Available online at www.sciencedirect.com
ScienceDirect

Journal of Catalysis 251 (2007) 453–458

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

# Organo-bridged silsesquioxane titanates for heterogeneous catalytic epoxidation with aqueous hydrogen peroxide

Yi Meng Wang [a,b], Pieter C.M.M. Magusin [a], Rutger A. van Santen [a,*], Hendrikus C.L. Abbenhuis [b]

[a] *Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, 116023 Dalian, China*

Received 2 May 2007; revised 16 July 2007; accepted 17 July 2007

---

## Abstract

Organo-bridged silsesquioxane titanates for heterogeneous catalytic epoxidation with aqueous hydrogen peroxide were synthesized through the acid-catalyzed hydrolysis and co-condensation of organotrialkoxysilane monomers and $\alpha,\omega$-bis(trialkoxysilyl) alkane cross-linkers in ethanol–water solution, with subsequent titanium grafting. These hybrid catalysts show high activity and selectivity in the epoxidation of cyclooctene with both aqueous hydrogen peroxide and *tert*-butyl hydroperoxide (TBHP) as oxidants, although they are nonporous. The catalysts can be reused at least six times with no loss of activity with TBHP as the oxidant and at least four times (although with gradual activity loss) with aqueous $H_2O_2$ as the oxidant. Furthermore, the catalytic activities of these hybrid titanates relate to the nature and the composition of the starting materials used. The epoxidation activity of the catalysts using aqueous $H_2O_2$ as the oxidant seems to increase with increasing carbon length in the starting organosilane cross-linkers. UV–vis DRS and XPS measurements indicate that tetrahedrally coordinated Ti species are the active centers.

*Keywords:* Organosilica support; Titanate; Silsesquioxane; Epoxidation; Aqueous; Hydrogen peroxide; Nonporous

---

## 1. Introduction

The development of heterogeneous epoxidation catalysts remains of considerable interest and a challenge from the standpoint of both fundamental chemistry and modern industrial processes. $Ti^{IV}$, which is not the most effective homogeneous epoxidation catalyst, forms various efficient and truly heterogeneous catalysts [1]. An early and successful example, $Ti(IV)/SiO_2$, was commercialized by Shell in the 1970s for the epoxidation of propene with ethylbenzene hydroperoxide [2]. However, the $Ti(IV)/SiO_2$ catalyst, a hydrophobic molecular sieve, is ineffective for epoxidation with aqueous hydrogen peroxide. TS-1, developed by Enichem in the 1980s, shows high epoxidation activity with aqueous hydrogen peroxide under very mild conditions [3]. Although some large-pore molecular sieves, including zeolite $\beta$ [4], mordenite [5], ZSM-12 [6], and MCM-22 [7], with isomorphous substitution of part of the silicon for titanium, have broadened the possible uses of titanium molecular sieves as (ep)oxidation catalysts, the relatively small pore size (usually $<0.8$ nm) of these titanium molecular sieves restricts their application to the epoxidation of small organic substrates. Therefore, titanium catalysts with high stability in the epoxidation with aqueous hydrogen peroxide and easy accessibility to bulky substrates remain in great demand.

Up to now, some titanium-supported amorphous silicas and ordered mesoporous silicas have been claimed to have high epoxidation activity with hydrogen peroxide [8–12]. However, certain organic solvents, such as acetonitrile, 1-phenylethanol, and *tert*-butanol [8–12], co-react in the epoxidation reaction.

Another route is to mimic the hydrophobicity in TS-1. Some hydrophobic mixed titania–silica oxides containing Si–C bonds have been prepared by sol–gel methods [13–16] or by subsequent trimethylsilylation of the surface [17,18]. An alternative approach involves the incorporation of titanium containing polyhedral oligosilsesquioxane (POSS) units into a hydrophobic polymer backbone [19,20]; however, as yet this has not yet resulted in catalysts with sufficient activity and reusability with aqueous hydrogen peroxide as the oxidant.

---

[*] Corresponding author. Fax: +31 40 2455054.
*E-mail address:* r.a.v.santen@tue.nl (R.A. van Santen).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2007.07.023

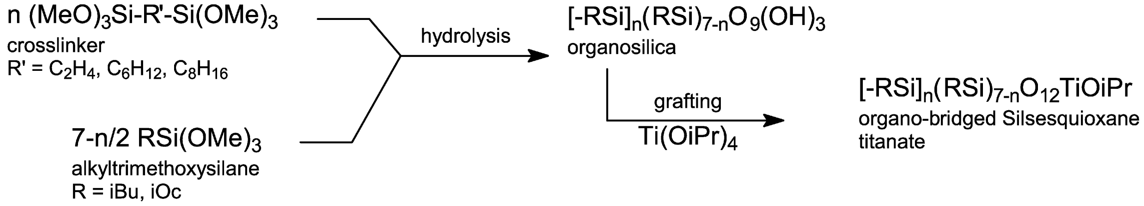


Chart 1. Synthesis of organo-bridged silsesquioxane titanates.

Incompletely condensed POSS units with silanols can be used as models to study silica surfaces [21]. Incorporation of these units into solid materials may render catalyst supports with molecularly defined metal docking sites. Here we report a one-pot method to prepare hybrid organosilica supports. After post-titanium grafting, these catalysts have a high epoxidation activity and good reusability using aqueous hydrogen peroxide as the oxidant without the assistance of an organic solvent (Chart 1).

## 2. Experimental

### 2.1. Catalyst synthesis

Bis(trialkoxysilyl) alkane or a mixture of alkyltrimethoxysilane and such a dimeric organosilane, containing 20 mmol Si, was added to a solution of 20 ml of 37% HCl and 40 mL of ethanol, and the mixture was refluxed for 6 h. Then the solid was recovered by filtration, washed in water and ethanol, and dried at room temperature. The bridged organosilane was selected from 1,2-(trimethoxysilyl)ethane (BTME), 1,6-(trimethoxysilyl)hexane (BTMH), and 1,8-(triethoxysilyl)octane (BTEO), and the alkyltrimethoxysilane was selected from *iso*-butyl trimethoxysilane (*i*BTMS) and *iso*-octyl trimethoxysilane (*i*OTMS). All silanes were used as received from Gelest.

A 0.5-g sample of each of the aforementioned hybrid solids was reacted with 0.1 g $Ti(O^iPr)_4$ in 50 ml of hexane at reflux temperature for 8 h under argon. The titanium catalyst was recovered by filtration, washed in hexane and ethanol, and dried at room temperature.

### 2.2. Characterization

Nitrogen sorption was measured on a Tristar 3000 Micromeritics apparatus that allowed the analysis of up to three solids at one time. Before measurements, the samples were pretreated at 423 K under a nitrogen flow for 2 h.

X-ray photo-electron spectroscopy (XPS) was conducted with a VG Escalab 200 using a standard aluminum anode ($AlK\alpha$ 1486.3 eV) operating at 510 W. Spectra were recorded at room temperature at normal emission at background pressure of $5 \times 10^{-10}$ mbar. All binding energies were referenced to the Si 2p peak at 103.3 eV.

UV–vis spectra were recorded on a Shimadzu UV-2401 PC spectrometer in diffuse–reflectance mode with a 60-mm integrating sphere. $BaSO_4$ was used as a reference sample.

The solid-state NMR experiments were performed on a Bruker DMX500 spectrometer operating at 500.13 MHz for $^1H$ and 99.36 MHz for $^{29}Si$. A magic-angle spinning (MAS) probe head equipped with a 4-mm rotor spinning at 12.5 kHz was used. Quantitative $^{29}Si$ MAS spectra were obtained using a Hahn decoupling pulse sequence with a 90° pulse of 5 µs and a delay time of 120 s. $^1H/^{29}Si$ cross-polarization experiments were conducted using a 5-s delay time and a 5-ms contact time. The number of scans collected for each spectrum varied between 128 and 1024. The $^{29}Si$ chemical shifts were referenced to TMS.

Infrared (IR) spectra were recorded on a Bruker IFS-113v Fourier Transform IR spectrometer with a DTGS detector at a resolution of 2 $cm^{-1}$. Typically, a sample was evacuated in vacuo (pressure $<10^{-6}$ mbar) at 423 K for 30 min, and the spectra were recorded at 423 K and room temperature, respectively.

### 2.3. Catalyst activity testing

Aqueous $H_2O_2$: (1.8 mmol, 35% aqueous solution; Acros), catalyst (0.06 g), and neat cyclooctene (7.2 mmol) were mixed together in the reaction vessels (cyclooctene/$H_2O_2$ molar ratio = 4:1), with 1,3,5-trimethylbenzene (TMB, Acros, 99%) added as the internal standard. The epoxidation reaction was performed at 333 K for 4 h. Samples (0.1 mL) were taken from the reactors and filtered through syringe filters (0.45 µm); then the organic top layer was injected into gas chromatography (GC) vials containing MeOH (0.9 mL), and analyzed by GC; additional GC analysis of the water layer showed no traces of diols.

In epoxidations with TBHP (*tert*-butyl hydroperoxide) as the oxidant, cyclooctene (7.2 mmol), TBHP (1.8 mmol, 2.0 M in isooctane), catalyst (0.06 g), and TMB as an GC internal standard were transferred into the reaction vessels, with a cyclooctene/TBHP molar ratio of 4:1. The reaction was performed at 333 K for 4 h.

For recycling tests on the hybrid catalysts, before each cycle, the catalyst was recovered by filtration, washed with methanol three times, and dried. In the recycling reactions, the weight ratios of the catalyst, reactant, and oxidant were kept constant.

## 3. Results

### 3.1. $N_2$ adsorption–desorption

First, hybrid organosilica supports were synthesized by acid-catalyzed hydrolysis and co-condensation of bis(trialkoxysilyl) alkane monomers and trialkoxysilane. Then these hybrid supports were subjected to grafting titanium isopropoxide with no

Table 1
The composition and catalytic activity of titanium containing hybrid catalysts

| Catalysts | Composition (mmol) | | $S_{BET}$[a] ($m^2/g$) | Ti/Si[b] | Ti[d] (wt%) | Yield[c,e,f] (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | By $H_2O_2$ | By TBHP |
| TA-01Ti | 10/*i*BTMS | 5/BTEO | 4.6 | 0.101 | $2.7 \pm 0.1$ | 85.6 | 87.2 |
| TA-05Ti | 5/*i*BTMS | 7.5/BTEO | 9.8 | 0.177 | $1.4 \pm 0.1$ | 75.1 | 93.2 |
| TA-03Ti | 0/*i*BTMS | 10/BTEO | 24.9 | 0.323 | $0.9 \pm 0.1$ | 35.7 | 90.8 |
| TA-10Ti | 10/*i*BTMS | 5/BTMH | 0.8 | 0.184 | $1.2 \pm 0.1$ | 66.5 | 88.8 |
| TA-08Ti | 10/*i*BTMS | 5/BTME | 3.7 | 0.745 | $0.9 \pm 0.1$ | 29.2 | 83.9 |

[a] $S_{BET}$: surface area.
[b] Measured by XPS.
[c] Epoxidation reaction: cyclooctene/oxidant = 4 (mol/mol); 333 K.
[d] Titanium contents were determined by ICP analysis.
[e] Measured by GC with internal standard.
[f] Epoxide selectivity >95% in all cases.

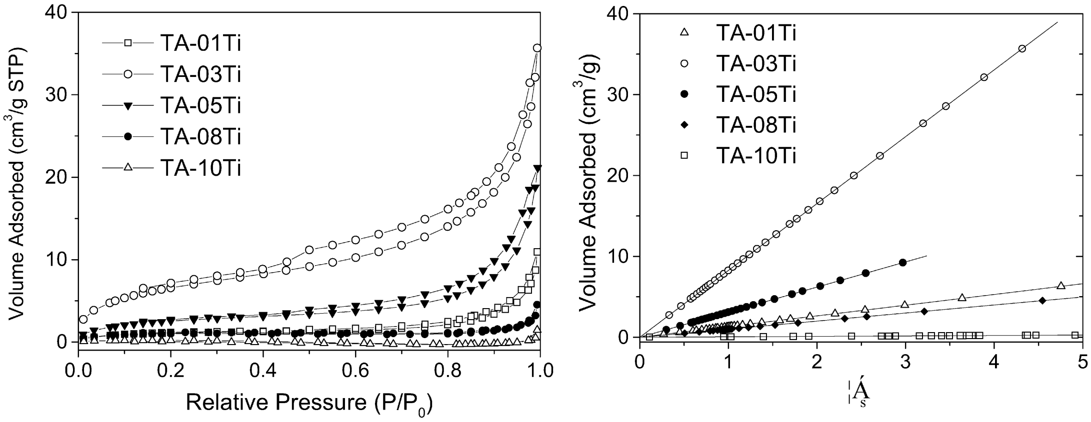


Fig. 1. $N_2$ adsorption–desorption isotherms (left) and $\alpha_s$ plots (right) on the hybrid titanium catalysts.

pretreatment under ambient conditions. As shown in Table 1, all of the catalysts had small surface areas. Fig. 1 gives $N_2$ adsorption–desorption isotherms and $\alpha_s$ plots; $\alpha_s$ is the ratio of the amount adsorbed (at the given $p/p_0$) to the amount adsorbed at $p/p_0 = 0.4$. All samples demonstrate linear $\alpha_s$ plots over the whole range of $p/p_0$, indicating that they are nonporous [22].

### 3.2. Epoxidation activity

The titanium catalysts were tested in the epoxidation of cyclooctene using 35% aqueous hydrogen peroxide solution or TBHP as the oxidant. As shown in Table 1, all titanium catalysts gave a high epoxide yield using TBHP as the oxidant, even though these hybrid titanium-containing catalysts were all nonporous. But they behaved quite differently when using aqueous hydrogen peroxide solution as the oxidant. With the incorporation of monosubstituted organosilane, *i*BTMS, the catalytic activity improved distinctly. Furthermore, the catalyst synthesized from *i*BTMS and BTEO with the longest carbon bridge showed the best catalytic activity.

### 3.3. XPS and UV–vis measurement

XPS and UV–vis were used to characterize the nature of the Ti species. As shown in Fig. 2, all samples except TA-08Ti had tetrahedrally coordinated Ti species with a Ti $2p_{3/2}$ peak situated at high binding energy (460 eV), whereas the TA-08Ti sample exhibited another contribution at lower binding energy (about 458 eV), which is the fingerprint of octahedrally coordinated Ti(IV) [17,23].

Moreover, diffuse reflectance UV–vis spectra demonstrated that these titanium catalysts had several overlapping absorption bands at 200–300 nm, as shown in Fig. 3. These broad absorptions are similar to those of amorphous silica-supported titanium catalysts, but quite different from the single peak at 210 nm for TS-1 [8].

The bands at 200–230, 260–290, and 330 nm give evidence of isolated framework Ti, octahedrally coordinated Ti species with low dispersion, and anatase Ti(IV) particles, respectively [24]. Moreover, the absorption bands at around 280, 220 and 200 nm can be assigned to the monofunctional, bifunctional, and multifunctional bonding of titanium atoms through –O–Si–O– bridges with the silica matrix, respectively [25]. Combined with XPS data, the band at around 260–280 nm in Fig. 3 can be assigned to tetrahedrally coordinated titanium species with less attachment to the silica support through Ti–O–Si linkages. Most samples demonstrated no absorption at 330 nm, indicating the absence of $TiO_x$ clusters. As shown in Fig. 3B, TA-08Ti showed the broadest absorption, with a small component at around 330 nm attributed to $TiO_x$ aggregates with octahedral coordination. This is in harmony with the XPS data.

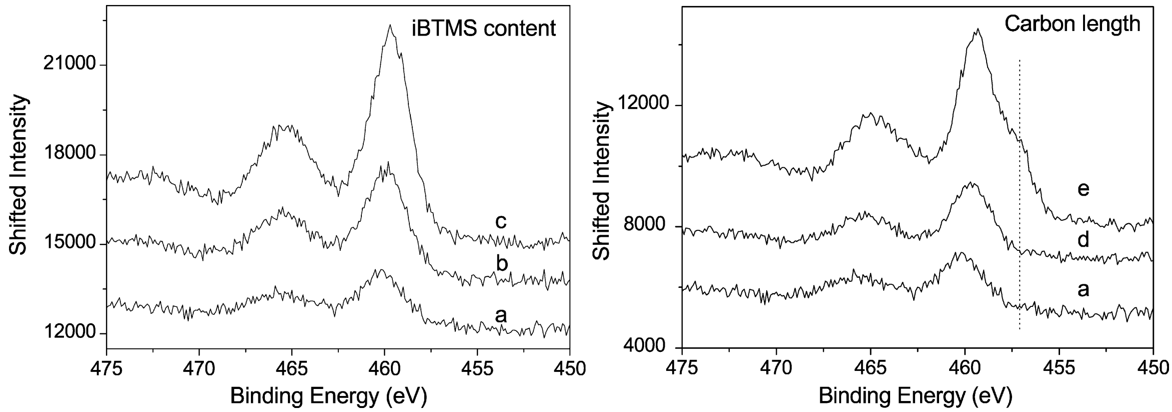
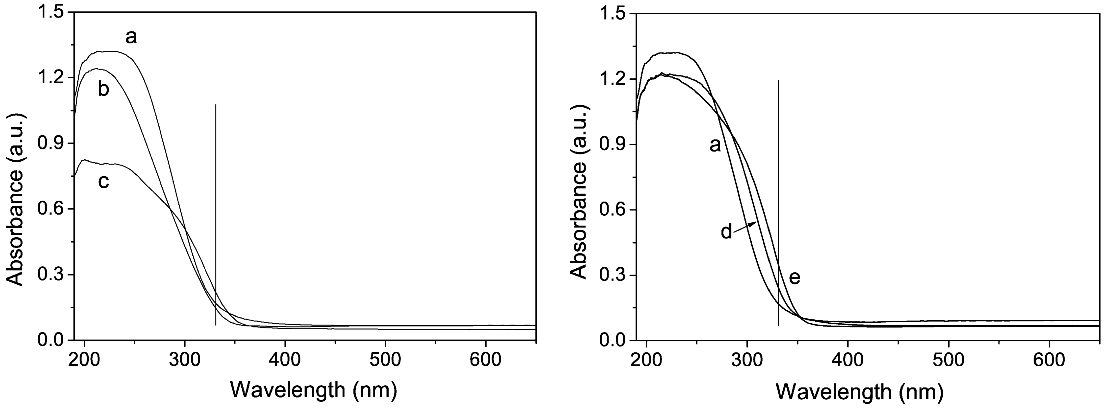


Fig. 2. XPS spectra for the samples: (a) TA-01Ti, (b) TA-05Ti, (c) TA-03Ti, (d) TA-10Ti, and (e) TA-08Ti.



(A)

(B)

Fig. 3. UV-DR spectra of the samples with different compositions: (a) TA-01Ti, (b) TA-05Ti, (c) TA-03Ti, (d) TA-10Ti, and (e) TA-08Ti.

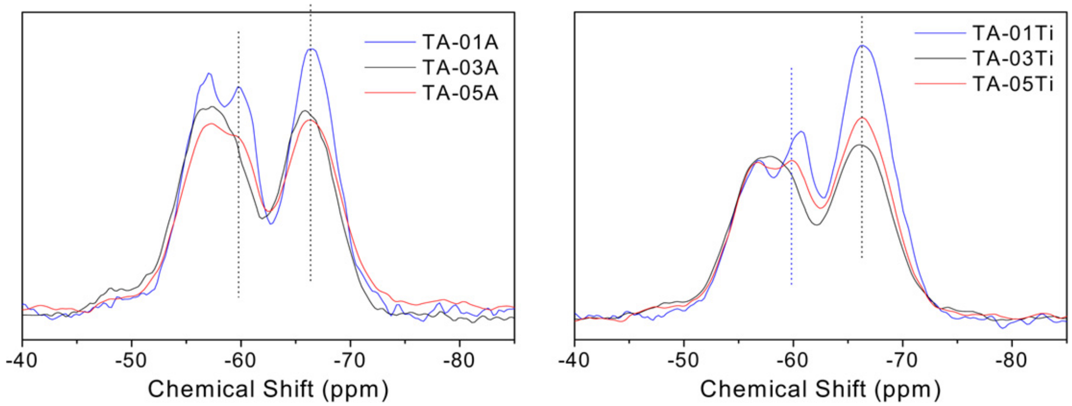


Fig. 4. The $^1$H/$^{29}$Si CP/MAS NMR spectra of the samples.

### 3.4. *NMR measurements*

Quantitative measurements of $^{29}$Si MAS NMR were used to characterize these supports and titanium catalysts, wherein $T^0$, $T^1$, $T^2$, and $T^3$ represent the number of siloxane bonds to a silicon atom. As shown in Table 1, the titanium catalysts exhibited better epoxidation activity using aqueous $H_2O_2$ as an oxidant with an increasing amount of *i*BTMS. However, the $T^2/T^3$ ratios for TA-01A and TA-03A before titanium grafting were almost the same (about 0.89). Two corresponding titanium catalysts exhibited distinct differences in the epoxidation with aqueous $H_2O_2$, indicating no direct correlation between the amount of silanol in the support and the amount of Ti grafted onto the catalysts.

Interestingly, the $T^2$ peak ($\delta_{Si} = -57.9$) split into two peaks ($\delta_{Si} = -57.1$ and $-60.0$) in the $^1$H/$^{29}$Si CP/MAS spectra of TA-01A and TA-05A with the incorporation of *i*BTMS, as shown in Fig. 4. However, TA-03A, composed of BTEO, showed only one peak of $T^2$ species, ($\delta_{Si} = -57.9$), in accordance with previously reported findings [26,27].

If the different aliphatic groups caused the splitting of the $T^2$ peak, then the $T^3$ peak attached to the same organic groups should exhibit similar splitting. Moreover, because $–CH_2–Si\equiv$ groups dominate in both BTEO and *i*BTMS compounds, the difference in the chemical shifts due to two aliphatic precursor compounds should be not so distinct [27]. Periodic mesoporous organosilicas synthesized by the hydrolysis and co-condensation of bis(triethoxysilyl)ethane and other organosilanes with different functional groups, including amino, vinyl, ethyl, glycidoxypropyl, and cyanopropyl units, showed no splitting of the $T^2$ peak [28]. Thus different organic groups cannot cause the splitting of the $T^2$ peak. Furthermore, substitution of OR′ for OH (hydrolysis) leads to a chemical shift between 0.4 and 0.8 ppm [29]; however, this splitting is 2.9 ppm, much larger than the shift caused by hydrolysis. This splitting most likely can be attributed to different silanol environments with certain organosilica structures, such as linear, cyclic, and caged structures.

In the case of the trialkoxysilane gels, the bands of $T^2$ silicons in the $-57$ to $-61$ ppm region can be interpreted by the existence of different diastereoisomers of an incompletely condensed octameric $Si_8(OH)_2$, whereas the sharp band at $-60.2$ ppm can be assigned to heptameric tri-silanol $Si_7(OH)_3$ [30,31]. Furthermore, the $T^2$ peak could move to a minus larger chemical shift after a longer condensation process, demonstrating an increase in the sterical hindrance around the silicon atom due to the growth of oligomers [32]. These two explanations do not contradict each other. Thus, the $T^2$ peak ($\delta_{Si} = -60.0$ ppm) here might be related to silanols situated in a close manner, similar to tetra-silanols and tri-silanols in POSS units.

### 3.5. IR spectroscopy

The presence of tetra-silanols and tri-silanols is supported by the IR spectra measured under vacuum. Before titanium grafting, a vibration of intramolecular mono-hydrogen bond centering at 3440 $cm^{-1}$ overlapped some small vibrations from 3080 to 3650 $cm^{-1}$ (Fig. 5). There was no obvious difference between TA-01A and TA-03A. After titanium grafting, a shoulder appeared (but at a different wavenumber) in the spectra of both titanium catalysts collected at room temperature (not shown). But these vibration bands at lower wavenumber were distinct in the spectra collected at 423 K. The signal of TA-01Ti was at ∼3180 $cm^{-1}$, and that of TA-03Ti was at ∼3271 $cm^{-1}$. The former may correspond to the vibration of vicinal tri-silanol or tetra-silanol; the latter, to that of di-silanol [21]. Therefore, the surface properties of these two samples are quite different.

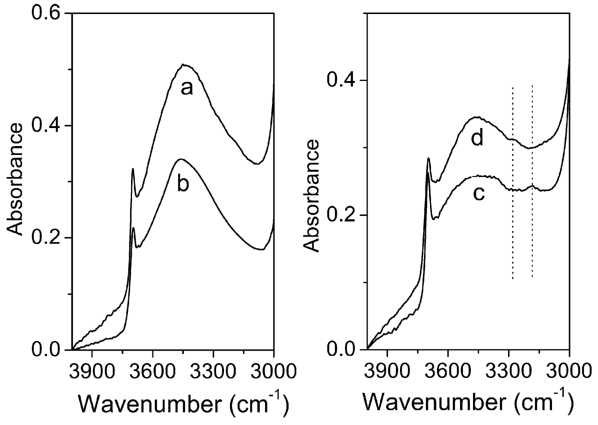


Fig. 5. The infrared spectra of samples: (a) TA-01A, (b) TA-03A before titanium grafting collected at room temperature, (c) TA-01Ti and (d) TA-03Ti after titanium grafting collected at 423 K.

## 4. Discussion

All of the hybrid titanium catalysts discussed here are nonporous. Nonporous xerogels can be synthesized from bis(trialkoxysilyl) monomers containing longer alkylene bridges due to the microphase separation of the long aliphatic $C_8$ groups and the framework of siloxane [26]. Interestingly, the titanium catalysts synthesized from BTME and BTMH with shorter alkylene bridges also are nonporous, probably due to the incorporation of *i*BTMS.

The XPS and UV–vis diffuse reflectance spectra demonstrated that all of the titanium catalysts except TA-08Ti have only tetrahedrally coordinated Ti species. All of these catalysts gave a high epoxide yield using TBHP as the oxidant. This confirms that tetrahedrally coordinated Ti species are the active centers in the epoxidation reaction for all of these hybrid titanium catalysts. However, the content of the surface Ti species had no direct correlation with catalytic activity. Even the titanium catalysts with high surface species content exhibited low epoxidation activity with $H_2O_2$ as the oxidant, as shown in Table 1. Apparently, tetrahedrally coordinated Ti with a unique environment is required.

The different catalytic activities demonstrated when $H_2O_2$ was used as an oxidant may be related to the nature and composition of the catalyst preparation starting materials. As shown in Table 1, the epoxidation activity of the catalysts increased with increasing length of the alkylene bridge in the bis(trialkoxysilyl) monomers. The titanium-containing hybrid catalyst synthesized from BTEO and *i*BTMS exhibited the highest epoxide yield: 85.6% based on $H_2O_2$. Using BTMH and BTME instead of BTEO, the yields decreased to 66.5 and 29.2%, respectively. A similar phenomenon occurred with regard to the length of the organic group in the organotrialkoxysilanes. Using *i*OTMS instead of *i*BTMS, the epoxide yield for the catalyst from BTME and *i*OTMS increased from 29.2 to 57.2% with $H_2O_2$. Apparently, the epoxidation activity of the hybrid catalysts has a direct correlation to the length of organic groups, that is, the hydrophobicity.

But hydrophobicity alone is not the ultimate solution to the epoxidation with aqueous hydrogen peroxide. It has been shown that the titanium centers embedded in highly hydrophobic polystyrene backbone undergo some leaching. These titanium catalysts could not be reused in a second run with $H_2O_2$ as the oxidant [20]. In contrast, the catalyst TA-01Ti could be recovered by filtration and reused at least six times with no loss of epoxide yield, which remained around 87.2% based on TBHP. When using aqueous $H_2O_2$ as the oxidant, the epoxide yield for TA-01Ti decreased only gradually, from 85.6 to 78.3% and finally to 68.7%, corresponding to the first, second, and third runs of the epoxidation with $H_2O_2$ as the oxidant. XPS data confirmed the titanium loss during epoxidation with aqueous $H_2O_2$.

NMR and IR results indicated the presence of tri-silanols or tetra-silanols. More tri-silanols or tetra-silanols in the vicinal situation may favor the stable grafting of guest species through the reaction of titanium centers with two or three attachments through –O–Si–O– bridges with silica matrix, which may inhibit, although not prevent, leaching. Combined with the hydrophobicity of microseparated aliphatic domains, increasing the number of attachments between titanium centers and hybrid supports improves the reusability of the catalysts against the titanium leaching.

For the materials discussed here, the hydrophobic domains in our nonporous materials due to the microphase separation of the long aliphatic groups and the framework of siloxane could solubilize the organic substrate molecules, similar to the hydrophobic cores in amphiphilic micelles, making epoxidation possible. Meanwhile, these hydrophobic domains could prevent water molecules from accessing Ti centers, thus inhibiting or decreasing titanium leaching.

## 5. Conclusion

We have synthesized hybrid titanium–silica catalysts with high epoxidation activity by a sol–gel process and a subsequent titanium-grafting step. These hybrid catalysts can be reused at least four times, although with decreasing activity, after reaction with aqueous hydrogen peroxide and at least six times using TBHP as the oxidant. Furthermore, the surface properties of these hybrid supports can be fine-tuned by the choice of solvent and the nature and the composition of the starting materials. This method provides a one-pot route to generate a POSS-like structure in hybrid silicas.

## Acknowledgments

Financial support was provided by NRSC-Catalysis. The authors thank M.W.G.M. Verhoeven for providing the XPS measurements, T. Staring for providing technical support, B. Mezari for assisting with the NMR measurements, N. Rane for helping with material characterization, and G. Gerritsen and L. Zhang for sharing valuable discussions.

## References

[1] K.A. Jørgensen, Chem. Rev. 89 (1989) 431.

[2] H.P. Wulff, US Patent 3 923 843 (1975), to Shell Oil Company.

[3] M. Taramasso, G. Perego, B. Notari, US Patent 4 410 501 (1983), to Snamprogetti S.p.A.

[4] M.A. Camblor, A. Corma, A. Martínez, J. Pérez-Pariente, J. Chem. Soc. Chem. Commun. (1992) 589.

[5] P. Wu, T. Komatsu, T. Yashima, J. Phys. Chem. 100 (1996) 10316.

[6] A. Tuel, Zeolites 15 (1995) 236.

[7] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Phys. Chem. B 105 (2001) 2897.

[8] M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, M.P. de Fruto, A. Padilla Polo, Chem. Commun. (2000) 855.

[9] M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, J. Catal. 217 (2003) 195.

[10] J.M. Fraile, J.I. García, J.A. Mayoral, E. Vispe, Appl. Catal. A 245 (2003) 363.

[11] M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, J. Catal. 234 (2005) 488.

[12] G.A. Eimer, S.G. Casuscelli, G.E. Ghione, M.E. Crivello, E.R. Herrero, Appl. Catal. A 298 (2006) 232.

[13] S. Klein, W.F. Maier, Angew. Chem. Int. Ed. 35 (1996) 2230.

[14] H. Kochkar, F. Figueras, J. Catal. 171 (1997) 420.

[15] C.A. Müller, M. Schneider, T. Mallat, A. Baiker, J. Catal. 189 (2000) 221.

[16] M.P. Kapoor, A. Bhaumik, S. Inagaki, K. Kuraoka, T. Yazawa, J. Mater. Chem. 12 (2002) 3078.

[17] M.B. D'Amore, S. Schwarz, Chem. Commun. (1999) 121.

[18] R.L. Brutchey, D.A. Ruddy, L.K. Andersen, T. Don Tilley, Langmuir 21 (2005) 9576.

[19] M.D. Skowronska-Ptasinska, M.L.W. Vorstenbosch, R.A. van Santen, H.C.L. Abbenhuis, Angew. Chem. Int. Ed. 41 (2002) 637.

[20] L. Zhang, H.C.L. Abbenhuis, G. Gerritsen, N. Ní Bhriain, P.C.M.M. Magusin, B. Mezari, W. Han, R.A. van Santen, Q. Yang, C. Li, Chem. Eur. J. 13 (2007) 1210.

[21] T.W. Dijkstra, R. Duchateau, R.A. van Santen, A. Meetsma, G.P.A. Yap, J. Am. Chem. Soc. 124 (2002) 9856.

[22] M.R. Bhambhani, P.A. Cutting, K.S.W. Sing, D.H. Turk, J. Colloid Interface Sci. 38 (1972) 109.

[23] D. Chandra, N.K. Mal, M. Mukherjee, A. Bhaumik, J. Solid State Chem. 179 (2006) 1802.

[24] D. Ji, R. Zhao, G. Lv, G. Qian, L. Yan, J. Suo, Appl. Catal. A 281 (2005) 39.

[25] Q. Yuan, A. Hagen, F. Roessner, Appl. Catal. A 303 (2006) 81.

[26] H.W. Oviatt Jr., K.J. Shea, J.H. Small, Chem. Mater. 5 (1993) 943.

[27] D.A. Loy, B.M. Baugher, C.R. Baugher, D.A. Schneider, K. Rahimian, Chem. Mater. 12 (2000) 3624.

[28] M.A. Wahab, I. Imae, Y. Kawakami, C.-S. Ha, Chem. Mater. 17 (2005) 2165.

[29] M. Oubaha, M. Dubois, B. Murphy, P. Etienne, J. Sol-Gel Sci. Technol. 38 (2006) 111.

[30] L. Matějka, O. Dukh, D. Hlavatá, B. Meissner, J. Brus, Macromolecules 34 (2001) 6904.

[31] F.J. Feher, D.A. Newman, J.F. Walzer, J. Am. Chem. Soc. 111 (1989) 1741.

[32] M. Feuillade, C. Croutxé-Barghorn, C. Carré, Prog. Solid State Chem. 34 (2006) 87.