



Organic functionalization of the surface of silica with arylsilanes. A new method for synthesizing organic–inorganic hybrid materials

Norihisa Fukaya^{a,*}, Hisato Haga^b, Teruhisa Tsuchimoto^b, Syun-ya Onozawa^a, Toshiyasu Sakakura^a, Hiroyuki Yasuda^{a,*}

^aNational Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

^bDepartment of Applied Chemistry, School of Science and Technology, Meiji University, Higashimita, Tama-ku, Kawasaki, 214-8571, Japan

ARTICLE INFO

Article history:

Received 23 June 2010

Received in revised form

9 August 2010

Accepted 17 August 2010

Available online 24 August 2010

Keywords:

Organic–inorganic hybrid materials

Mesoporous silica

Immobilization

Arylsilane

Dearylation

ABSTRACT

Organic functionalization of a silica surface has been realized by employing arylsilanes. Grafting reactions of aryl(3-chloropropyl)dimethylsilanes (aryl = *p*-anisyl, *p*-tolyl, phenyl) with silica were carried out in heptane at 80 °C for 24 h. The ²⁹Si and ¹³C CP/MAS spectra of the obtained silica materials clearly showed that the 3-chloropropyl dimethylsilyl moieties were cleanly grafted onto silica via a siloxane (Si–O–Si) bond accompanied by the release of the aryl groups. The loading amounts on FSM-type mesoporous silica (TMPS-4) with aryl(3-chloropropyl)dimethylsilanes were comparable to those with 2-propenylsilane and the most commonly used methoxysilane.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Organic–inorganic hybrid materials have attracted increasing attention because the combination is expected to provide excellent and unique properties [1–3]. In particular, hybrid materials obtained by modifying the surface of inorganic oxides such as silica with organic functional groups are valuable, and utilized or expected to be applied in various fields, including packing materials for chromatography, chiral selectors, adsorbents, chemical sensors, immobilized catalysts, etc [4–6]. A general method for organic functionalization of a silica surface is based on the reaction between silanol groups on silica and “silane coupling reagents”, which are organosilanes containing alkoxy, halo, acyloxy, or amino groups on silicon atoms as leaving groups [7]. However, silane coupling reagents are occasionally difficult to handle under hydrolytic conditions and are hard to purify by chromatography in air because they are easily hydrolyzed and subsequently condensed to the corresponding siloxane compound.

Recently, a method that modifies the silica surface utilizing deallylation of 2-propenylsilane derivatives has been reported [8–10]. 2-Propenylsilanes are less sensitive to moisture than conventional silane coupling reagents. Although they can be

purified easily, they are still chemically unstable. Thus, a synthetic strategy for constructing organic functional moieties is limited due to the high reactivity of the propenyl leaving groups. Moreover, an acid catalyst like scandium triflate is necessary to modify silica with methallylsilanes [10]. In this paper, we report the organic modification of a silica surface with less reactive arylsilanes. To date, employing arylsilanes to graft organic functional groups on silica has yet to be reported.

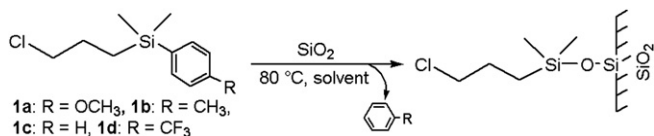
2. Results and discussion

Grafting reactions of aryl(3-chloropropyl)dimethylsilanes **1a–1d** with amorphous silica (CARIACT Q-3, hereafter abbreviated as “Q-3”) and ordered mesoporous silica (TMPS-4) were carried out in heptane at 80 °C for 24 h (Scheme 1). For comparison, the reactions of general silane coupling reagents, (3-chloropropyl)-2-propenyl dimethylsilane **2**, (3-chloropropyl) dimethylmethoxysilane **3**, and chloro(3-chloropropyl) dimethylsilane **4** with Q-3 and TMPS-4 were also conducted.

Fig. 1 shows the ¹³C and ²⁹Si CP/MAS spectra of the material obtained by reacting **1a** with Q-3. The ¹³C CP/MAS spectrum exhibited four signals, which were assigned to the carbons of the propyl moiety (δ 47.4, 26.3, and 14.5 ppm) and the methyl groups on the silicon atom (δ – 1.5 ppm) [8]. Surprisingly, signals due to the *p*-anisyl group were not present in the aromatic region. In

* Corresponding authors. Tel.: +81 29 861 9399; fax: +81 29 861 4580.

E-mail addresses: n.fukaya@aist.go.jp (N. Fukaya), h.yasuda@aist.go.jp (H. Yasuda).



Scheme 1. Grafting of arylsilanes on silica.

In addition to the silica peaks in the ^{29}Si CP/MAS spectrum, one signal corresponding to the silicon attached to silica (δ 14.4 ppm) was observed. The chemical shifts in the ^{13}C and ^{29}Si CP/MAS spectra were essentially the same as those for the materials obtained using **2–4**. These data clearly show that the 3-chloropropyl dimethylsilyl moiety in **1a** was cleanly grafted onto Q-3 via a siloxane (Si–O–Si) bond accompanied by the release of the *p*-anisyl group. Actually, anisole was detected on the GC–MS analysis of the reaction solution of **1a** and Q-3. The materials obtained by reacting **1b** or **1c** with Q-3 also gave ^{13}C and ^{29}Si CP/MAS spectra similar to Fig. 1 (see Supplementary Data, Figs S1 and S2), but grafting of the 3-chloropropyl dimethylsilyl group in **1d** was negligible.

The grafted (3-chloropropyl)dimethylsilyl groups on silica were quantified using elemental analysis of chlorine. Table 1 summarizes the results. The loading amounts of **1a–1c** on Q-3 and TMPS-4 were 0.51 to 0.54 and 0.9 to 1.4 mmol/g, respectively (entries 1–3 and 8–10). The elemental analysis results were supported by quantitative solid-state ^{29}Si dipolar decoupling/magic angle spinning (DD/MAS) NMR spectroscopy. In the ^{29}Si DD/MAS spectrum of the material from **1a** and TMPS-4, the loading amount of the organic moieties calculated from the integrated intensity ratio between the silicon due to **1a** and the silicon due to silica was 1.06 mmol/g, which agreed well with the value from chlorine analysis (see Supplementary Data, Fig. S3). Interestingly, the loading amounts on TMPS-4 with **1a–1c** were comparable to those with 2-propenylsilane and the most commonly used methoxysilane (entries 12 and 13).

Next, the applicability of the present grafting method onto other silica supports was examined. Using **1a–1c**, the 3-chloropropyl dimethylsilyl group was grafted onto familiar mesoporous silica, MCM-41 (0.48–1.1 mmol/g) (entries 15–17). On the other hand, the loading amount on another type of mesoporous silica, SBA-15, was smaller than those on TMPS-4 and MCM-41 (entries 19–21). The grafting of organic groups on Q-3 with arylsilanes gave a moderate amount, whereas grafting onto another commercial

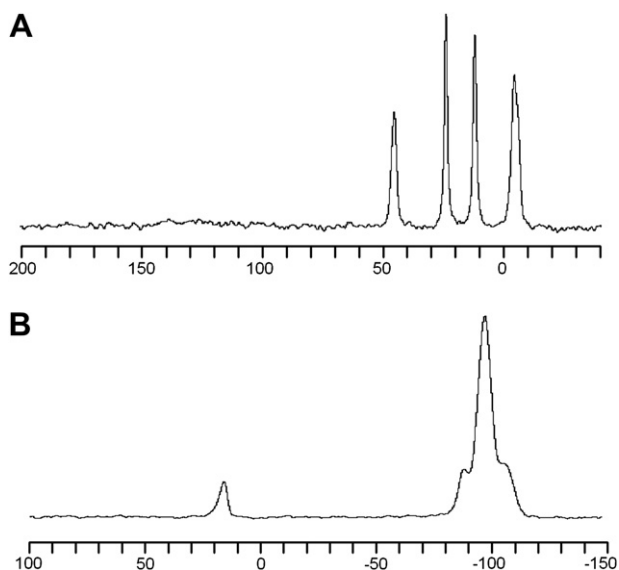


Fig. 1. (A) ^{13}C and (B) ^{29}Si CP/MAS spectra of modified silica obtained by the reaction of **1a** with Q-3.

Table 1
Grafting of (3-chloropropyl)dimethylsilanes on silica.

Entry	Silane	Silica	Solvent	Loading ^a (mmol/g)
1	1a	Q-3	heptane	0.51
2	1b	Q-3	heptane	0.54
3	1c	Q-3	heptane	0.52
4	1d	Q-3	heptane	trace
5	2	Q-3	heptane	0.95
6	3	Q-3	heptane	0.74
7	4	Q-3	heptane	1.10
8	1a	TMPS-4	heptane	1.04
9	1b	TMPS-4	heptane	0.90
10	1c	TMPS-4	heptane	1.40
11	1d	TMPS-4	heptane	trace
12	2	TMPS-4	heptane	1.40
13	3	TMPS-4	heptane	1.00
14	4	TMPS-4	heptane	1.86
15	1a	MCM-41	heptane	1.11
16	1b	MCM-41	heptane	0.48
17	1c	MCM-41	heptane	0.80
18	1d	MCM-41	heptane	trace
19	1a	SBA-15	heptane	0.17
20	1b	SBA-15	heptane	0.17
21	1c	SBA-15	heptane	0.07
22	1d	SBA-15	heptane	trace
23	1a	Aerosil 200	heptane	0.17
24	1a	TMPS-4	toluene	1.09
25	1a	TMPS-4	n-Bu ₂ O	0.50

^a Determined by elemental analysis of chlorine.

amorphous silica, Aerosil 200, was scarce (entry 23). Table 2 compares the density of the surface silanol groups on the silica supports estimated by TG-DTA [11] and the percentage of utilization of the silanol groups in the grafting with **1a**. Silanol utilization varied among the supports; MCM-41 and TMPS-4 showed higher percentages. Therefore, the loading amount is not simply influenced by the surface silanol density. Although the most predominant factor of silica that determines the reactivity of arylsilanes is not clear at present, the local environment around the silanol groups and/or the acidity of silanol may play an important role [12].

Additionally, solvent choice is important for grafting organic functional groups with arylsilanes. For the reaction of **1a** and TMPS-4, toluene (80 °C) was as effective as heptane, but di-*n*-butyl ether (80 °C) reduced the loading by about half that of heptane (Table 1, entries 24 and 25).

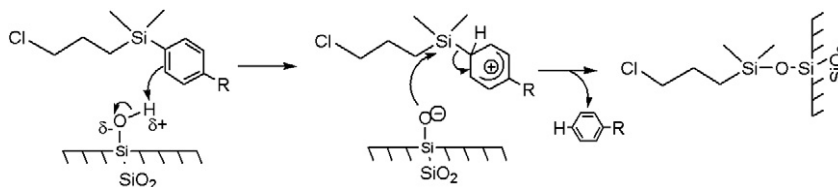
Aryl groups in arylsilanes are removed from silicon with strong Brønsted acid such as hydrochloric acid, trifluoromethanesulfonic acid, and supercritical water [13–16]. The cleavage of the carbon–silicon bond in arylsilanes using solid acids like montmorillonite KSF has also been reported [17]. In the present grafting reaction with arylsilanes, we hypothesized that the acidic silanol groups on the silica surface promote dearylation. That is, the hydrogen of a silanol group acts as a proton to add electrophilically to the arylsilane and accompanies the nucleophilic attack on silicon in arylsilane by the oxygen of silica, resulting in the elimination of the aryl group from silicon (Scheme 2). The protonation of the olefinic carbon–carbon double bonds with the silanol groups on

Table 2
Utilization of silanol groups in grafting with **1a**.

Entry	Silica	Si–OH ^a (/nm ²)	Loading ^b (/nm ²)	Utilization (%)
1	MCM-41	1.6	0.67	43
2	TMPS-4	1.6	0.60	38
3	SBA-15	1.2	0.11	9
4	Q-3	4.9	0.43	9
5	Aerosil 200	4.1	0.51	12

^a Determined by TG-DTA.

^b Determined by elemental analysis of chlorine.



Scheme 2. Possible mechanism of grafting of arylsilanes on silica.

Table 3
Textural properties of silica.

Silica	Surface area ^a (m ² /g)	Pore volume ^b (cm ³ /g)	Pore diameter ^c (nm)
Q-3	713	0.52	2.4
Aerosil 200	199	–	–
TMPS-4	1039	1.46	3.8
MCM-41	1056	1.06	2.9
SBA-15	947	1.01	7.0

^a BET surface area.

^b Pore volume ($P/P_0 = 0.99$).

^c Average pore diameter by the BJH method.

silica has also been assumed in the organic functionalization with 2-propenylsilanes [8]. If one accepts the above mechanism, the less reactivity of **1d** can reasonably be explained by the difficulty of protonation due to the electronegative p -CF₃ group on the aryl ring. However, the order of the loading amounts on silica among **1a–1c** did not agree with the predicted tendency for protonation (p -MeO > p -Me > H). This disagreement suggests that the efficiency of dearylation might be decided not only by the protonation of the aryl groups but also the steric effect and/or the electrophilicity on the silicon atom of arylsilanes that could influence on the rate of the nucleophilic attack by the oxygen of silica.

3. Conclusion

We have realized organic functionalization of a silica surface via the reaction of silica with fairly stable arylsilanes without the aid of a catalyst. We believe the present methodology has great potential in the synthesis of versatile organic–inorganic hybrid materials.

4. Experimental

4.1. General remarks

All preparation of arylsilanes and organic functionalization of silicas were performed under an inert gas using Schlenk techniques. All solid-state NMR spectra were recorded on a Bruker AVANCE 400WB spectrometer equipped with a 4 mm MAS probehead. The surface area and the pore volume were measured by nitrogen adsorption at -196 °C using BEL Japan BELSORP-mini II. The pore size distribution was calculated from the adsorption branch of nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method. The density of the surface silanol groups on the silica supports was determined by the weight loss of silica powders over a temperature range of 25–1000 °C which was monitored by TG-DTA (Bruker AXS, TG-DTA200SA).

4.2. Materials

As silica supports, two types of amorphous silica (Fuji Silysia Chemical Ltd., CARIACT Q-3 and Nippon Aerosil Co. Ltd., Aerosil 200) and three types of ordered mesoporous silica (Taiyo Kagaku Co. Ltd., TMPS-4 (FSM-type mesoporous silica with a 2D hexagonal structure), MCM-41, and SBA-15) were used in this work. MCM-41

[18] and SBA-15 [19] were prepared according to the literature. The textural properties of silica are summarized in Table 3. All silicas were dried at 80 °C under vacuum for 3 h prior to use. Aryl(3-chloropropyl)dimethylsilanes **1a–1d** were prepared according to the reported procedures [20].

4.3. Grafting of 3-chloropropylsilanes on silica

A typical procedure is given for the reaction of p -anisyl(3-chloropropyl)dimethylsilane (**1a**) with silica: To a suspension of dried silica (0.25 g) in 5 mL of heptane was added p -anisyl(3-chloropropyl)dimethylsilane (**1a**) (0.36 g, 1.5 mmol), and the mixture was stirred at 80 °C for 24 h. The resulting modified silica was filtered and washed successively with ethyl acetate (10 ml) and dichloromethane (10 ml). Then the modified silica was dried at 80 °C under a vacuum for 3 h.

Acknowledgements

This research was financially supported by the Development of Microspace and Nanospace Reaction Environment Technology for Functional Materials Project of NEDO, Japan.

Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.jorgchem.2010.08.023.

References

- [1] Special Issue on Organic–Inorganic Nanocomposites, Chem. Mater. 13 (2001) No. 10.
- [2] C. Sanchez, P.G. Romero, Functional Hybrid Materials. Wiley-VCH, Weinheim, 2004.
- [3] G. Kimmelbick, Hybrid Materials, Synthesis, Characterization and Applications. Wiley-VCH, Weinheim, 2007.
- [4] A.P. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589–3614.
- [5] A. Corma, H. Garcia, Adv. Synth. Catal. 348 (2006) 1391–1412.
- [6] Special Issue on Functional hybrid materials, J. Mater. Chem. 15 (2005) 35–36.
- [7] E.P. Plueddemann, Silane Coupling Agents, second ed., Plenum, New York, 1991.
- [8] T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki, T. Hayashi, J. Am. Chem. Soc. 125 (2003) 4688–4689.
- [9] K. Aoki, T. Shimada, T. Hayashi, Tetrahedron Asymmetry 15 (2004) 1771–1777.
- [10] Y.R. Yeon, Y.J. Park, J.S. Lee, J.W. Park, S.G. Kang, C.H. Jun, Angew. Chem. Int. Ed. 47 (2008) 109–112.
- [11] R. Mueller, H.K. Kammler, K. Wegner, S.E. Pratsinis, Langmuir 19 (2003) 160–165.
- [12] The difference in the surface morphology and the local environment of silanol between MCM-41 and SBA-15, and their influences on the surface organic functionalization have been described, see: I.G. Shenderovich, D. Mauder, D. Akcakayran, G. Buntkowsky, H.-H. Limbach, G.H. Findenegg J. Phys. Chem. B. 111 (2007) 12088.
- [13] C. Eaborn, Pure Appl. Chem. 19 (1969) 375–388.
- [14] H. Gilman, F.J. Marshall, J. Am. Chem. Soc. 71 (1949) 2066–2069.
- [15] W. Uhlig, Chem. Ber. 125 (1992) 47–53.
- [16] K. Itami, K. Terakawa, J. Yoshida, O. Kajimoto, J. Am. Chem. Soc. 125 (2003) 6058–6059.
- [17] Y. Zafrani, E. Gershonov, I. Columbus, J. Org. Chem. 72 (2007) 7014–7017.
- [18] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834–10843.
- [19] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548–552.
- [20] T. Nakashima, R. Fujiyama, H.J. Kim, M. Fujio, Y. Tsuno, Bull. Chem. Soc. Jpn. 73 (2000) 429–438.