

Surface Functionalization of Silica by Si–H Activation of Hydrosilanes

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Supporting Information

ABSTRACT: Inspired by homogeneous borane catalysts that promote Si–H bond activation, we herein describe an innovative method for surface modification of silica using hydrosilanes as the modification precursor and tris(pentafluorophenyl)borane (B(C₆F₅)₃) as the catalyst. Since the surface modification reaction between surface silanol and hydrosilane is dehydrogenative, progress and termination of the reaction can easily be confirmed by the naked eye. This new metal-free process can be performed at room temperature and requires less than 5 min to complete. Hydrosilanes bearing a range of functional groups, including alcohols and carboxylic acids, have been immobilized by this method. An excellent preservation of delicate functional groups, which are otherwise decomposed in other methods, makes this methodology appealing for versatile applications.

Functionalization of pre-designed silica supports such as particles and monoliths, regardless of crystalline and glassy states, with desired organic moieties by stable covalent linkage has been attracting huge attention because of its widespread applications in drug delivery,¹ bioimaging,² catalysis,³ optics,⁴ and polymer brushes.⁵ The surface reaction between silanol (Si–OH) of silica and functionalized organosilicon compounds such as chlorosilanes (denoted as precursor) is leveraged in many cases to form covalent siloxane (Si–O–Si) bonds (denoted as grafting).⁶ However, due to high reactivity and moisture sensitivity of the traditional alkoxy-, halo-, amino-, and acyloxysilanes,⁷ purification is often the critical for these hydrolyzable precursors. These problems can be partially circumvented by using stable allylsilanes as the precursor.⁸ In addition, significant progress has been made in the surface functionalization of silica with the recent development of catalytic grafting processes using methallyl-⁹ and vinylsilane¹⁰ precursors. These processes can be performed at room temperature, use transition and noble metal catalyst (3–10 mol%), and require 6–12 h for completion depending on the precursors. For this process to reach its full potential, it is desirable to be able to efficiently graft organics on silica in a shorter duration of time at room temperature to prevent decomposition of the delicate functional groups and to extend its applications to nanolithography, which requires fast surface reaction for the controlled modification of surfaces on the nanometer to micrometer scale.¹¹

Since the invention of the hydrosilylation reaction, hydrosilanes, which are moisture stable and can be purified by standard laboratory techniques such as extraction and silica gel column chromatography, have been used extensively in organic chemistry for several decades.¹² Thus, unlike allyl-, methallyl-, or vinylsilanes, various hydrosilanes are commercially available (more than 200 from Sigma-Aldrich (USA), Tokyo Chemical Industry (Japan), and Gelest (USA)), and numerous protocols are already established for their synthesis as well.¹³ Around 20 years ago, Piers and co-workers first reported the reduction of ketones and esters by hydrosilanes using the strong Lewis acid tris(pentafluorophenyl)borane (B(C₆F₅)₃) as the catalyst (denoted as Cat.).¹⁴ The proposed mechanism^{14b} and a recent theoretical study¹⁵ describe the role of the catalyst in the catalytic cycle as an activator of Si–H groups by coordination [Si–H---B(C₆F₅)₃], which largely decreases the electron density at the silicon center, making it susceptible to be attacked by electron-rich substrates. This concept has been extended toward dehydrogenative addition of hydrosilane to alcohols using zinc catalysts, and these reactions are extremely fast and quantitative.¹⁶ Also, this process represents a fascinating similarity where the Si–OH moiety is replaced with C–OH. By fostering these reports, we herein present for the first time a fast (5 min), room temperature, catalytic grafting protocol for surface modification of amorphous silica with a variety of functional groups using hydrosilanes as the precursor and B(C₆F₅)₃ as the Si–H bond activation catalyst.

Initially, a benchmark reaction between amorphous mesoporous silica microparticles (MCM-41, **1**, with specific surface area 850 m² g⁻¹) and (3-chloropropyl)dimethylsilane (**2**) in the presence of Cat. was performed under various conditions for optimization of the condition (Figure 1a,b). All the reactions were performed under the anhydrous condition by suspending 0.1 g of dry **1** in 3 mL of dichloromethane (DCM) containing 0.5 mmol of **2**. All the surface-grafted products were purified by vigorous washing, followed by drying under vacuum. The addition of 5 mol% of Cat. in the aforementioned reaction mixture leads to an intensive evolution of hydrogen, which terminates within a few minutes. The elemental analysis on the samples reacted for 60 min (G2, entry 1, Table 1) and 5 min (G2, entry 2) shows almost identical loading of organics (1.68 and 1.65 mmol g⁻¹, respectively), indicating the completion of reaction within 5 min. Decreasing the Cat. loading to 1 mol% (G2, entry 3) did not change the reaction rate and comparable

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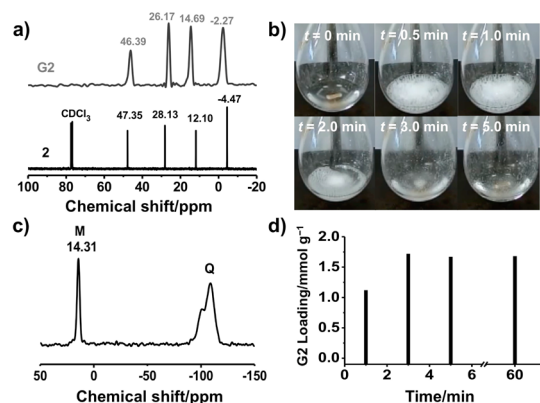


Figure 1. (a) Solid-state ^{29}Si CPMAS NMR spectrum of **G2**. (b) Solid-state (gray, top) and liquid-state (black, bottom, in CDCl_3 solvent) ^{13}C CPMAS NMR spectra of **G2** and **2**, respectively. (c) Time-dependent loadings of **2** on **G2**. (d) Photographs of grafting reaction (using the same condition as entry 3 in Table 1; $t = 0$ shows the onset of addition of Cat.), which can be visually confirmed by evolution of hydrogen.

Table 1. Optimization of Reaction Conditions for Immobilization of 2 on 1 in the Presence of Cat. at Room Temperature

entry	Cat./mol%	solvent, amount/ mL	time/ min	loading on G2 / mmol g^{-1}
1	5.00	CH_2Cl_2 , 3	60	1.68
2	5.00	CH_2Cl_2 , 3	5	1.65
3	1.00	CH_2Cl_2 , 3	5	1.67
4	1.00	none	5	1.71
5	1.00	none (0°C)	5	1.69
6	0	CH_2Cl_2 , 3	1440	0.00

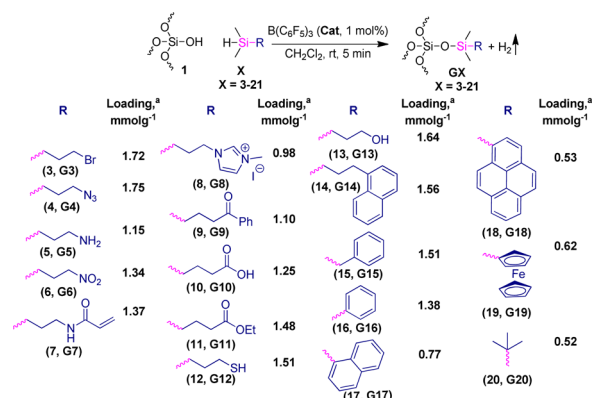
(1.67 mmol g^{-1}) loading of organics was obtained within 5 min. Furthermore, the reaction proceeded without diminishing its rate in the absence of solvent (**G2**, entry 4), and can be performed at even lower temperature (0°C , **G2**, entry 5). It is noteworthy that no detectable loading of organics was found in the absence of Cat. even after 24 h (**G2**, entry 6). The solid-state ^{13}C CPMAS NMR (Figure 1a) spectra of **G2** (entry 3) revealed that all the carbons in **2** remained unchanged after grafting. Advantages of this procedure are that it can be observed by the naked eye and the end of grafting can easily be confirmed (Figure 1b).

Spectroscopic characterizations of **G2** (entry 3) by solid-state ^{29}Si CPMAS NMR (Figure 1c) unambiguously proved the immobilization of **2** on the silica surface by Si–O–Si bonding by the appearance of sharp M signal (silicon species with one siloxane bond) at 14.3 ppm, which corresponds to the surface-bound silicon from **2**. These measurements suggest the proposed surface formula of **G2** is reasonable. A time-dependent study was performed for investigating the rate of loading of **2** on **1** under the identical condition with entry 3. Surprisingly, 1 min after the addition of 1 mol% of Cat. shows a loading of 1.12 mmol g^{-1} by elemental analysis, and the loading increases to 1.69 after 3 min and remains almost constant after another 57 min (Figure 1d). This proves the termination of

grafting of **2** on silica **1** within 3 min, which is also supported by the visual evidence.

In order to extend the methodology, we synthesized hydrosilanes bearing diverse functional groups using simple traditional synthetic methods (section 5 in SI). All the compounds after synthesis were purified by using conventional laboratory procedures like extraction and silica gel column chromatography, giving high yields and purity. Grafting of these functionalized hydrosilanes on **1** was performed using the same condition as entry 3, and in all the cases, grafting was finished within 5 min irrespective of the functional groups on hydrosilanes. The loading efficiencies vary between 1.75 and 0.52 mmol g^{-1} (Chart 1), with a surface coverage (number of molecules per nm^2 , section 7 in SI) ranging from 1.23 to 0.37 nm^{-2} , depending on the functional groups (section 6 in SI for FT-IR spectra).

Chart 1. Catalytic Immobilization of Hydrosilanes Containing Various Functional Groups onto Silica^a



^aDetermined by elemental analysis of carbon, bromine, nitrogen, and sulfur.

Although hydrosilanes have been used as the reducing agent in homogeneous reactions,^{12a,14,17} the fast heterogeneous reactions between surface silanols and hydrosilanes with functional groups such as azido (**4**, **G4**), nitro (**6**, **G6**), acrylamido (**7**, **G7**), ketone (**9**, **G9**), and ester (**11**, **G11**) with their entirety are remarkable; these functional groups may otherwise be reduced instead of being grafted. Carboxylic acid **10** and alcohol **13** functional groups are difficult to maintain in most of the silylated precursors for transesterification and acid-catalyzed decomposition in the case of allyl- and methallyl-silanes. Hydrosilanes show distinct advantages, not only because these molecules are stable against water and air but also because they can be purified by column chromatography. Indeed, similar to the results shown above, these molecules were also grafted on the silica surface (**G10**, **G13**) with high enough loading within 5 min. In addition, even amine **5**¹⁸ was successfully grafted to give the aminopropylsilica **G5** containing 1.15 mmol g^{-1} of 3-aminopropyltrimethylsilyl group without catalytic inhibition by the formation of Cat. and **5** complex.¹⁹ However, a systematic decrease of loading of organics with increasing size of organic substituent adjacent to the silicon center was observed. For example, as the size of organic substituent was increased from phenyl (**15**, **G15**) to pyrenyl (**18**, **G18**), the loading gradually decreased from 1.51 to 0.53 mmol g^{-1} . This trend was also observed for ferrocenyl (**19**, **G19**) and *tert*-butyl (**20**, **G20**). It is noteworthy that the most

efficient methodology available until now required at least 6 h for grafting various functional groups. The present method drastically decreased the time required from the fastest known methodology⁹ by a factor of 72.

The possibility of preservation of delicate functional groups on the hydrosilanes was investigated. As allylsilanes are known to react with silica surface⁸ and can be hydrolyzed,²⁰ we have chosen allyldimethylsilane **21** as a model compound for this experiment. Two parallel reactions were performed: one without the catalyst at 60 °C and the other with 1 mol% of Cat. at room temperature. In the absence of catalyst at 60 °C, the allyl group on **21** reacted with silica for 48 h to yield Si–H-terminated silica surface (**G21a**, Figure 2), whereas in the

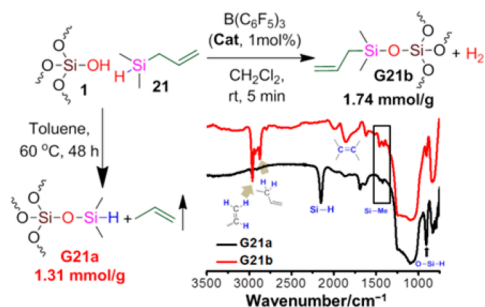


Figure 2. Grafting of hydrosilane bearing hydrolyzable allyl group **21** on silica **1**.

presence of 1 mol% of Cat. the Si–H group was reacted to yield the allyl group-terminated silica surface (**G21b**). The loading was higher in **G21b** (1.74 mmol g⁻¹) than **G21a** (1.31 mmol g⁻¹). In addition, the preservation of Si–H moiety in **G21a** proves the inertness of Si–H bond in the absence of catalyst and which becomes reactive in the presence of Cat., signifying the catalytic grafting method proceeds through Si–H activation by Cat. This experiment not only proves the high selectivity but also distinguishes the efficiency of this method by higher loading of organics.

The grafting of coumarin derivative **22** on **1** is interesting as it can be visualized by UV light. In order to differentiate physisorbed hydrosilanes from covalently grafted ones, two parallel experiments were designed (Figure 3). Both of these

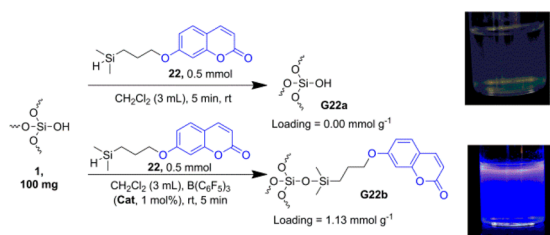


Figure 3. Immobilization of **22** on silica particles and their photographic image under UV lamp after dispersion in water.

experiments were carried out at room temperature under identical reaction conditions except for the catalyst: one reacted in the absence of catalyst (product **G22a**) and the other in the presence of Cat. (product **G22b**). After vigorous washing, the materials were dried, dispersed in water, and placed under UV light. A characteristic intense blue emission from the immobilized coumarin moiety was detected in the product **G22b**, whereas no emission was observed in **G22a**.

This process also works on silica materials with different morphology and material shape such as SBA-15 (specific surface area 450 m² g⁻¹, loading 1.54 mmol g⁻¹) and macroporous silica monolith (specific surface area 150 m² g⁻¹, loading 0.58 mmol g⁻¹). In addition, (3-chloropropyl)-methylsilane was also found to be suitable (loading 1.72 mmol g⁻¹, section 4b in SI). Spherical silica gel beads for packing HPLC columns have also been modified with octadecyldimethylsilane (section 8 in SI). The carbon content of the ODS-modified beads was 25.4% in contrast to 11.7% of standard commercial product (ODS-4, GL Sciences, Inc., Saitama, Japan). Moreover, columns packed with hydrosilane-modified beads exhibited stronger relative retentions than ODS-4 for aromatic compounds which are in accordance with the higher carbon content.

This protocol can also be extended to modify flat surfaces like microscope glass slides (Figure 4), which were pretreated

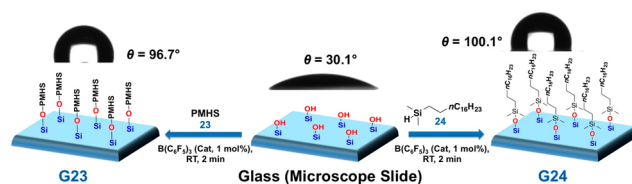
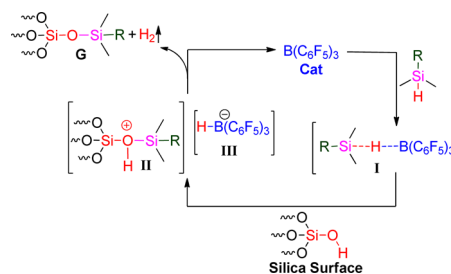


Figure 4. Modification of a microscope glass slide using monomeric and polymeric hydrosilanes and corresponding water contact angle measurement results.

in the piranha solution to activate the surface Si–OH groups. After the reaction with octadecyldimethylsilane (**24**, **G24**), the glass slide becomes hydrophobic after the reaction; the contact angle of water increased from 30.1° to 100.1° after the modification. We also found that the polymeric hydrosilanes such as polymethylhydrosiloxane (PMHS, **23**) also react in a similar fashion and alter the contact angle of water, proving the extendibility of this protocol from monomeric to polymeric hydrosilanes. The polymeric hydrosilanes may be useful for formation of polymer brushes on solid supports.⁵ It is worth mentioning that these modifications on flat surface can also be performed with or without solvent. In addition, due to high accessibility of surface silanols on the flat surface, the grafting proceeds almost instantaneously and terminates within a few seconds, exhibiting the high possibility of application to lithographic and printing techniques.

On the basis of the previous reports on Si–H activation by boranes¹⁴ and the aforementioned observations, we propose here the mechanism of this grafting procedure as depicted in Scheme 1. Initially Cat. reacts with hydrosilanes to form the highly active intermediate **I**.²¹ The silicon atom in **I** is electron-

Scheme 1. A Plausible Mechanism of the Catalytic Grafting of Hydrosilane on Silica Surface



deficient and therefore attacks the electron-rich oxygen of silanol on the silica surface to form the intermediate **II**. One of the possible explanations of this fast reaction between hydrosilane and silanol on silica is the acidic character of surface silanol ($pK_a = 4.9-8.5$),²² which makes the oxygen of silanol highly prone to electrophilic attack by the electron-deficient silicon of **I**. Finally, the basic tris(pentafluorophenyl)-borane hydride (**III**) intermediate snatches the proton from acidic and cationic intermediate **II**, forming hydrogen and immobilized product **G** and regenerating the catalyst in the reaction medium.

In summary, we have established a highly efficient, selective, extremely fast, room temperature, metal-free catalytic grafting method for surface functionalization of silica through Si-H bond activation of functionalized hydrosilanes by the $B(C_6F_5)_3$ catalyst. The grafting protocol is dehydrogenative; thus, the end of grafting can be easily recognized as termination of the hydrogen evolution by the naked eye. We believe that this grafting procedure can be extended to other metal oxides and polymer substrates, giving it greater potential in the development of lithographic/printing patterning techniques. Such efforts are currently underway in our laboratory.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed synthesis and characterizations of hydrosilanes; general procedure and characterizations of grafting. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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