Surface Modification

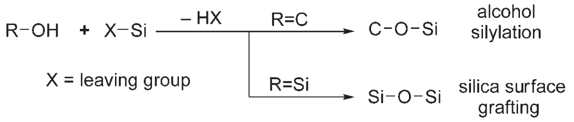
DOI: 10.1002/ange.200703112

Sc(OTf)$_3$-Mediated Silylation of Hydroxy Functional Groups on a Solid Surface: A Catalytic Grafting Method Operating at Room Temperature**

*Ye-Rim Yeon, Young Jun Park, Ji-Sung Lee, Jung-Woo Park, Sin-Gun Kang, and Chul-Ho Jun**

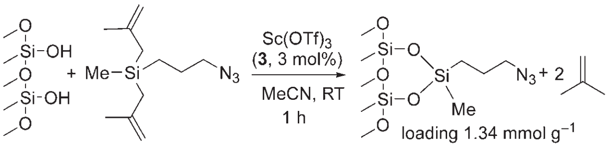
In memory of Yoshihiko Ito

The versatility of Si–O–Si bond-forming reactions has had a great impact on silica (glass or gel) surface modification, formation of organosilicon compounds containing organic or biological functions, and materials science.[1–3] Following the increased interest in surface technologies, such as dip-pen lithography,[4] these methods have now been extended to the preparation of modified surfaces at micrometer to nanometer scale.[5] Most silica surface-grafting methods are based on the reaction between the surface and alkoxy-[1,2] or allylsilanes[6] and are forced by heating to reflux, or very reactive silanes containing halides, acyloxy, and amino leaving groups are used.[3] However, there are no Si–O–Si bond-forming reactions with moisture-stable silylating reagents using a catalyst in the grafting process onto the silica surface at room temperature. Such a catalytic grafting method might be useful because of controllability of the reaction and experimental ease. There is an intriguing analogy between the grafting procedure and the silylation of alcohols,[7] where the Si–OH moiety takes the place of C–OH (Scheme 1).



Scheme 1. Correlation between alcohol silylation and silica surface grafting.

In our study of Rh^I-catalyzed O-silylation of alcohols with vinylsilane,[8] we found that methallylsilanes were an appropriate choice not only for their easy preparation and stability, but also for well-studied O-silylation reactions with alcohols with a variety of Lewis acid catalysts.[9] Based on this strategy, we describe herein the first catalytic post-grafting method for facile chemical modification of the silica surface with a variety of functional groups using a Sc(OTf)$_3$ catalyst (OTf = trifluoromethylsulfonate) at room temperature [Eq. (1)].



1 **2a** **4a** (1)

Silylation of silanols on the amorphous silica gel surface was carried out with 3-azidopropyldimethallylmethylsilane (**2a**, 5 mmol).[10] When the silica gel (1 g) was suspended in acetonitrile solution in the presence of Sc(OTf)$_3$ (**3**, 3 mol% based on **2a**) at room temperature for one hour, the isobutene that was liberated during the reaction could be detected in situ by ^{1}H NMR spectroscopy (see Supporting Information, Figure S1). After the reaction, 3-azidopropylmethylsilyl-group-grafted silica gel **4a** was obtained (1.11 g) and the amount of 3-azidopropylmethylsilyl moiety loaded on **4a** was determined by elemental analysis to be 1.34 mmol g^{-1}.[11] Characteristic ^{13}C CP-MAS NMR spectra for **4a** revealed that all ^{13}C signals of methallyl group in **2a** (Figure 1a) were now absent but the rest of signals corresponding to the four carbon atoms of 3-azidopropyl and methyl groups remained (Figure 1b). This observation shows that the surface formula proposed for **4a** is reasonable.

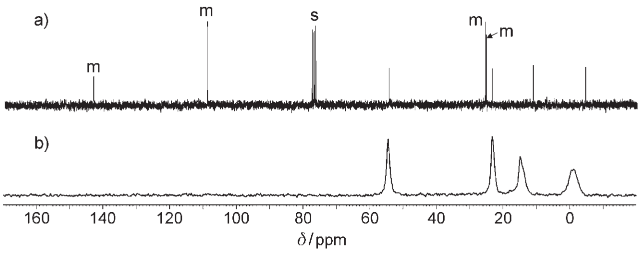


Figure 1. ^{13}C NMR spectra of **2a** (a) and ^{13}C CP-MAS NMR spectra of **4a** (b). The peaks marked with letters m and s correspond to carbon atoms of the methallyl group and the residual solvent CDCl$_3$, respectively.

---

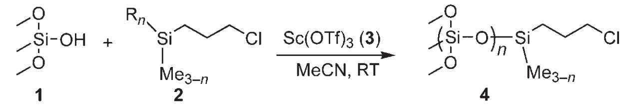
[*] Y.-R. Yeon, Dr. Y. J. Park, J.-S. Lee, J.-W. Park, S.-G. Kang, Prof. Dr. C.-H. Jun
Department of Chemistry and Center for Bioactive Molecular Hybrid (CBMH), Yonsei University, Shin-chon dong, Seodaemun-gu
Seoul 120-749 (Korea)
Fax: (+) 82-2-3147-2644
E-mail: junch@yonsei.ac.kr

[**] This work was supported by the CBMH and grant No. R01-2005-000-10548-0 from the Basic Research Program of the Korea Science & Engineering Foundation. We thank Dr. J.-S. Bae in KBSI for XPS measurements. J.-W.P. and S.-G.K. acknowledge the fellowship of the BK21 program from the Ministry of Education and Human Resources Development.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

We examined the correlation between immobilization efficiency and the number of methallyl groups on the silicon atom using mono- (**2b**), di- (**2c**) and trimethallylsilanes (**2d**) bearing a 3-chloropropyl group (Table 1) at room temperature. The catalyst **3** appeared to be essential for this transformation with monoallylsilane **2b**, as no reaction proceeded at all without the catalyst (Table 1, entry 1). The loading in **4b** was 0.84 mmol g^{-1} under 2 mol % **3** and a one-hour reaction time (Table 1, entry 2). Further increases in the amount of catalyst (up to 5 mol %) and a prolonged reaction time (12 h) had no significant effect on the efficiency of loading (Table 1, entries 3–5). When the grafting reagent was replaced by dimethallylsilane **2c**, loading of the 3-chloropropylsilyl group on silica gel increased by a factor of more than two, and 3 mol % **3** gave the optimal loading in **4c**; the loading efficiency could reach 1.92 mmol g^{-1} (Table 1, entries 6–9).[12] For trimethallylsilane **2d**, as much of methallyl group and its isomer (internal olefin)[13] were observed at the modified silica-gel surface in **4d** with ^{13}C CP-MAS NMR spectroscopy (Supporting Information, Figure S2). The exact amount of methallyl group in **4d** could not be determined. Presuming **4d** has one unreacted methallyl group, we estimated the loading efficiency to be 0.84 mmol g^{-1} with 3 mol % **3** and 1.19 mmol g^{-1} with 5 mol % **3** (Table 1, entries 10 and 11).

Table 1: Loading efficiency of **4** from the reaction of **1** and silane derivatives **2** under different reaction conditions.[a]

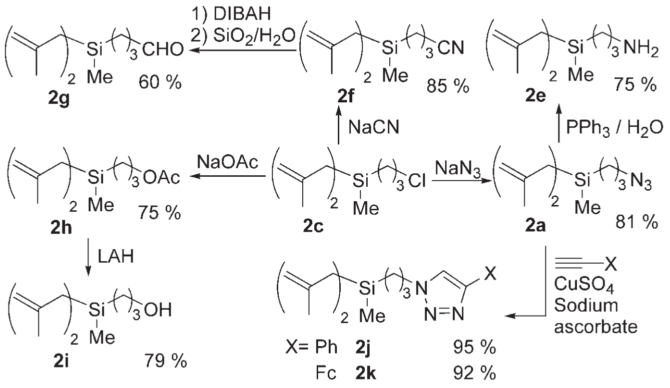


Entry	n		Sc(OTf)$_3$ [mol %][b]	t [h]	Loading[c] [mmol g^{-1}]	
1	1	**2b**	0	24	0	**4b**
2		**2b**	2	1	0.84	**4b**
3		**2b**	2	12	0.83	**4b**
4		**2b**	3	1	0.70	**4b**
5		**2b**	5	1	0.71	**4b**
6	2	**2c**	2	1	1.02	**4c**
7		**2c**	3	1	1.92	**4c**
8		**2c**	3	12	1.89	**4c**
9		**2c**	5	1	1.93	**4c**
10	3	**2d**	3	1	0.84	**4d**[d]
11		**2d**	5	1	1.19	**4d**[d]

[a] All reactions were performed in 3 mL of MeCN solution and all surface-modified silica-gel products were purified by Soxhlet extraction with EtOH for 24 h followed by vacuum drying. R = methallyl. [b] Based on **2**. [c] Determined by carbon elemental analysis. [d] Loading was calculated based on the assumed structure of $n = 2$ and R^2 = methallyl for **4d**.

Other silica materials were also found to be suitable. The loading rate (mmol g^{-1}) was 3.84 for SBA-15, 1.54 for MCF-5F, and 1.15 for ultrapure spherical silica balls, where **2c** was used as a grafting reagent.

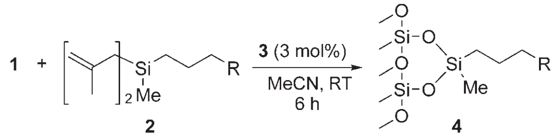
The dimethallylsilane moiety was chosen as a model system to immobilize a variety of organic functional groups on **1** and its chemical compatibility was investigated. Facile chemical transformations of the chloro group in **2c** were successfully achieved in good to high yields by various functional group interconversion reactions and routine workup processes (Scheme 2). In addition, the products derived from **2c** with a variety of functional groups could be readily purified by standard silica-gel column chromatography.



Scheme 2. Chemical transformation of the functional groups of **2c**. DIBAH = diisobutylaluminum hydride, Ac = acetyl, Fc = ferrocenyl, LAH = lithium aluminum hydride.

Catalytic grafting reactions of **1** with dimethallylsilanes **2** having various functional groups were performed in the presence of 3 mol % **3** (Table 2). Many different kinds of silica surface (**4**) modified by the corresponding functional groups of **2** could be obtained. The loading efficiencies were between 0.30 and 1.82 mmol g^{-1} depending on the functional groups.

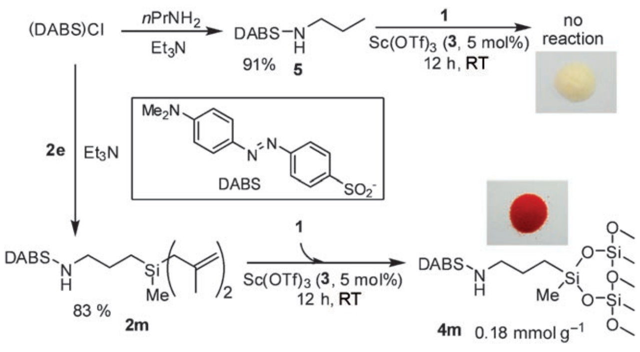
Table 2: Grafting with various functional groups.



Entry	R	4	Loading[a] [mmol g^{-1}]	Entry	R	4	Loading[a] [mmol g^{-1}]
1	N$_3$ (**2a**)	**4a**	1.40	5	OCOCH$_3$ (**2h**)	**4h**	1.76
2	NH$_2$ (**2e**)	**4e**	1.37[b]	6	OH (**2i**)	**4i**	1.82
3	CN (**2f**)	**4f**	1.43	7	4-Ph-R′[c] (**2j**)	**4j**	0.54
4	CHO (**2g**)	**4g**	1.72	8	4-Fc-R′[c] (**2k**)	**4k**	0.30

[a] Determined by elementary analysis of carbon and nitrogen. [b] Determined by elementary analysis of nitrogen. [c] R′ = 1,2,3-triazol-1-yl.

In particular, dimethallylsilane **2m** (not shown in Table 2) bearing a red dye, DABS (4-(dimethylamino)azobenzene-4′-sulfonyl), was noteworthy because the covalent immobilization of **2m** on **1** could be inspected with the naked eye. To discriminate covalently grafted DABS from physisorbed dye, a control experiment was carried out with **5** and **1** as shown in Scheme 3. During Soxhlet extraction with methanol for 24 h, the initial red color of the silica gel **4m** did not change significantly, implying that the DABS dye moiety was covalently bonded to the silica gel surface. In contrast, the



Scheme 3. Immobilization of **1** with a DABS group using DABS-dimethallylsilane **2m**.

redness of another silica gel derived from **1** and **5** completely disappeared.

The grafting method could be applied to physically or chemically different surfaces, such as microscope slides and indium tin oxide (ITO) glass, which had both been soaked in piranha solution (7:3 mixture of H_2SO_4 and 34.6% H_2O_2) for 30 minutes to activate surface hydroxy groups. When the microscope slide glass was reacted with octadecyldimethallylmethylsilane (**2n**) in the presence of **3**, the glass surface of **4n** became significantly hydrophobic relative to the surface before the reaction (estimated from the measurement of contact angle of each surface, 35° and 96°; Figure 2a).

In the case of ITO glass, the resulting ferrocene-functionalized glass of **4o** (Figure 2b) was investigated as an electrode by cyclic voltammetry (CV) in phosphate-buffered aqueous solution (pH 7.0). The CV revealed that the ferrocenyl group on the ITO surface is electrochemically active and shows reversible $Fc^{0/+}$ redox behavior, as expected for ferrocene oxidation (Figure 2c). Interestingly, the loading amount of the ferrocenyl group on ITO glass could be controlled by the used amounts of the catalyst **3**. For example, when the mole percent of **3** relative to **2o** was varied from 2 to 10, the loading of **4o** increased from 0.15×10^{-7} to 0.28×10^{-7} mmol per 1 cm^2 of ITO glass.[14]

In summary, we have developed a new catalytic grafting system composed of $Sc(OTf)_3$ and methallylsilane derivatives for the rapid surface modification of the hydroxy-terminated solids at room temperature. In addition, we believe that this catalytic grafting procedure has great potential in the development of special materials based on SiO_2 or ITO surfaces. Such efforts are underway in our laboratory.

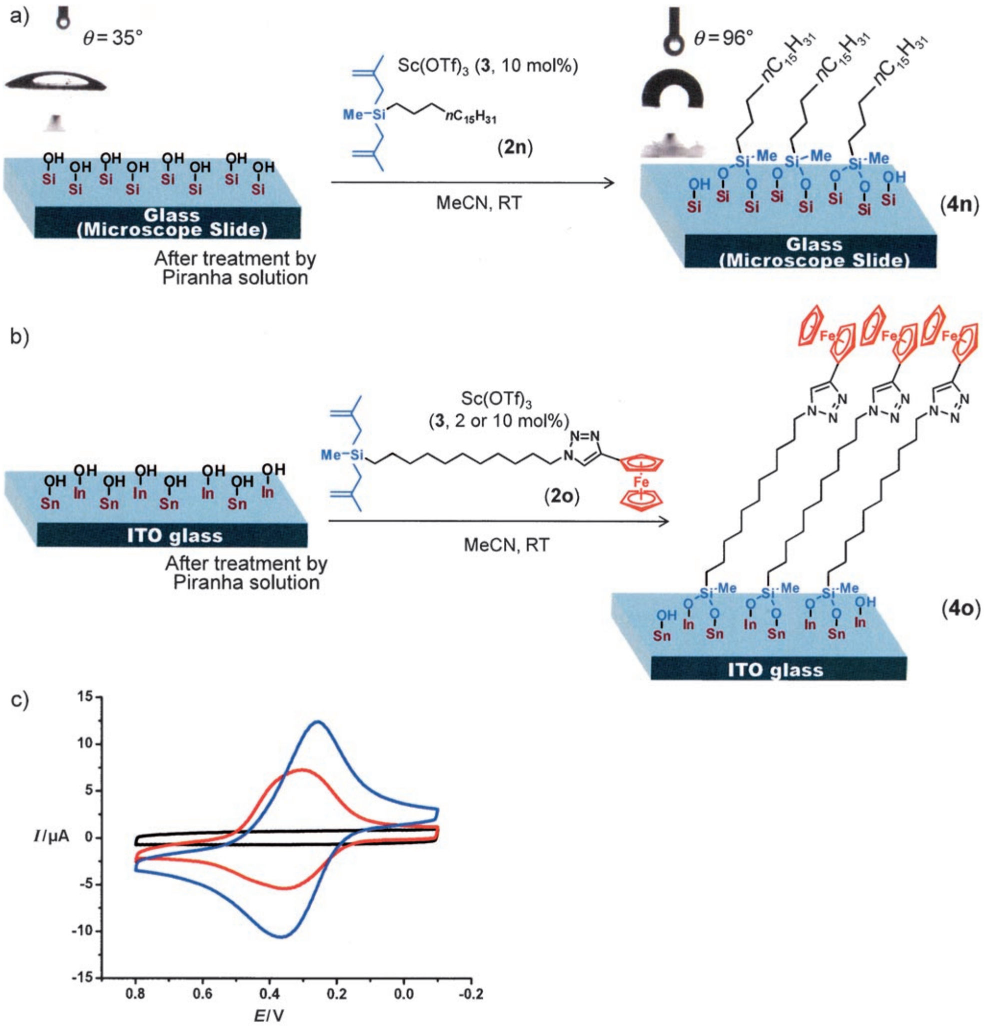


Figure 2. Glass surface modification using methallylsilane derivatives. a) Microscope glass slide showing the change in contact angle θ after reaction with octadecylmethallylmethylsilane. b) ITO glass of **4o** showing c) reversible redox behavior of the grafted ferrocenyl group. Bare ITO: black, Fc-functionalized ITO: red (2 mol%), blue (10 mol%). Reference electrode: Ag/AgCl. Scan rate: 50 mV s^{-1}.

Received: July 12, 2007
Revised: September 18, 2007

Keywords: glasses · methallylsilane · scandium · silicon · surface chemistry

---

[1] a) K. B. Yoon, *Acc. Chem. Res.* **2007**, *40*, 29, and references therein; b) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.* **2006**, *118*, 3290; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216; c) A. B. Descalzo, R. Martínez-Máñez, F. Sancenó, K. Hoffmann, K. Rurack, *Angew. Chem.* **2006**, *118*, 6068; *Angew. Chem. Int. Ed.* **2006**, *45*, 5924; d) G. J. A. A. Soler-Illia, P. Innocenzi, *Chem. Eur. J.* **2006**, *12*, 4478; e) I. Slowing, B. G. Trewyn, V. S. Y. Lin, *J. Am. Chem. Soc.* **2006**, *128*, 14792; f) A. Corma, H. Garcia, *Adv.*

Synth. Catal. **2006**, *348*, 1391; g) C. M. Crudden, M. Sateesh, R. Lewis, *J. Am. Chem. Soc.* **2005**, *127*, 10045; h) E. J. Acosta, C. S. Carr, E. E. Simanek, D. F. Shantz, *Adv. Mater.* **2004**, *16*, 985; i) Y. Fujimoto, A. Shimojima, K. Kuroda, *Chem. Mater.* **2003**, *15*, 4768; j) P. Judeinstein, C. Sanchez, *J. Mater. Chem.* **1996**, *6*, 511.

[2] Special issues on functional hybrid materials: a) *J. Mater. Chem.* **2005**, *15*, 3541; b) *Chem. Mater.* **2001**, *13*, 3059.

[3] E. F. Vansant, P. Van Der Voort, C. Vrancken in *Studies in Surface Science and Catalysis*, *Vol. 93*, *Part II* (Eds.: B. Delmon, T. Yates), Elsevier, Amsterdam, **1995**.

[4] a) S. Krämer, R. R. Fuierer, C. B. Gorman, *Chem. Rev.* **2003**, *103*, 4367; b) D. S. Ginger, H. Zhang, C. A. Mirkin, *Angew. Chem.* **2004**, *116*, 30; *Angew. Chem. Int. Ed.* **2004**, *43*, 30.

[5] a) A. Ivanisevic, C. A. Mirkin, *J. Am. Chem. Soc.* **2001**, *123*, 7887; b) H. Jung, R. Kulkarni, C. P. Collier, *J. Am. Chem. Soc.* **2003**, *125*, 12096; c) D. J. Pena, M. P. Raphael, J. M. Byers, *Langmuir* **2003**, *19*, 9028.

[6] T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki, T. Hayashi, *J. Am. Chem. Soc.* **2003**, *125*, 4688.

[7] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd ed., Wiley, New York, **1999**.

[8] J.-W. Park, H.-J. Chang, C.-H. Jun, *Synlett* **2006**, 771.

[9] a) T. Suzuki, T. Watahiki, T. Oriyama, *Tetrahedron Lett.* **2000**, *41*, 8903; b) T. Morita, Y. Okamoto, H. Sakurai, *Tetrahedron Lett.* **1980**, *21*, 835; c) G. A. Olah, A. Husain, B. G. B. Gupta, G. F. Salem, S. C. Narang, *J. Org. Chem.* **1981**, *46*, 5212; d) A. Hosomi, H. Sakurai, *Chem. Lett.* **1981**, 85; e) G. A. Olah, A. Husain, B. P. Singh, *Synthesis* **1983**, 892.

[10] For experimental procedures, see the Supporting Information.

[11] The loading rates were determined by simultaneous elemental analysis of carbon and nitrogen.

[12] Compared to **2c**, the loading of dialkoxy version (3-chloropropyldiethoxymethylsilane) in a separate experiment was 1.27 $\mathrm{mmol\,g^{-1}}$ even after heating in toluene to reflux for 24 hours.

[13] The terminal olefins of trimethallylsilanes could be isomerized into internal olefins without silica (**1**) in the presence of **3** in CD_3CN solution. For details of ^1H NMR experiments, see the Supporting Information, Scheme S2.

[14] Such trends were also observed by the XPS measurements on each sample of **4o** and DABS-functionalized glasses (Supporting Information, Figure S3). The loading on ITO surface was evaluated by integrating the CV curve after subtracting non-Faradaic current.