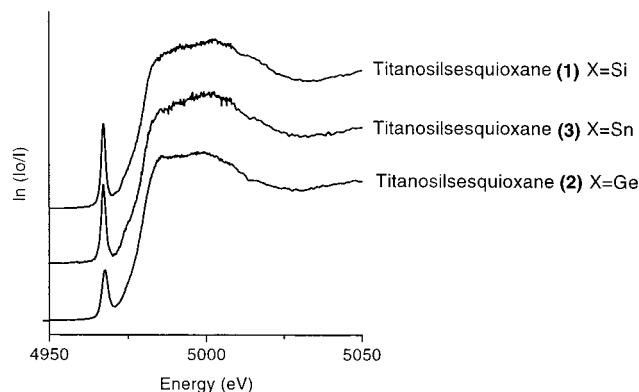


Figure 4. Room-temperature Ti K-edge XANES spectra for the titanosilsesquioxanes catalysts (1), (2), and (3). Note that the data were collected using the as-synthesized solids.

the triphenylsilanol byproduct. This leaves behind a surface rich in $(\text{>Si}-\text{O})_3-\text{Ti}-\text{OSiPh}_3$ groups (as depicted in Figure 1c) and a catalyst that we find exhibits greater catalytic activity than those prepared by grafting titanocene onto MCM-41.^{2,3}

A comparison of the XANES data of the silicon-(1), germanium-(2), and tin-(3) derivatized titanosilsesquioxane catalysts (see Figure 4) provides an insight into their relative catalytic activity. Unlike the model compounds (Figure 2), the pre-edge intensities of these three catalysts are markedly different from one another (see Table 1), with the germanium analogue (2) having the least and the silicon analogue (1) having the most intense pre-edge peak. This could either be due to (a) the presence of some octahedrally coordinated titanium centers, similar to the ones found in TiO_2 or in ETS-10, along with tetrahedral species or (b) interaction of Ti centers with atmospheric water, thereby resulting in a distorted, octahedral coordination similar to that present in heterogeneous titanosilicates. The former can be clearly ruled out, since the germanium-containing silsesquioxane shows the minimum pre-edge intensity (and maximum catalytic activity). Furthermore, it is well-known that both TiO_2 or ETS-10 are not active in catalytic epoxidation. The latter is the more likely possibility, since this behavior is similar to that of the heterogeneous catalysts. (It is not sensible to dehydrate these materials at temperatures similar to those used for heterogeneous titanium-

containing silicate catalysts i.e., in the range 400–500 °C since these titanosilsesquioxanes are unstable at such temperatures.) To examine if any loosely bound water molecules are present in the silsesquioxane catalysts, we separately dehydrated the Ge form at 55 °C, in a vacuum, for 2 h and we find that the pre-edge intensity peak does indeed increase (from 0.36 to 0.54). This mirrors the behavior of titanium-containing heterogeneous catalysts, where the pre-edge intensity decreases significantly during reaction upon attachment of the reactant species. Thus our XANES data show that, in the solid state, the degree of accessibility of the Ti active center decreases in the order Ge > Sn > Si which closely follows with the order of catalytic activity.

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References and Notes

- (1) Murugavel, R.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36* (6), 477.
- (2) Maschmeyer, T.; Rey, F.; Sankar, G.; Thomas, J. M. *Nature* **1995**, *378*, 159.
- (3) Oldroyd, R. D.; MacFaul, P. A.; Maschmeyer, T.; Thomas, J. M.; Snelgrove, D. W.; Ingold, K. U.; Wayner, D. D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2787.
- (4) Marchese, L.; Gianotti, E.; Dellarocca, V.; Maschmeyer, T.; Rey, F.; Coluccia, S.; Thomas, J. M. *PCCP* **1999**, *1*, 585.
- (5) Thomas, J. M. *Eur. J. Chem.* **1997**, *3*, 1557.
- (6) Oldroyd, R. D.; Thomas, J. M.; Sankar, G. *J. Chem. Soc., Chem. Commun.* **1997**, 2025.
- (7) Oldroyd, R. D.; Sankar, G.; Thomas, J. M.; Ozkaya, D. *J. Phys. Chem. B* **1998**, *102*, 1849.
- (8) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741.
- (9) Feher, F. J.; Gonzales, S. L.; Ziller, J. W. *Inorg. Chem.* **1988**, *27*, 3440.
- (10) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3859.
- (11) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205.
- (12) Voigt, A.; Murugavel, R.; Montero, M. L.; Wessel, H.; Liu, F. Q.; Roesky, H. W.; Uson, I.; Albers, T.; Parisini, E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1001.
- (13) Maschmeyer, T.; Klunduk, M. C.; Martin, C. M.; Shephard, D. S.; Thomas, J. M.; Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1997**, 1847.
- (14) Klunduk, M. C.; Maschmeyer, T.; Thomas, J. M.; Johnson, B. F. G. *Eur. J. Chem.* **1999**, *5*, 1481.
- (15) Klunduk, M. C.; Thomas, J. M.; Johnson, B. F. G.; Maschmeyer, T. *J. Organomet. Chem.*, submitted.
- (16) Crocker, M.; Herold, R. H. M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1997**, 2411.
- (17) Crocker, M.; Herold, R. H. M. *Pat. Appl. PCT/EP96/05873*, **1997**.
- (18) Abbenhuis, H. C. L.; Krijnen, S.; van Santen, R. A. *J. Chem. Soc., Chem. Commun.* **1997**, 331.
- (19) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Thiele, S. K. H.; van Tol, M. F. H. *Organomet.* **1998**, *17*, 5222.
- (20) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K. H.; van Tol, M. F. H. *Organomet.* **1998**, *17*, 5663.
- (21) Buys, I. E.; Hambley, T. W.; Houlton, D. J.; Maschmeyer, T.; Masters, A. F.; Smith, A. K. *J. Mol. Catal.* **1994**, *86*, 309.
- (22) Field, L. D.; Lindall, C. M.; Maschmeyer, T.; Masters, A. F. *Aust. J. Chem.* **1994**, *47*, 1127.
- (23) Wada, K.; Nakashita, M.; Bundo, M.; Ito, K.; Kondo, T.; Mitsudo, T. *Chem. Lett.* **1998**, 659.
- (24) Notari, B. *Adv. Catal.* **1996**, *41*, 253.
- (25) Klunduk, M. C.; Sankar, G.; Martin, C. M.; Thomas, J. M.; Johnson, B. F. G. Manuscript in preparation.
- (26) Zeitler, V. A.; Brown, C. A. *J. Am. Chem. Soc.* **1957**, *79*, 4616.
- (27) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
- (28) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organomet.* **1991**, *10*, 2526.
- (29) Dannley, R. L.; Farrant, G. C. *J. Org. Chem.* **1969**, *34*, 2428.
- (30) Discover Code, MSI, San Diego, **1996**.
- (31) *X-ray Absorption, Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*; Koningsberger, D. C., Prins, R., Eds.; Wiley: New York, 1988.
- (32) Iwasawa, Y. *Proceedings of the 11th International Congress on Catalysis*, Baltimore, 1996; Hightower, J. W., Delgass, W. N., Bell, A. T., Iglesia, E., Eds.; Elsevier: Amsterdam, 1996; p 21.
- (33) Sankar, G.; Rey, F.; Thomas, J. M.; Greaves, G. N.; Corma, A.; Dobson, B. R.; Dent, A. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2279.
- (34) Blasco, T.; Camblor, M. A.; Corma, A.; Prez-Pariente, J. *J. Am. Chem. Soc.* **1993**, *115*, 11806.
- (35) Tozzola, G.; Mantegazza, M. A.; Raghino, G.; Petrini, G.; Bordiga, S.; Ricchiardi, G.; Lamberti, C.; Zulian, R.; Zecchina, A. *J. Catal.* **1998**, *179*, 64.
- (36) Thomas, J. M. *Faraday Discuss.* **1996**, *105*, 1.
- (37) Sankar, G.; Thomas, J. M. *Topics in Catal.* **1999**, *8*, 1.
- (38) Sankar, G.; Thomas, J. M.; Catlow, C. R. A. Submitted for publication.