

## Functionalization on Silica Gel with Allylsilanes. A New Method of Covalent Attachment of Organic Functional Groups on Silica Gel

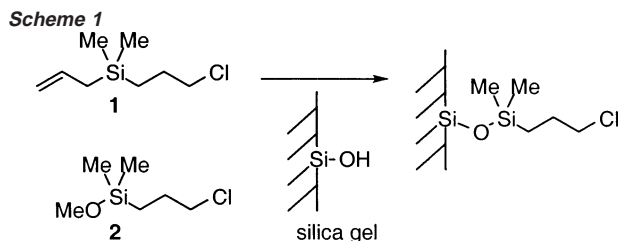
Toyoshi Shimada,<sup>\*,†</sup> Kazuko Aoki,<sup>†</sup> Yo Shinoda,<sup>†</sup> Tomoaki Nakamura,<sup>†</sup> Norihito Tokunaga,<sup>†</sup> Shinji Inagaki,<sup>‡</sup> and Tamio Hayashi<sup>\*,†</sup>

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan, and Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan

Received February 17, 2003; E-mail: thayashi@kuchem.kyoto-u.ac.jp

Binding of an organic functional group to a silica surface via a covalent bond is the most reliable method of modification and functionalization of the silica surface.<sup>1</sup> The covalent bond used for the binding is mostly the Si–O–Si bond, where one of the silicon atoms is on the silica surface and the other comes from organosilicon compounds, and the Si–O–Si bond is formed by the reaction of an Si–OH group on the silica gel surface with organosilicon compounds containing a leaving group of high reactivity on the silicon atom. The organosilicon compounds most commonly used are those containing an alkoxy leaving group ( $R_n\text{-SiX}_{4-n}$ ; X = OR').<sup>2</sup> Halides, acyloxy, and amino groups on the silicon atom (X = halide, OCOR', and NR'<sub>2</sub> in  $R_n\text{-SiX}_{4-n}$ ) have been also used for the Si–O–Si bond formation.<sup>1c</sup> Unfortunately, these functional groups are so reactive toward hydrolysis that the silicon compounds cannot be handled under hydrolytic conditions or cannot be purified by silica gel chromatography. Here we wish to report a new method of functionalizing a silica surface, which is realized by use of (allyl)organosilanes (Scheme 1). They are stable under regular hydrolytic conditions but undergo deallylation forming a Si–O–Si bond on the silica under certain conditions.

We chose 2-propenyl(3-chloropropyl)dimethylsilane (**1**) as an organo-functionalized allylsilane,<sup>3</sup> which is stable enough to be purified by silica gel column chromatography at room temperature (40 °C or lower), and we examined its reactivity toward silica gel at higher temperature. It was found that the Si–O–Si bond formation on the silica surface takes place efficiently with the allylsilane **1** at the temperature of refluxing toluene. The results obtained for the reaction of allylsilane **1** with FSM-16<sup>4</sup> and amorphous silica<sup>5</sup> are summarized in Table 1, which also contains the data obtained with alkoxydimethylsilane, methoxy(3-chloropropyl)dimethylsilane (**2**),<sup>6</sup> for comparison. As a typical experimental procedure (entry 2), 1.0 g of FSM-16 was treated with 0.89 g (5.0 mmol, 1.0 equiv of SiOH on the silica gel) of allylsilane **1** in 30 mL of refluxing toluene for 15 h. Filtration and Soxhlet extraction with methanol for 24 h and with benzene for 48 h followed by drying at 120 °C for 15 h under 0.2 mmHg gave 1.14 g of the functionalized FSM-16. Introduction of the 3-chloropropyl dimethylsilyl group onto the silica gel was confirmed by <sup>29</sup>Si and <sup>13</sup>C NMR spectra (vide infra), and its amount was determined to be 1.3 mmol per 1.0 g of the starting FSM-16 by elemental analysis of the chlorine atom. The use of a greater amount of the allylsilane **1** under otherwise the same conditions gave the silica gel containing a greater amount of the 3-chloropropyl dimethylsilyl group, 1.7 mmol per 1.0 g of the FSM-16 being obtained with 15 mmol of **1** (entry 4). It should be noted that the present method using the allylsilane **1** is more efficient than that using methoxydimethylsilane **2**, which has been often used for the functionalization. With a smaller amount



**Table 1.** Loadings of (3-Chloropropyl)silanes **1** and **2** on Silicas<sup>a</sup>

entry	organosilane (mmol)	silica gel	time (h)	loading <sup>b</sup> (mmol g <sup>-1</sup> )
1	<b>1</b> (3)	FSM-16	15	1.1
2	<b>1</b> (5)	FSM-16	15	1.3
3	<b>1</b> (10)	FSM-16	15	1.6
4	<b>1</b> (15)	FSM-16	15	1.7
5	<b>1</b> (10)	FSM-16	0.5	1.1
6	<b>1</b> (10)	FSM-16	48	1.6
7	<b>2</b> (3)	FSM-16	15	0.8
8	<b>2</b> (5)	FSM-16	15	0.8
9	<b>2</b> (10)	FSM-16	15	1.2
10	<b>2</b> (15)	FSM-16	15	1.3
11	<b>2</b> (10)	FSM-16	0.5	0.6
12	<b>2</b> (10)	FSM-16	48	1.6
13	<b>1</b> (10)	amorphous silica	15	0.3
14	<b>2</b> (10)	amorphous silica	15	0.5

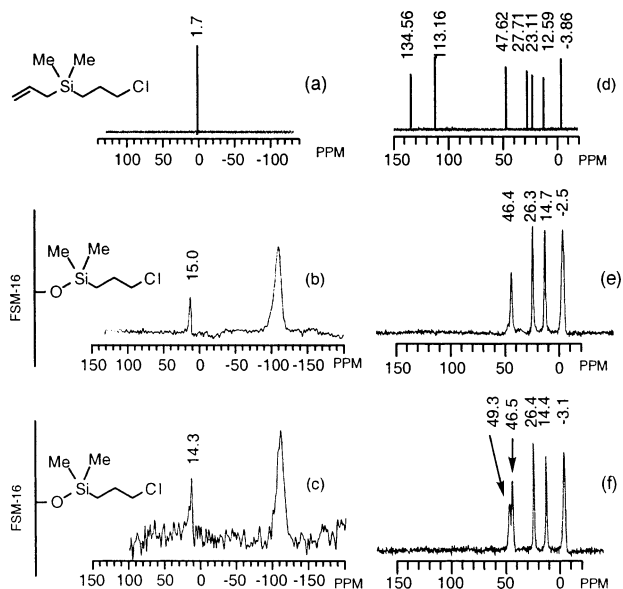
<sup>a</sup> All reactions were carried out for 1.0 g of silica gel support in 30 mL of refluxing toluene. <sup>b</sup> Obtained by elemental analysis of Cl.

of the organosilicon compounds and in a shorter reaction time, a greater amount of the silyl group is introduced on the silica gel (compare entries 1–6 with entries 7–12). The present method of functionalization using the allylsilane is also applicable to amorphous silica gel, although the amount of the attached silyl group is lower with allylsilane **1** than with methoxydimethylsilane **2** (entries 13 and 14).

The Si–O–Si bond formation between the 3-chloropropyl dimethylsilyl group and the FSM-16 surface was demonstrated by <sup>29</sup>Si and <sup>13</sup>C CP-MAS NMR spectra. Figure 1 contains the NMR spectra for allylsilane **1** (a and d), FSM-16 treated with allylsilane **1** (b and e), and FSM-16 treated with methoxydimethylsilane **2** (c and f). The resonance of <sup>29</sup>Si at 1.7 ppm observed for allylsilane **1** (a) was replaced by the resonance at 15.0 ppm by treatment with FSM-16 (b). This chemical shift is a typical value for trialkylsilyloxy groups on the silica surface<sup>1g,7</sup> and is essentially the same as that in the FSM-16 (c), which is obtained by a standard procedure for the modification of a silica surface with a 3-chloropropyl dimethylsilyl group using methoxydimethylsilane **2**.<sup>8</sup> Three <sup>13</sup>C singlets at 23.11, 113.16, and 134.56 ppm which are assigned to the allyl carbons on the allylsilane **1** (d) disappeared by treatment with FSM-16 (e). The other four singlets remained on the FSM-16, indicating that the

<sup>†</sup> Kyoto University.

<sup>‡</sup> Toyota Central R&D Laboratories, Inc.



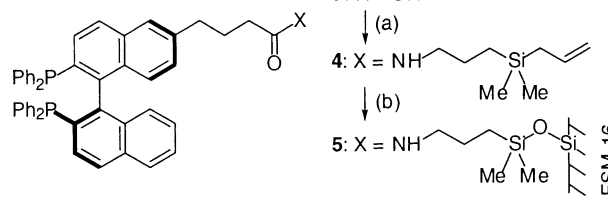
**Figure 1.**  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra of 2-propenyl(3-chloropropyl)dimethylsilane **1** in  $\text{CDCl}_3$  (a and d),  $^{29}\text{Si}$  and  $^{13}\text{C}$  CP-MAS NMR spectra of the reaction products of **1** with FSM-16 (b and e), and those of **2** with FSM-16 (c and f).

3-chloropropyl)dimethylsilyl group was attached to the silica surface while the allyl group was lost from the allylsilane **1**.<sup>8</sup> It is worth noting that the allylsilane **1** is a better modifying reagent than methoxysilane **2** with respect to the chemical purity of the silica surface. With methoxysilane **2**, which releases the methanol at the Si–O–Si bond formation, a considerable amount of methoxy group on the silica gel is observed at 49.3 ppm (f).<sup>9</sup> In the reaction with allylsilane **1**, the leaving molecule from the silicon atom is propene,<sup>10</sup> which is not reactive toward silica gel and is readily removed from the reaction mixture. It is likely that the reaction proceeds, as the protodesilylation of allylic silanes,<sup>11</sup> by way of a  $\beta$ -silyl cation intermediate which is formed by the protonation of the allyl group with silanol on the silica surface and undergoes nucleophilic attack by the silanol oxygen leaving propene.

The present method makes it possible to modify the silica gel surface with heavy organo-functional groups, which cannot be purified by distillation due to their nonvolatility. For example, the BINAP skeleton was attached to the FSM-16 surface by use of allylsilane **4**, which was obtained by the amide bond formation of BINAP-carboxylic acid **3**<sup>12</sup> with 2-propenyl(3-aminopropyl)dimethylsilane. The BINAP-allylsilane **4** (3.96 g, 4.7 mmol), which was purified by silica gel chromatography (hexane/ethyl acetate = 2/1), was treated with FSM-16 (0.91 g) in refluxing toluene for 15 h to give the FSM-16 **5** containing 0.3 mmol/g of the BINAP unit (Scheme 2).

To summarize, we found a new method for the modification of the silica gel surface by use of (allyl)organosilanes. In refluxing toluene, deallylation on the allylsilane takes place to form the Si–O–Si bond with the silicon on the silica gel. The present method will have broad applications in the surface-modifying technology

### Scheme 2<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a)  $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiMe}_2\text{CH}=\text{CH}_2$ , EDC, HOBt, DMF, 83%; (b) FSM-16, toluene, reflux.

on the silica gel as a reliable functionalization method. Immobilization of a catalyst on a silica surface is one of the examples.<sup>13</sup>

**Acknowledgment.** This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

**Supporting Information Available:** Experimental procedures, spectroscopic and analytical data for the substrates and products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

### References

- (1) (a) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons, Ltd.: New York, 1979; Chapter 6. (b) Pesek, J. J.; Leigh, I. E., Eds. *Chemically Modified Surfaces*; Royal Society of Chemistry: Cambridge, 1994. (c) Vansant, E. F.; Van Der Voort, P.; Vrancken, C. In *Studies in Surface Science and Catalysis*; Delmon, B.; Yates, T., Eds.; Elsevier: Amsterdam, 1995; Vol. 93, Part II. (d) Pesek, J. J.; Matyska, M. T.; Abuelafiya, R. R., Eds. *Chemically Modified Surfaces: Recent Developments*; Royal Society of Chemistry: Cambridge, 1996. (e) Vankelecom, I. F. J.; Jacobs, P. A. In *Chiral Catalyst Immobilization and Recycling*; De Vos, D. E.; Vankelecom, I. F. J.; Jacobs, P. A., Eds.; Wiley-VCH: New York, 2000; Chapter 2. (f) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons, Ltd.: New York, 2000; Chapter 10. (g) Tao, T.; Maciel, G. E. *J. Am. Chem. Soc.* **2000**, *122*, 3118.
- (2) (a) Plueddemann, E. P. *Silane Coupling Agents*, 2nd ed.; Plenum: New York, 1991. (b) Tertykh, V. A.; Belyakova, L. A. *Stud. Surf. Sci. Catal.* **1996**, *99*, 147.
- (3) Voronkov, M. G.; Kirpichenko, S. V.; Abrosimova, A. T.; Albanov, A. I.; Keiko, V. V.; Lavrent'yev, V. I. *J. Organomet. Chem.* **1987**, *326*, 159.
- (4) (a) Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc., Chem. Commun.* **1993**, 680. (b) Ishikawa, T.; Matsuda, M.; Yasukawa, A.; Kandori, K.; Inagaki, S.; Fukushima, T.; Kondo, S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1985. The sample used here has a surface area of  $966\text{ m}^2\text{ g}^{-1}$ , pore diameter of 2.8 nm, and 5.0 mmol silanol groups  $\text{g}^{-1}$ , and it was dried at  $140\text{ }^\circ\text{C}$  for 17 h under vacuum at  $10^{-5}\text{ mmHg}$ .
- (5) Silica gel (Davisil), with a particle diameter range of 100–200 mesh and a surface area of  $480\text{ m}^2\text{ g}^{-1}$ , was purchased from Aldrich.
- (6) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297.
- (7) Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Chromatogr.* **1981**, *205*, 438.
- (8)  $^{13}\text{C}$  CP-MAS NMR for the 3-chloropropylsiloxy group on silica surface has been reported: Hays, G. R.; Clague, A. D. H.; Huis, R.; Van Der Velden, G. *Appl. Surf. Sci.* **1982**, *10*, 247.
- (9) Schenk, U.; Hunger, M.; Weitkamp, J. *Magn. Reson. Chem.* **1999**, *37*, S75.
- (10) The generation of propene was confirmed by the detection of 1,2-dibromopropane, which is formed by treatment of the evolved gas with bromine.
- (11) (a) Sommer, L. H.; Tyler, L. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2872. (b) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (c) Morita, T.; Okamoto, Y.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 835.
- (12) Bayston, D. J.; Fraser, J. L.; Ashton, M. R.; Baxter, A. D.; Polywka, M. E. C.; Moses, E. *J. Org. Chem.* **1998**, *63*, 3137.
- (13) As a pertinent review on supported chiral catalysts on inorganic materials: Song, C. E.; Lee, S.-G. *Chem. Rev.* **2002**, *102*, 3494.

JA034691L