A Sol−Gel Method Using Tetraethoxysilane and Acetic Anhydride: Immobilization of Cubic *μ*-Oxo Si−Ti Complex in a Silica Matrix

Masahiro Fujiwara,*,† Helge Wessel,‡ Hyung S. Park,‡ and Herbert W. Roesky‡

AIST (National Institute of Advanced Industrial Science and Technology) Kansai, 1 Midorigaoka, Ikeda, Osaka 563-8577, Japan, and Institut für Anorganische Chemie der Universität, Göttingen University, Tammannstrasse 4, D-37077 Göttingen, Germany

A sol−gel procedure using acetic anhydride as a substitute for water using a condensing reagent for the tetraethoxysilane (TEOS) to silica conversion is reported. The mixed solution obtained from the reaction of TEOS and acetic anhydride at 110 °C was allowed to stand in air for several weeks, resulting in gel formation of the solution. This prepared silica was mesoporous based on the nitrogen adsorption−desorption isotherms. Even when the gelation was performed in the presence of a large amount of benzene, silica was also obtained. The immobilization of a cubic *μ*-oxo Si−Ti complex, which is a good homogeneous catalyst for the epoxidation of olefins, in a silica matrix was achieved by using this technique. Although the complex readily afforded TiO_2 anatase on treatment with water, no free TiO_2 phase was found in the solid obtained by this procedure according to XRD, DR−UV−vis, and Raman spectra. The titanium was highly dispersed in the silica matrix. On the other hand, a solid prepared by the same procedure using titanium tetra-isopropoxide as the titanium source contained the TiO_2 anatase phase. The obtained SiO_2−TiO_2 mixed oxide solid was an effective heterogeneous catalyst for the highly efficient epoxidation of cyclohexene in the liquid phase by *tert*-butylhydroperoxide.

Introduction

The preparation of inorganic materials using metal alkoxides and their analogues is one of the most important and well-developed subjects in modern material science. In particular, the sol−gel method presents a novel route for preparing inorganic materials under very mild conditions (often at room temperature) and has been actively studied for the creation of functional materials.[1] The key step of this technique is the hydrolysis of a metal alkoxide or other substrates such as acetylacetonates to form hydroxy metal species followed by their condensation to metal−oxygen−metal (M−O−M) bonds. During these procedures, the utilization of water, generally in excess, is essential and alcoholic solvents such as ethanol are often required to homogenize the solution. As the common sol−gel procedure allows for only limited use of organic substrates due to their low solubility and stability in aqueous and protic solutions, some new variations of the sol−gel method are required. The combination of organic and inorganic materials (organic−inorganic composite materials) is becoming more important in the technologies of the new century.[1,2] Recently, some procedures were reported for preparing metal oxides from metal alkoxides without the utilization of water.[3−6] One of these procedures is represented by the so-called "nonhydrolytic sol−gel process", which involves the reaction of metal alkoxides and metal halides.[3,5] It is also reported that acetic acid and sometimes acetic anhydride can be alternatives to water as a condensation reagent.[6,7] For silica preparation,[8] the employment of comparatively expensive and unstable silicon acetates[9] is not required if the acetates are directly produced from silicon alkoxide and acetic acid or anhydride.

In the first part of this paper, we wish to report the successful preparation of silica from silicon alkoxide and acetic anhydride via transesterification (Scheme 1). In
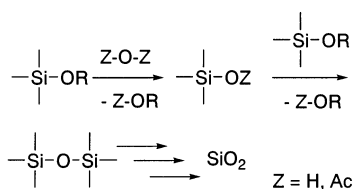
* To whom correspondence should be addressed. Phone: +81-727-51-9253. Fax: +81-727-51-9628. E-mail: m-fujiwara@aist.go.jp.
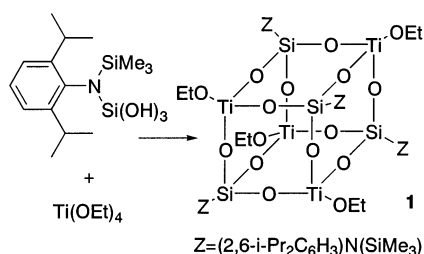† AIST Kansai.
‡ Göttingen University.

(1) (a) Corriu, R. J. P. *Eur. J. Inorg. Chem.* **2001**, 1109. (b) Brinker, C. J., Scherer, G. W., Eds.; *Sol−Gel Science: The physics and chemistry of sol−gel processing*; Academic Press: San Diego, 1990.

(2) (a) Boury, B.; Corriu, R. J. P. *Adv. Mater.* **2000**, *12*, 989. (b) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403. (c) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633. (d) Tamaki, R.; Horiguchi, T.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2749.

(3) (a) Grader, G. S.; Shter, G. E.; Avnir, D.; Frenkel, H.; Sclar, D.; Dolev, A. *J. Sol−Gel Sci. Technol.* **2001**, *21*, 157. (b) Hay, J. N.; Porter, D.; Raval, H. M. *J. Mater. Chem.* **2000**, *10*, 1811. (c) Vioux, A. *Chem. Mater.* **1997**, *9*, 2292. (d) Andrianainarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1665. (e) Acosta, S.; Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1994**, *170*, 234. (f) Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1992**, *4*, 961. (g) Corriu, R. J. P.; Leclercq, D.; Lefèvre, P.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1992**, *2*, 673.

(4) (a) Terry, K. W.; Lugmair, C. G.; Gantzel, P. K.; Tilley, T. D. *Chem. Mater.* **1996**, *8*, 274. (b) Terry, K. W.; Lugmair, C. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 9745. (c) Wada, K.; Nakashita, M.; Bundo, M.; Ito, K.; Kondo, T.; Mitsudo, T. *Chem. Lett.* **1998**, 659. (d) Juwiler, D.; Blum, J.; Neumann, R. *J. Chem. Soc., Chem. Commun.* **1998**, 1123.

(5) (a) Hay. J. N.; Raval, H. M. *J. Mater. Chem.* **1998**, *8*, 1233. (b) Hay, J.; Porter, D.; Raval, H. *J. Chem. Soc., Chem. Commun.* **1999**, 81.

(6) Hay, J. H.; Raval. H. M. *Chem. Mater.* **2001**, *13*, 3396.

Scheme 1

Scheme 2

the second part, the immobilization of a metal complex into a silica matrix is described. A cubic μ-oxo Si–Ti complex (complex **1** in Scheme 2),[11,12] which is an effective catalyst for the epoxidation of olefins in organic solutions by *tert*-butylhydroperoxide (TBHP),[13] was immobilized in a silica matrix. This SiO_2–TiO_2 mixed oxide acted as a solid heterogeneous catalyst for the epoxidation of the olefin in the liquid phase.

Experimental Section

Measurements and Materials. IR spectra were measured using a Jasco FT/IR-230 spectrometer by KBr pellets or neat liquid with KBr plates. Laser-Raman spectra were recorded by a Nicolet FT-Raman 960 spectrometer. DR–UV–vis spectra were measured by a Jasco V-560 double-beam spectrometer with a diffuse reflectance accessory. The Kubelka–Munk function was plotted versus the wavelength (in nm). GC-MS measurement was carried out using a Shimadzu GCMS-QP5000 spectrometer. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded using a JEOL AL-400 spectrometer. Power X-ray diffraction patterns were obtained using a MAC Science MO3X diffraction meter with Cu Kα radiation. Nitrogen adsorption–desorption isotherms were measured by a BELSORP 28 (BEL Japan Inc.). The BET plot and the BJH method (using the adsorption branch of the isotherms) were used to determine the specific surface area, pore volume, and pore size distribution. Elemental analysis was performed by fluorescent X-ray detection using a Shimadzu VXQ150A spectrometer.

Most of the commercially available reagents were used without further treatment. The purity of acetic anhydride we

used was more than 98% (confirmed by ^1H NMR spectrum). Titanium tetraethoxide and titanium tetra-isopropoxide (TPOT) were distilled and stored under dry argon. Acetoxy triethoxy-silane was prepared by a previously described method.[10] The cubic μ-oxo Si–Ti complex **1** was obtained from a hindered silanetriol [RN(SiMe₃)(Si(OH)₃], R = 2,6-iso-$Pr_2C_6H_3$][14] and titanium tetraethoxide by our procedure[12] and purified by recrystallization from *n*-pentane. The dichloromethane solution of TBHP was prepared by the method described by Sharpless and co-workers.[15]

Procedure for Sol–Gel Processing of Tetraethoxysilane Using Acetic Anhydride. The mixture of tetraethoxysilane (20 mmol; TEOS) and acetic anhydride (40 mmol) was refluxed at 110 °C for 24 h under dry argon. The resulting solution was transferred into a suitable glass beaker and then allowed to stand in air with a paper cover. The gelation was performed in our experimental room with ambient air, where the temperature and humidity were monitored using a common thermometer and hygrometer, respectively. The gelation of the solution occurred after about 1–3 weeks. This gel was crushed, washed three times with benzene (approximately 100 mL each) (**Warning: benzene is a human carcinogen**), and dried at 80 °C for 18 h. No calcination was carried out. The final gel was labeled **G-TEOS**.

Preparation of Gel Using Complex 1. Complex **1** (0.21 g, 0.125 mmol; Ti: 0.50 mmol) was dissolved in TEOS (2.92 g, 14 mmol) and then acetic anhydride (3.06 g, 30 mmol) was added. The resulting clear solution was heated at 60 °C for 20 h under dry argon. After the reaction, the solution was cooled to room temperature. The formed white precipitate was filtered and dried at 80 °C for 24 h. The resulting solid was designated as **P-comp1**. On the other hand, the filtrate permitted to stand in air became a clear gel after about 1 week. The treatment of this gel in a manner similar to **G-TEOS** gave the granular gel **G-comp1**.

Preparation of Precipitate from TEOS and TPOT Complex 1. To a mixed solution of TEOS (3.75 g, 18 mmol) and TPOT (0.57 g, 2 mmol) acetic anhydride (4.08 g, 40 mmol) was added. This resulting solution was heated at 60 °C for 20 h under dry argon. After the solution was cooled to room temperature, the formed white precipitate was filtered and dried at 80 °C for 24 h (**P-TPOT**). This precipitate was added to ethanol (50 mL) and refluxed for 21 h. The final solid was designated as **P-EtOH**.

Typical Epoxidation Procedure. To the suspension of the obtained solid material (60 mg) in cyclohexene (5 mL), 2 mL of a dichloromethane solution of TBHP (4.0 M solution; 8 mmol) was added at room temperature. The resulting solution was heated at 40 °C with vigorous stirring for 21 h. After filtration of the catalyst, the conversion of TBHP was estimated by the common iodometric titration method. The products were identified and determined by capillary GC (Shimadzu GC-17) and GC-MS.[13]

Results and Discussion

Preparation of Silica Using Acetic Anhydride. We first examined the reaction of TEOS with acetic anhydride (2 equiv to TEOS) at 110 °C for 24 h. The obtained clear transparent solution was transferred to a glass beaker after cooling to room temperature and then permitted to stand at room temperature in contact with air. After about 1–3 weeks, the solution became a gel. In this colorless and transparent gel, no phase separation was visually observed. This gel was crushed, washed three times with benzene, and dried at 80 °C for 18 h. The obtained gel **G-TEOS** was confirmed to be amorphous by powder X-ray diffraction measure-

(7) (a) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin. P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1925. (b) Andrianainarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Mutin. P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1665. (c) Jansen, M.; Guenther, E. *Chem. Mater.* **1995**, *7*, 2110. (d) Caruso, J.; Hampden-Smith, M. J.; Rheingold, A. L.; Yap, G. *J. Chem Soc., Chem. Commun.* **1995**, 157. (e) Caruso, J.; Hampden-Smith, M. J.; Duesler, E. N. *J. Chem Soc., Chem. Commun.* **1995**, 1041.

(8) Auner, N., Weis, J., Eds.; *Organosilicon Chemistry IV.; From Molecules to Materials*; Wiley-VCH: Weinheim, 2000.

(9) Coltrain, B. K.; Kelts, L. W.; Armstrong, N. J. *J. Sol-Gel Sci. Technol.* **1994**, *3*, 83.

(10) Roth, M. J.; Brook, M. A.; Penny, H. B. *J. Organomet. Chem.* **1996**, *521*, 65.

(11) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205. (b) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183.

(12) (a) Voigt, A.; Murugavel, R.; Chandrasekhar, V.; Winkhofer, N.; Roesky, H. W.; Schmidt, H.-S.; Usón, I. *Organometallics* **1996**, *15*, 1610. (b) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352.

(13) Fujiwara, M.; Wessel, H.; Park, H.-S.; Roesky, H. W. *Tetrahedron* **2002**, *58*, 239.

(14) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-S.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298.

(15) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.
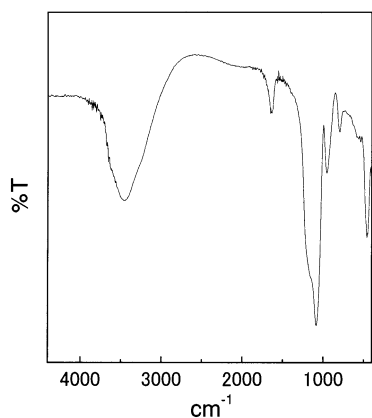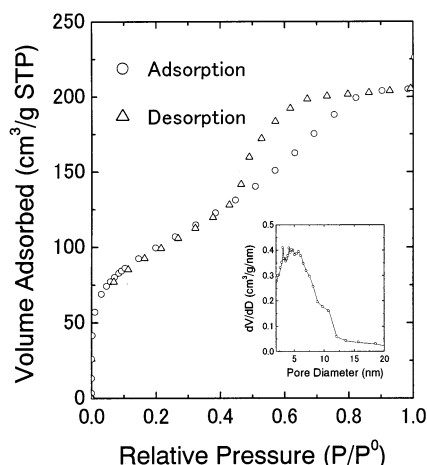
Figure 1. IR spectrum of **G-TEOS**.

Figure 2. Nitrogen adsorption−desorption isotherm and BJH pore size distribution (inset) of **G-TEOS.**

Figure 3. ^{29}Si NMR spectrum of the solution of TEOS and acetic anhydride with the complete conversion of acetic anhydride after the removal of the volatiles.

ment. The IR spectrum of **G-TEOS** showed the typical absorption patterns of silica without organic moieties (Figure 1). The nitrogen adsorption−desorption isotherm of **G-TEOS** is illustrated in Figure 2. The specific surface area and the pore volume were calculated to be 353.4 m^2/g or 0.288 cm^3/g, respectively. The inset in Figure 2 illustrates the pore size distribution of the mesopores estimated by the BJH method using an adsorption branch. Mesopores widely distributed from 2 to 12 nm were observed. Thus, it is ascertained that a silica material could be prepared from the solution produced by TEOS and acetic anhydride.

The solution obtained from the reaction of TEOS and acetic anhydride was analyzed. GC analysis of the resulting solution indicated that over 90% of TEOS was converted and a large amount of ethyl acetate, whose quantification was not performed because ethyl acetate is thought to partially evaporate at the reaction temperature over its boiling point (ca. 77 °C). In the IR spectrum of the resulting solution, the absorption of the acetoxy silane species was clearly observed at 1742 cm^{-1}.[10,16] GC and GC-MS analyses indicated that acetoxy triethoxysilane was formed based on the comparison with a standard sample obtained from a known method.[10] The transesterification of TEOS and acetic anhydride afforded some silicon acetate species. Iden-
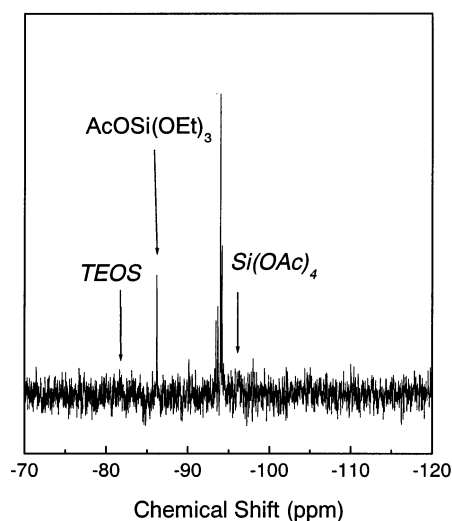
tifying other silicon acetates by infrared spectrometry was not practical because the absorption of the mono-acetate[10] (1742 cm^{-1}) and tetra-acetate[16a] (1745 cm^{-1}) are reported to be in approximately the same area. The solution after the complete conversion of acetic anhydride (about 4 days reaction and confirmed by GC) was analyzed using an NMR spectrometer after the removal of the volatiles (ethyl acetate, etc.). In the ^{1}H and ^{13}C NMR spectra, the determination of the silicon acetates was not effective because the peaks of the acetyl groups in the silicon acetates were observed in approximately the same ranges. However, in the ^{29}Si NMR spectrum (Figure 3), various peaks, which are not assigned to TEOS ($\delta = -81.8$), acetoxy triethoxysilane ($\delta = -86.6$), and silicon tetra-acetate ($\delta = -96.1$), were found. These peaks were detected (from $\delta = -93$ to $\delta = -95$) between acetoxy triethoxysilane and silicon tetra-acetate. It is likely that silicon diacetate [(AcO)$_2$Si(OEt)$_2$], the tri-acetates [(AcO)$_3$SiOEt], and their derivatives with =Si−O−Si= groups were formed. Thus, the condensation of TEOS with acetic anhydride by transesterification significantly occurred.

This gelation was promoted by contact with humid air. The average temperature and humidity, where these experiments were carried out, were around 25 °C and 70%, respectively. Even under drier conditions (around 15 °C and 40% humidity), the same kind of gel was obtained, although a longer time was required for the gelation. When the gelation was performed in a flask with a calcium chloride tube to prevent contact with humid air, the solution did not become a gel even after 1 month. According to GC analysis, the benzene solution used for washing the gel contained acetic acid with a large amount of ethyl acetate. It is likely that silanol from acetoxy silane with water in humid air reacted with another acetoxy silane or silanol to give Si−O−Si bonds.[9,17] Therefore, the formation of Si−O−Si bonds to afford the silica gel was induced not only by the transesterification of acetoxy silane but also by the

(16) (a) Straughan, B. P.; Moore, W.; McLaughlin, R. *Spectrochim. Acta* **1986**, *42A*, 451. (b) Okawara, R.; Webster, D. E.; Rochow, E. G. *J. Am. Chem. Soc.* **1960**, *82*, 3287.

(17) (a) Hernandez, A.; Torres-Martinez, L. M.; Lopez, T. *Mater. Lett.* **2000**, *46*, 340. (b) Bokhimi, X.; Munoz, E.; Boldu, J. L.; Adem, E.; Navaro, O.; Lopez, T.; Rojas, F.; Gomez, R.; Garcia-Ruiz, A. *J. Sol-Gel Sci. Technol.* **2000**, *17*, 219.
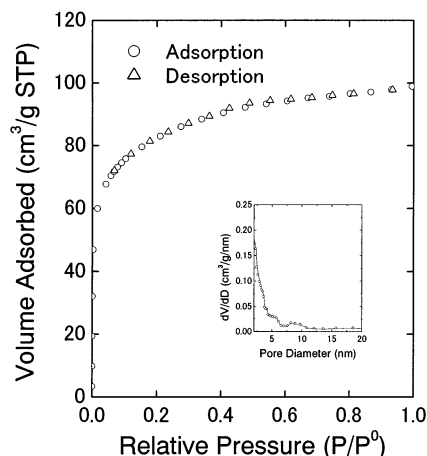
Figure 4. Nitrogen adsorption−desorption isotherm and BJH pore size distribution (inset) of **G-PhH**.

condensation of silanol obtained by the hydrolysis of acetoxy silane with water vapor. It is interesting that the addition of a large amount of benzene (1 L to 1 mol of TEOS) to the resulting solution of TEOS and acetic anhydride also made a one-phase clear transparent solution. After some weeks (longer than no solvent case), a clear transparent gel swelled by benzene was obtained. The microporous structure of this gel **G-PhH** was confirmed by the nitrogen adsorption−desorption isotherm (Figure 4). The specific surface area of the silica was estimated to be 307 m^2/g. From the BJH calculation, there are few mesopores in the silica **G-PhH** (inset in Figure 4) and the pore volume was estimated to be 0.069 cm^3/g. Thus, it was found that the addition of benzene influenced the pores of the silica, although the effect of benzene was not clear (under investigation). It seems that many kinds of organic substrates can be mixed in the solution system of TEOS and acetic anhydride because a large amount of benzene (1 L to 1 mol of TEOS) was successfully incorporated. This procedure is advantageous for creating novel materials under lipophilic conditions with organic solutions. The next part of this paper introduces an example of preparing an inorganic solid in the lipophilic organic solution.

Immobilization of a Cubic μ-Oxo Si−Ti Complex in Silica. Various applications of this sol−gel technique can be expected. The preparation of organic−inorganic composite materials[1,2] seems to be the most appropriate variation. As most organic substrates and solvents can be dissolved in the solution obtained from TEOS and acetic anhydride, molecular imprinting[18] into silica[19] is regarded as another potential development. On the other hand, the immobilization of catalysts in a silica matrix[20,21] is also considered to be favorable by using this sol−gel method. Although most of these approaches involve grafting catalytic species onto a silica surface,[20] the direct build-in of a catalytic species into a silica

matrix is not common and a typical example is the fixing of enzymes in silica.[21] It is expected that various metal complexes can be fixed into a silica matrix by using the described sol−gel method. In the second part of this paper, we wish to propose a new approach for the immobilization of metal complex catalysts into a silica matrix. Our cubic μ-oxo Si−Ti metal complex **1**[12,13] is selected as an example of this methodology.

The cubic complex **1** is readily soluble in organic solvents such as *n*-hexane, whereas it scarcely dissolves in protic solvents such as ethanol. This complex is also comparatively moisture-sensitive. When an aqueous solution of 2-propanol with the insoluble complex **1** was mixed at room temperature for 1 h, a considerable amount of the complex could be recovered. However, when the solution with complex **1** was refluxed for 24 h, a white precipitate, which did not dissolve in *n*-hexane, was obtained. After drying at 150 °C and calcining at 400 °C, sharp peaks assigned to TiO$_2$ anatase were observed by X-ray diffraction. Therefore, the aqueous treatment decomposed complex **1** to form TiO$_2$. However, it was also confirmed that complex **1** was not seriously sensitive to water probably because of its bulky substituent on the silicon. Although the direct syntheses of metal oxides from some μ-oxo metal complexes have been recently developed,[4] the direct thermal decomposition of complex **1** afforded a mixed oxide with TiO$_2$ anatase phase (sharp peaks of TiO$_2$ anatase were confirmed by X-ray diffraction). The next trial to immobilize this complex into silica involved mixing complex **1** with an aqueous 2-propanol solution including prehydrolyzed TEOS.[22] Even in this case, the complex scarcely dissolved in the solution and finally TiO$_2$ anatase was found in the resulting solid. Furthermore, a two-phase reaction consisting of an organic phase with dissolved complex **1** and an aqueous phase was unsuccessful, and TiO$_2$ anatase was likewise produced. In all these attempts using common sol−gel techniques with water, the Ti−O bonds, being less stable than Si−O bonds in complex **1**, preferentially react with water to form TiO$_2$ species. It is thought that the effective transformation and immobilization of complex **1** into solid silica free from the TiO$_2$ phase must be performed in an organic solution which dissolves complex **1**. Therefore, the sol−gel technique described in the first part of this article is advantageous.

The solution system obtained from complex **1**, TEOS, and acetic anhydride was next investigated. This clear homogeneous solution was heated at 60 °C for 20 h. A temperature lower (60 °C) than the simple silica synthesis (110 °C) was employed because it is well-known that titanium alkoxide catalyzes transesterification to

(18) (a) Wulff, G. *Chem. Rev.* **2002**, *102*, 1. (b) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812. (c) Davis, M. E.; Katz, A.; Ahmad, W. R. *Chem. Mater.* **1996**, *8*, 1820. (d) Sellergren, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1031. (e) Haupt, K.; Mosbach, K. *Chem. Rev.* **2000**, *100*, 2495. (f) Asanuma, H.; Hishiya, T.; Komiyama, M. *Adv. Mater.* **2000**, *12*, 1019.

(19) (a) Katz, A.; Davis, M. E. *Nature* **2000**, *403*, 286. (b) Hunnius, M.; Rufiñska, A.; Maier, W. F. *Microporous Mesoporous Mater.* **1999**, *29*, 389. (c) Pinel, C.; Loisil, P.; Gallezot, P. *Adv. Mater.* **1997**, *9*, 582.

(20) (a) Bourque, S. C.; Maltais, F.; Xiao, W.-J.; Tardif, O.; Alper, H.; Arya, P.; Manzer, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 3035. (b) Petrucci, M. G. L.; Kakkar, A. K. *Chem. Mater.* **1999**, *11*, 269. (c) Yang, H.; Gao, H.; Angelici, R. J. *Organometallics* **1999**, *18*, 2285. (d) Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52. (e) Krijnen, S.; Abbenhuis, H. C. L.; Hanssen, R. W. J. M.; van Hooff, J. H.; van Santen, R. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 356. (f) Pirrung, M. C. *Chem. Rev.* **1997**, *97*, 473. (g) Maschmeyer, T.; Rey, F.; Sankar, G.; Thomas, J. M. *Nature* **1995**, *378*, 159. (h) Fraile, M.; García, J. I.; Mayyoral, J. A.; de Mènorval, L. C.; Rachdi, F. *J. Chem. Soc., Chem. Commun.* **1995**, 539. (i) Kurusu, Y.; Neckers, D. C. *J. Org. Chem.* **1991**, *56*, 1981.

(21) (a) Gill, I.; Ballesteros, A. *Trend Biotechnol.* **2000**, *18*, 282. (b) Gill, I.; Ballesteros, A. *J. Am. Chem. Soc.* **1998**, *120*, 8587. (c) Reetz, M. T. *Adv. Mater.* **1997**, *9*, 943.

(22) Thangaraj, A.; Kumar, R.; Mirajkar, S. P.; Ratnasamy, P. *J. Catal.* **1991**, *130*, 1.
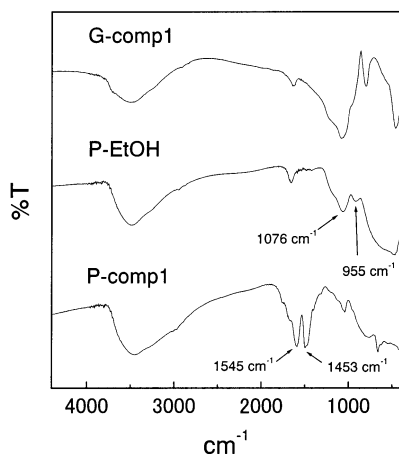
Immobilization of Cubic μ-Oxo Si–Ti Complex

Chem. Mater., Vol. 14, No. 12, 2002 **4979**

Figure 5. IR spectra of **P-comp1**, **P-EtOH**, and **G-comp1**.

Figure 6. Nitrogen adsorption–desorption isotherm and BJH pore size distribution (inset) of **G-comp1**.

promote the condensation process,[23] and the lower temperature seems to prevent the decomposition of complex **1** during the reaction. After a few hours, a small amount of a white precipitate was gradually formed. After the filtration of this **P-comp1** precipitate, the filtrate was allowed to stand at room temperature in air. After about 1 week, gelation of the solution was observed. Generally, the gelation time of the solution with complex **1** was shorter than that of the solution obtained from only TEOS and acetic anhydride. The transparent gel was crushed, washed with benzene, and dried (however, no calcination was carried out), and finally a white granular gel was obtained (**G-comp1).** In the X-ray diffraction pattern of **G-comp1,** a typical amorphous silica spectrum, no peaks from TiO_2 anatase were detected. This suggested that **G-comp1** was an amorphous silica-based material free from a TiO_2 phase. In the same type of experiment with titanium tetra-isopropoxide (TPOT) instead of complex **1** (at 60 °C for 20 h), a large amount of a white precipitate (**P-TPOT**) was obtained and the filtrate did not become a gel.

Two types of precipitates obtained from the cubic complex **1** (**P-comp1**) or TPOT (**P-TPOT**) were analyzed by IR spectrometry. The two spectra were approximately the same and were characterized by two strong absorptions at around 1545 and 1453 cm^{-1} (Figure 5). The precipitate bearing two similar absorptions was also obtained from the reaction of TPOT with acetic anhydride (without TEOS).[24] These absorptions are assigned to a bidentate titanium acetate species[25] and are not attributed to the unidentate acetoxy silane, which have absorptions of the carbonyl groups at 1725–1765 cm^{-1} as already mentioned.[16] When these precipitates (**P-comp1** and **P-TPOT**) were treated by refluxing of ethanol or calcining at 400 °C, these two strong absorptions completely disappeared and the absorptions at 1076 and 955 cm^{-1} appeared, and were assigned to Si–O–Si[26] and Si–O–Ti stretchers,[12,27] respectively.

(23) Otera, J. *Chem. Rev.* **1993**, *93*, 1449.
(24) (a) Thiele, K.-H.; Panse, M. *Z. Anorg. Allg. Chem.* **1978**, *441*, 23. (b) Pande, K. C.; Mehrotra, R. C. *Z. Anorg. Allg. Chem.* **1957**, *290*, 95.
(25) Doeuff, S.; Henry, M.; Sanchez, C.; Livage, J. *J. Non-Cryst. Solids* **1987**, *89*, 206.
(26) Dutoit, D. C. M.; Schneider, M.; Baiker, A. *J. Catal.* **1995**, *153*, 165.
(27) (a) Vayssilov, G. N. *Catal. Rev.-Sci. Eng.* **1997**, *39*, 209. (b) Notari, B. *Catal. Today* **1993**, *18*, 163. (c) Camblor, M. A.; Corma, A.; Pérez-Pariente, J. *J. Chem. Soc., Chem. Commun.* **1993**, 557.
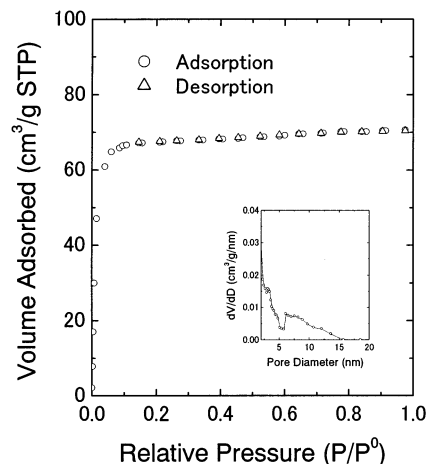
Figure 5 also shows the IR spectrum of a gel (**P-EtOH**) that was obtained by the reflux treatment of ethanol with **P-TPOT**. It is assumed that the titanium acetate species that existed in the silica matrix was decomposed by heating with alcohol or by calcination, thus forming Si–O–Ti bonds with the silanol of silica. On the other hand, the gel **G-comp1** from the cubic complex **1** with TEOS had neither absorptions at 1545 nor 1453 cm^{-1} (Figure 5). The absorption patterns were consistent with those of **G-TEOS** (see Figure 1). This suggested that no titanium acetate existed and that the titanium atoms were dispersed in the silica matrix as already mentioned. The elemental analysis of the **G-comp1** showed that the molar ratio of Ti and Si was 0.026 (Ti/Si), whereas the molar ratio in the starting materials was 0.034 (see Experimental Section). It is thought that the formation of the **P-comp1** resulted in the loss of Ti species from **G-comp1**. Another gel produced by a procedure similar to that of **G-comp1** had approximately the same ratio of Ti and Si (Ti/Si = 0.028). Figure 6 is the nitrogen adsorption–desorption isotherm of **G-comp1**, indicating that **G-comp1** was a microporous solid and the specific surface area was calculated to be 298.0 m^2/g, whereas **G-TEOS** was found to have mesopores (Figure 2). The titanium alkoxide part of complex **1** catalyzes the transesterification,[23] so the polymerization of TEOS to silica seems to be promoted. The shorter gelation time of **G-comp1** than that of **G-TEOS** also suggests that titanium accelerates the formation of Si–O–Si bonds and the silica matrix. It is likely that the gel **G-comp1** is crammed with silica particles by the promoted transesterification with titanium. This effect prevents the formation of wider pores and finally only micropores, which are probably formed by the templating effect of ethyl acetate and ethanol as byproducts, were fabricated in the gel.

The gel **G-comp1** and the precipitate **P-EtOH** were further analyzed by ultraviolet diffuse reflectance spectrometry (DR–UV–vis). **P-EtOH** clearly contained the TiO_2 anatase phase as is shown by Figure 7. The absorption from 310 to 330 nm was derived from extra lattice titanium. On the other hand, the spectrum of **G-comp1** showed no absorption at around 310–330 nm (Figure 7). The band around 270 nm indicates isolated
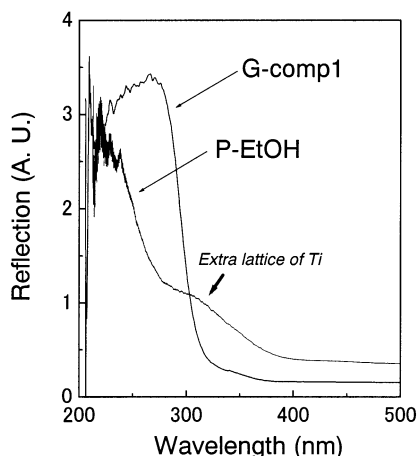
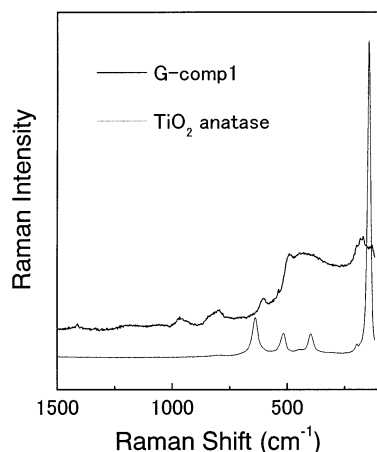**Figure 7.** DR−UV−vis spectra of **P-EtOH** and **G-comp1**.

Figure 8. Laser Raman spectrum of **G-comp1** and TiO_2 anatase.

framework titanium in tetrahedral coordination.[27,28] Furthermore, in the laser-Raman spectrum of **G-comp1**, no absorptions from TiO_2 anatase (about 140, 390, 513, and 637 cm^{-1}) were found (Figure 8). In conclusion, the formation of TiO_2 phase was prevented using complex **1** as the titanium source, where titanium is fixed to the silica-like cube with four-coordination. It is assumed that the aggregation of the titanium species into TiO_2 by the reaction with acetic anhydride and water from humid air is considerably depressed by this fixed coordination structure.

The stoichiometric reaction of acetoxy triethoxysilane and complex **1** at 110 °C for 15 h in toluene (acetoxy triethoxysilane/titanium in complex **1** = 1) afforded products of the transesterification of acetoxy triethoxysilane. After the removal of the volatiles by evaporation, no acetoxy group and only the peaks of complex **1** (partly decomposed) and ethoxy groups were observed in the ^1H NMR spectrum (Figure 9). The acetoxy group in acetoxy triethoxysilane was completely converted into Si−O−Si bonds. As ethyl acetate as a byproduct of transesterification was removed by evaporation, only ethoxy groups were detected in the ^1H NMR spectrum. It is likely that some oligomeric siloxanes such as −O−
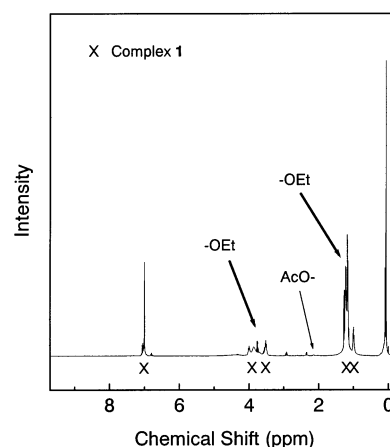
(28) (a) Thomas, J. M.; Sanker, G.; Klunduk, M. C.; Attfield, M. P.; Maschmeyer, T.; Johnson, B. F. G.; Bell, R. G. *J. Phys. Chem. B* **1999**, *103*, 8809. (b) Bordiga, S.; Coluccia, S.; Lamberti, C.; Marchese, L.; Zecchina, A.; Boscherini, F.; Buffa, F.; Genoni, F.; Leofanti, G.; Petrini, G.; Vlaic, G. *J. Phys. Chem.* **1994**, *98*, 4125.

Figure 9. ^1H NMR spectrum of the products obtained from the reaction of complex **1** and acetoxy triethoxysilane at 110 °C for 15 h in toluene.

Table 1. Epoxidation of Cyclohexene Catalyzed by SiO_2−TiO_2 Mixed Oxide[a]

run	catalyst	conv. of TBHP (%)	yield of cyclohexene oxide[b] (%)	efficiency of TBHP[c] (%)
1	**G-TEOS**	<5	0	0
2	**G-comp1**	58	56	96
3	**G-comp1**[d]	59	58	>98
4[e]	**G-comp1**	73	72	>98
5	**P-TPOT**	82	64	78[f]
6	**P-TPOT**[g]	18	15	84
7	**P-TPOTcalcn**	21	17	82

[a] Reaction conditions: Catalyst 60 mg, TBHP 8 mmol (dichloromethane solution), cyclohexene 5 mL, Ar, 40 °C, 21 h. [b] Based on TBHP. [c] Ratio of converted TBHP used for epoxidation. [d] Used catalyst in run 2. [e] 80 °C, 6 h. [f] Solution became milky. [g] Used catalyst in run 5.

$Si(OEt)_2$−O−$Si(OEt)_2$−O− were produced. Thus, complex **1** accelerates the condensation reaction of silane acetates and produces a silica matrix surrounding the complex. Complex **1** is relatively stable under those conditions. During the final stage for silica matrix formation (gel formation) with humid air, the substituents on complex **1**, the alkoxides on titanium and the aniline derivatives on silicon, are gradually eliminated. Finally, the cubic core consisting of 12 Si−O−Ti bonds is fixed into a silica matrix. On the other hand, for the aqueous solution, these Ti−O−Si bonds were preferentially cleaved with water to form the TiO_2 phase. Furthermore, TPOT is also readily condensed to TiO_2 because of its very high reactivity. Titanium acetate itself is reported to consist of bimetallic species such as $[(AcO)_3Ti−O−Ti(OAc)_3]$,[24] and the Ti−O−Ti bond is already formed. It is thought that the formation of the TiO_2 phase was inevitable with TPOT even in the sol−gel process mentioned here.

Epoxidation of Cyclohexene by TBHP. The epoxidation of cyclohexene by TBHP was examined using various solids (Table 1). This reaction is also advantageous for estimating the coordination states of titanium in the solid. It is well-known that SiO_2−TiO_2 mixed oxides with a TiO_2 anatase phase decompose peroxides to decrease their efficiency for epoxidation and that the SiO_2−TiO_2 mixed oxides with no free TiO_2 anatase phase generally catalyze the epoxidation with high

peroxide efficiency (over 95%).[30] As shown in Table 1, **G-TEOS** without titanium naturally had no epoxidation activity (run 1). Although the precipitate **P-TPOT** without any treatment had catalytic activity (run 5), the solution after the reaction was milky. The recovered **P-TPOT** had a lower activity (run 6). It is thought that the titanium species dissolved in the solution mainly catalyzed the epoxidation in the case of the fresh **P-TPOT**. The precipitate after calcination at 400 °C (**P-TPOTcalcn**) had poor activity and the efficiency of TBHP for epoxidation was moderate, although the solution was clear (run 7). The comparatively low efficiency of TBHP for epoxidation resulted from its decomposition of the peroxide by the TiO_2 anatase in the silica matrix, as was confirmed by DR−UV−vis.[27,28,30] On the other hand, the gel **G-comp1** was found to be a selective epoxidation catalyst. The conversion and the efficiency of TBHP for epoxidation were 58% and 96%, respectively (run 2). The recovered catalyst used for a second time had a completely similar activity (run 3). Moreover, the residue of the filtrate of run 2 after complete evaporation (the weight of the residue was negligible; under 10 mg.) had no activity for epoxidation. Thus, no leaching of titanium species occurred and **G-comp1** can be repeatedly utilized as a catalyst. Even in the reaction at a higher temperature (80 °C), the high efficiency of TBHP for epoxidation was maintained (run 4). The relatively low activity of **G-comp1** for epoxidation compared with the reported SiO_2−TiO_2 mixed oxides[31,32] is considered to be caused by its microporosity. It is thought that comparatively bulky cyclohexene cannot easily access the pores of the SiO_2−TiO_2 mixed oxide, thus decreasing the reaction rate.[31] In the case of the titanosilicate, a shape selectiv-

ity for olefins, that is, linear olefins are active and bulky ones are less active, was also reported.[31] However, if some suitable molecules are imprinted in the silica matrix to control the pore character,[18,33] a new selective oxidation catalyst is expected.

Conclusions

The sol−gel preparation method using acetic anhydride, which substitutes for water, was studied. Transesterification is a key reaction of this process. With use of this procedure, not only silica but also a solid SiO_2−TiO_2 mixed oxide were prepared. The addition of benzene to the solution for this sol−gel method changed the porosity of the silica. In this process, a metal complex, which is decomposed by water, is applied. For the preparation of the SiO_2−TiO_2 mixed oxide with highly dispersed Ti atoms in a silica matrix, the cubic μ-oxo Si−Ti complex **1** was an essential titanium source. This solid was an effective catalyst for the epoxidation of cyclohexene by TBHP. On the other hand, the solid formed from TPOT was an unsuitable catalyst due to the low efficiency of TBHP for epoxidation. On the other hand, the high efficiency of TBHP for epoxidation by **G-comp1** suggested that the cubic center of complex **1** was directly immobilized into the silica matrix. The substituent on silicon is also a good leaving group. This sol−gel technique with acetic anhydride realized the immobilization of a water-sensitive cubic complex. The common sol−gel method was not applicable due to the low stability of the cubic complex in aqueous solution. Furthermore, this method has the potential for developing a new preparation technology for inorganic materials by using organic solutions, which is advantageous for the preparation of organic−inorganic composite materials, molecular imprinting, and so forth.

CM020424N

(29) Lippman, E.; Mägi, M.; Samason, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889.

(30) (a) Khouw, C. B.; Dartt, C. B.; Labinger, J. A.; Davis, M. E. *J. Catal.* **1994**, *149*, 195. (b) Huybrechts, D. R. C.; Buskens, P. L.; Jacobs, P. A. *J. Mol. Catal.* **1992**, *71*, 129.

(31) (a) Tatsumi, T.; Nakamura, M.; Yuasa, K.; Tominaga, H. *Catal. Lett.* **1991**, *10*, 259. (b) Tatsumi, T.; Nakamura, M.; Yuasa, K.; Tominaga, H. *Chem. Lett.* **1990**, 297.

(32) (a) Dusi, M.; Mallat, T.; Baiker, A. *Catal. Rev.* **2000**, *42*, 213. (b) Corma, A.; Diaz, U.; Domine, M. E.; Fornes, V. *J. Am. Chem. Soc.* **2000**, *122*, 2804. (c) Saxton, R. J. *Top. Catal.* **1999**, *9*, 43. (d) Gao, X.; Wachs, I. E. *Catal. Today* **1999**, *51*, 233. (e) Van der Waal, J. C.; van Bekkum, H. *J. Mol. Catal. A: Chem.* **1997**, *124*, 137. (f) Thiele, G. F.; Roland, E. *J. Mol. Catal. A: Chem.* **1997**, *117*, 351. (g) Klein, S.; Thorimbert, S.; Maier, W. F. *J. Catal.* **1996**, *163*, 476. (h) Hutter, R.; Dutoit, D. C. M.; Mallat, T.; Schneider, M.; Baiker, A. *J. Chem. Soc., Chem. Commun.* **1995**, 163. (i) Hutter, R.; Mallat, T.; Baiker, A. *J. Catal.* **1995**, *153*, 177.

(33) (a) Markowitz, M. A.; Kust, P. R.; Deng, G.; Schoen, P. E.; Dordick, J. S.; Clark, D. S.; Gaber, B. P. *Langumir* **2000**, *16*, 1759. (b) Davis, M. E. *Cattech* **1997**, 19. (c) Heilmann, J.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 471. (d) Morihara, K.; Kurihara, S.; Suzuki, J. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3991.