Recyclable Functionalization of Silica with Alcohols via Dehydrogenative Addition on Hydrogen Silsesquioxane

Nirmalya Moitra,[†] Toshiyuki Kamei,[‡] Kazuyoshi Kanamori,*[,†] Kazuki Nakanishi,*[,†] Kazuyuki Takeda,[†] and Toyoshi Shimada*[,‡]

[†]Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan
[‡]Department of Chemical Engineering, Nara National College of Technology, 22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan

Ⓢ Supporting Information

ABSTRACT: Synthesis of class II hybrid silica materials requires the formation of covalent linkage between organic moieties and inorganic frameworks. The requirement that organosilylating agents be present to provide the organic part limits the synthesis of functional inorganic oxides, however, due to the water sensitivity and challenges concerning purification of the silylating agents. Synthesis of hybrid materials with stable molecules such as simple alcohols, rather than with these difficult silylating agents, may therefore provide a path to unprecedented functionality. Herein, we report the novel functionalization of silica with organic alcohols for the first time. Instead of using hydrolyzable organosilylating agents, we used stable organic alcohols with a Zn(II) catalyst to modify the surface of a recently discovered highly reactive macro-mesoporous hydrogen silsesquioxane (HSQ, $HSiO_{1.5}$) monolith, which was then treated with water with the catalyst to form surface-functionalized silica. These materials were comprehensively characterized with FT-IR, Raman, solid-state NMR, fluorescence spectroscopy, thermal analysis, elemental analysis, scanning electron microscopy, and nitrogen adsorption−desorption measurements. The results obtained from these measurements reveal facile immobilization of organic moieties by dehydrogenative addition onto surface silane (Si−H) at room temperature with high loading and good tolerance of functional groups. The organic moieties can also be retrieved from the monoliths for recycling and reuse, which enables cost-effective and ecological use of the introduced catalytic/reactive surface functionality. Preservation of the reactivity of as-immobilized organic alcohols has been confirmed, moreover, by successfully performing copper-catalyzed azide−alkyne cycloaddition (CuAAC) "click" reactions on the immobilized silica surfaces.
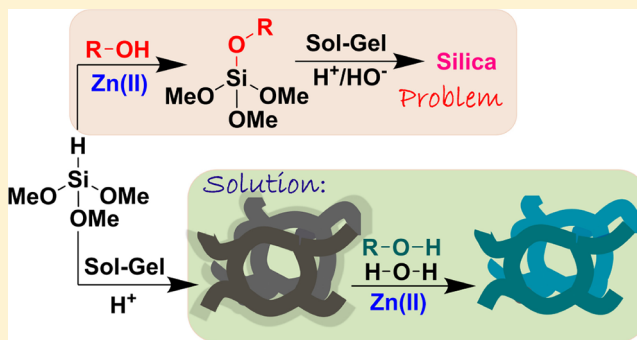
1. INTRODUCTION

Reliable techniques for immobilizing organic functional groups on silica with covalent bonds to form class II hybrids have been attracting a great deal of attention for applications in supported catalysis, drug delivery, and optics[1−3] for many years. Organically modified silicas based on Si−O−Si networks, in which an organic moiety is covalently bonded with silicon, have been widely exploited using methodologies such as sol−gel[4,5] and grafting.[6−11] In both the sol−gel and grafting processes, use of an organic moiety functionalized with a hydrolyzable chlorosilyl, alkoxysilyl, or allylsilyl group is essential to obtain class II hybrids. Synthesis of these silylated precursors starting from pure organic compounds often requires single or multiple step reactions.[12−17] Furthermore, the purification of these hydrolyzable compounds is a critical step for nondistillable or noncrystallizable compounds. Efforts have been made to eliminate the use of silylated-organic molecules for the synthesis of class II hybrid silica via postfunctionalization on hybrid silica supports containing reactive sites. In this connection, amino-[18] and chloro-functionalized[19] hybrid silica have been used for immobilization of nonsilylated organic molecules. Click methodologies such as copper-catalyzed azide−alkyne cycloaddition (CuAAC) reactions on azide-[20,21] or alkyne-functionalized[22] silica and radical-initiated thiol−ene click reactions on thiol-functionalized silica[23−25] have also been employed. These simple methodologies represent a significant step forward in the immobilization of nonhydrolyzable organic molecules on hybrid silica. In all the above-mentioned methods, reactive sites are chemically anchored to the pure silica matrices. Simplification of this system can be achieved by using silica containing highly reactive sites as an integral part of as-synthesized materials that can then react easily with organic molecules.

From another perspective, formation of organic monolayers on silicon surfaces has long been conducted with organic compounds using silane chemistry on hydride-terminated Si(100) and Si(111) surfaces.[26−28] Various methodologies are available for functionalizing Si surfaces with Si−C,[29] Si−N,[30]

and Si−O[31−33] covalent bonds.[34] In most cases, nonsilylated organic molecules with specific functionality are reacted with hydride-terminated Si surfaces. Extension of these methodologies to siloxane-based materials will provide a novel way to functionalize silica without using hydrolyzable silylated compounds, thus producing silica with unprecedented functionality.

Unlike silicon, hydride-terminated siloxane-based (silica-like) materials with controlled porosity are rare, a condition that inhibits the extension of these methodologies. From the viewpoint of organic chemistry, alcohols are generally stable in air and easy to synthesize and purify. Use of a transition-metal-catalyzed dehydrogenative process to add alcohols to monomeric and polymeric organosilanes containing an Si−H moiety, which yields alkoxysilanes, has already been reported.[35,36] Reactions between carboxylic acid and polymeric hydrosilanes to form silaesters using a palladium catalyst have also been described.[37] These reactions are fast and quantitative. In all these cases, the reactions were performed in homogeneous media, however, since both the reactants and products were liquid. In order to use this methodology for immobilization of alcohols on solid silica, we require a siloxane-based material with a built-in reactive Si−H moiety as a heterogeneous substitute for silyl hydrides. In this context, Ozin et al. reported the synthesis of periodic mesoporous hydrogen silsesquioxane (or hydridosilica) microparticles (HSiO$_{1.5}$, HSQ),[38] and more recently, we have reported the synthesis of hierarchically porous HSQ monoliths with a completely preserved highly reactive Si−H moiety.[39]

Herein, we demonstrate a Zn(II)-catalyzed dehydrogenative methodology for direct synthesis of class II hybrid silica from hierarchically porous HSQ monoliths and simple organic alcohols. The diversity of the resulting functional groups, reaction at room temperature, high loading of organics, functional group tolerance, and stability as bound organic moieties make this methodology attractive for future applications. The possibility of further modification and the preservation of the reactivity of the functional groups are verified by performing "click" reactions on the azide- and alkyne-functionalized materials. In addition, the immobilized alcohols can be removed and recycled by treatment with acidic water. The novelty of this functionalization methodology lies particularly in the avoidance of hydrolyzable silane precursors and the use of easily synthesizable organic alcohols, which are generally stable in air.

2. RESULTS AND DISCUSSION

2.1. Dehydrogenative Addition Reactions between Monomeric Hydrosilanes and Alcohols. We first investigated reactions between hydrosilanes and alcohols in homogeneous media as a step toward the functionalization of silica. Although the Zn-catalyzed dehydrogenative addition of alcohols to monomeric and polymeric hydrosilanes has been reported previously,[35,36] this is the first report on the use of this methodology for production of tetraalkoxysilane bearing functional moieties. The extension of this methodology to synthesis of tetraalkoxysilane (**1**) starting from trimethoxysilane (HTMS, Scheme 1) shows similar behavior. Indeed, the use of anhydrous zinc(II) acetate as a catalyst in the equimolar reaction system of HTMS and CD$_3$OD leads to the evolution of hydrogen, suggesting that the dehydrogenative alcohol addition proceeds successfully (Table 1, entry A). This reaction was carried out under a nitrogen atmosphere at room

Scheme 1. Dehydrogenative Addition Reaction between HTMS and Alcohols with Zn(II) as a Catalyst
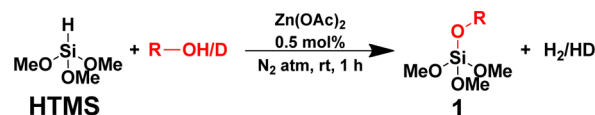

Table 1. Results of Dehydrogenative Addition Reaction between HTMS and Alcohols[a]

Entry	Alcohol	Product	Yield [%]
A	D$_3$C−OD	(H$_3$CO)$_3$Si−OCD$_3$ **1A**	92
B	∿OH	(MeO)$_3$Si−O∿ **1B**	89
C	∿OH (propargyl)	(MeO)$_3$Si−O∿ (propargyl) **1C**	93
D	benzyl alcohol	(MeO)$_3$Si−O−CH$_2$Ph **1D**	95
E	4-nitrobenzyl alcohol	(MeO)$_3$Si−O−CH$_2$C$_6$H$_4$NO$_2$ **1E**	91
F	tert-butyl alcohol	(MeO)$_3$Si−O−C(CH$_3$)$_3$ **1F**	0

[a]Reaction conditions: 2 mmol of HTMS, 2 mmol of alcohol, 1.8 mg of Zn(OAc)$_2$ (0.01 mmol), reaction time 1 h under a nitrogen atmosphere. Purification of the reaction mixture was carried out by filtration under a nitrogen atmosphere.

temperature in anhydrous solvent to prevent the addition of water instead of alcohols. Hydrogen evolution was completed after 1 h, at which time termination of the reaction was assumed. Isolation of the product was carried out by filtration of the reaction mixture under a nitrogen atmosphere, and the disappearance of the Si−H signal of HTMS at 4.2 ppm in the ^{1}H NMR spectrum of the product evidenced the conversion of Si−H (Figure 1a) into Si−OCD$_3$. The FT-IR spectrum of the starting reaction mixture reveals the presence of a CD$_3$ stretching vibration of CD$_3$OD, moreover, and Si−H and O−Si−H stretching vibrations of HTMS, while the disappearance of Si−H and O−Si−H are observed upon completion, indicating conversion of HTMS with preservation of the CD$_3$ (Figure 1b). Thus, after the reaction, partially deuterated tetramethoxysilane (TMOS) was obtained as the sole reaction product (**1A**, denoting product 1 of entry A). Application of this methodology for ethanol (**1B**) and benzyl alcohol (**1D**) gave similar results with quantitative yields. Furthermore,
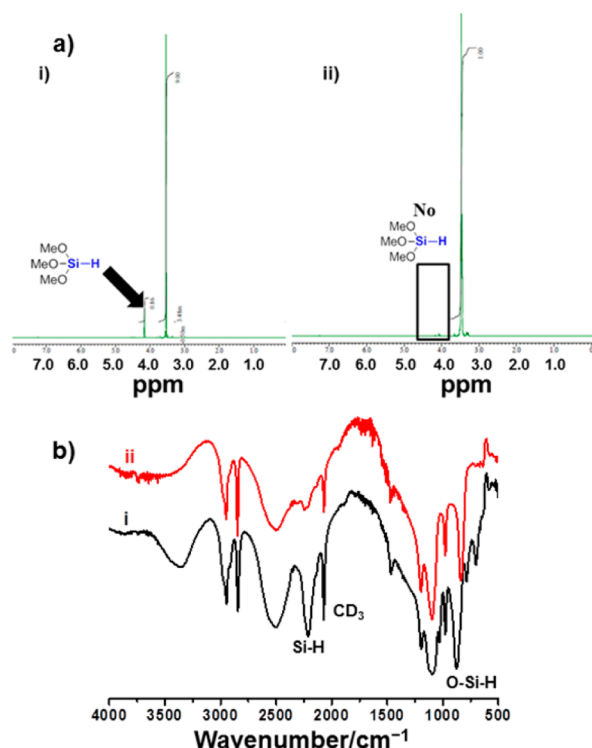
Figure 1. Spectroscopic study of entry A: (a) ^{1}H NMR of the reaction mixture of (i) before and (ii) after the reaction, showing the disappearance of the Si−H signal and the formation of a Si−O−C bond. (b) FT-IR spectrum (i) before and (ii) after the reaction, showing the disappearance of the Si−H and O−Si−H stretching vibrations with the characteristic CD$_3$ vibration preserved at 2077 cm^{-1}.

alcohols containing functional groups such as alkyne (**1C**) and nitro (**1E**) also reacted in similar fashion. In some cases, however, isomerization of the final product was observed by NMR (Supporting Information, S3). Increasing the bulkiness of the adjacent carbon atom of alcohol showed a decrease in the reaction rate. Indeed, in the case of *tert*-butyl alcohol (*t*-BuOH), no reaction between HTMS and *t*-BuOH was observed, indicating a stereochemical limitation of this methodology.

2.2. Dehydrogenative Addition Reactions between Si−H on Solid HSQ and Alcohols. Application of the aqueous sol−gel process to functionalized tetraalkoxysilanes

[(MeO)$_3$Si−OR] results in total or partial decomposition of the desired functional moiety R. Simple silica gel is therefore obtained without loading an organic functionality as a result of the sol−gel reaction of the obtained products **1A−1E**. An alternative solution using this methodology to functionalize silica involves reacting alcohols in the presence of a Zn(II) catalyst on preformed silica containing a built-in Si−H moiety that acts as a heterophase counterpart to HTMS. Herein, we report use of hierarchically porous hydrogen silsesquioxane (HSQ) synthesized directly from HTMS via acid-catalyzed sol−gel accompanied by phase separation (Supporting Information, S4).[39] The as-dried gel shows total preservation of the Si−H moiety in ^{29}Si solid-state NMR and a high specific surface area (800 m^2/g) with the mesopore distribution ranging mainly from 2 to 6 nm. In addition, SEM observation reveals the presence of a well-defined cocontinuous macroporous structure of the HSQ monolith with an average pore size of 1.3 μm. A general view of the functionalization process for alcohol-immobilized HSQ (**2**) and silica (**2′**) is presented in Scheme 2.

Unlike the zinc(II) acetate-catalyzed reaction between HTMS and methanol, the addition of 0.5 mol % catalyst to an equimolar mixture of CD$_3$OD and HSQ monolith (53 mg) in THF under a nitrogen atmosphere shows no evolution of hydrogen, indicating the absence of a reaction of alcohol with the surface Si−H. This is verified by the FT-IR spectra of the dried monolith, which are identical to the spectra of the original HSQ monolith (Table 2, entry G; FT-IR shown in Figure 2a). In this case, anhydrous THF was used as a solvent due to the rather hydrophobic nature of the HSQ monolith, and CD$_3$OD was used as a benchmark alcohol due to its distinctive absorption band in the FT-IR spectrum at 2077 cm^{-1}. Water content in the system should be as low as possible to avoid the dehydrogenative addition of water, which is faster than that of alcohols. A successful proceeding of the reaction with a prolonged reaction time of 72 h was observed when increasing the catalyst loading from 0.5 to 10 mol % (entry H). An increase in the reaction temperature from room temperature to 50 °C reduced the reaction time from 72 to 10 h (entry I). This reduction in the reaction rate when changing from HTMS to HSQ monoliths can be attributed to the immobilized Si−H in the solid phase and the low solubility of zinc(II) acetate in the reaction medium. Changing the catalyst from zinc(II) acetate to zinc(II) 2-ethylhexanoate (Zn(2-EH)$_2$), which shows higher solubility in THF, reduced the reaction time from 10 to 1 h under similar reaction conditions (entry J). An increase in the reaction time from 1 to 3 h was observed on decreasing the

Scheme 2. Dehydrogenative Addition Reaction between Solid HSQ and Alcohols with Zn(II) as a Catalyst (Step 1), Followed by Treatment in Water with the Zn(II) Catalyst To Obtain Alcohol-Immobilized Silica Gel (Step 2)
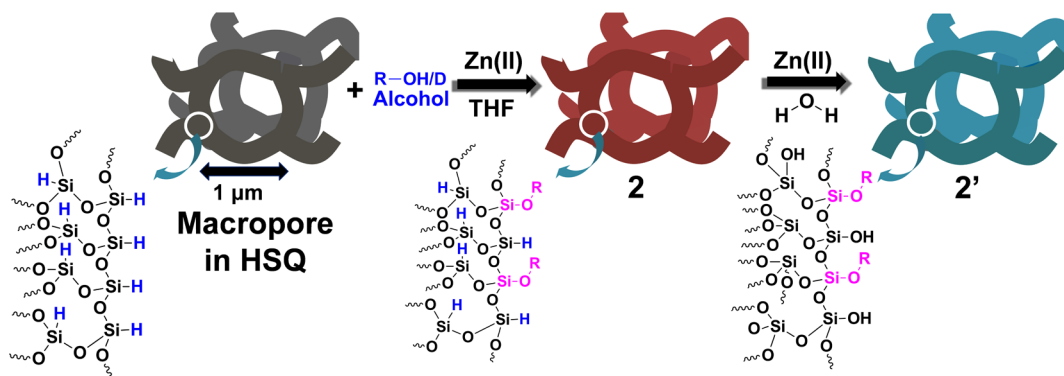
Table 2. Reaction Conditions for Dehydrogenative Addition of Alcohols to HSQ^a

entry	Zn(II) catalyst	alcohol	catalyst loading [mol %]	temp [°C]	time^b [h]	material after step 1	material after step 2
G	$Zn(OAc)_2$	CD_3OD	0.5	rt	NA	**2G**	NA
H	$Zn(OAc)_2$	CD_3OD	10	rt	72	**2H**	NA
I	$Zn(OAc)_2$	CD_3OD	10	50	10	**2I**	NA
J	$Zn(2\text{-}EH)_2$	CD_3OD	10	50	1	**2J**	NA
K	$Zn(2\text{-}EH)_2$	CD_3OD	5	rt	3	**2K**	**2′K**

^{a}Reaction conditions: step 1: HSQ (53 mg, ~1 mmol), CD_3OD (1 mmol), and Zn(II) catalyst in THF (2 mL) under a nitrogen atmosphere. Step 2: resulting material dispersed in 10 mL of water and reacted with a Zn(II) catalyst (see Supporting Information S4 for details). ^{b}Reaction time determined by the completion of hydrogen evolution and FT-IR.
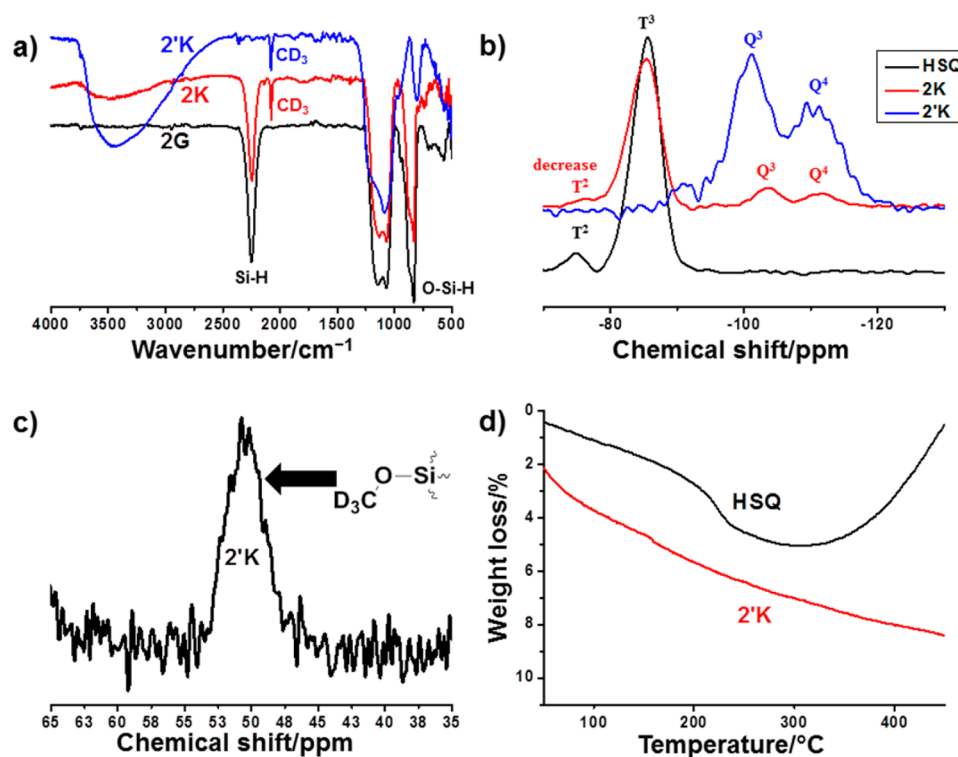
Figure 2. (a) FT-IR spectra of **2G** (Table 1, entry G) showing no incorporation of CD_3OD. Dried material **2K** shows the presence of CD_3 at 2077 cm^{-1} and unreacted Si−H at 2250 cm^{-1}. After treatment with water, the resultant material **2′K** shows the preservation of CD_3 and disappearance of Si−H. (b) ^{29}Si CP/MAS solid-state NMR showing the changes in the silicon environment in the materials after treatment with alcohol followed by treatment with water. (c) Presence of CD_3 indicated by ^{13}C CP/MAS solid-state NMR. (d) Thermogravimetric analysis of HSQ and **2′K**. An increase in weight due to the oxidation of Si−H is observed in the case of HSQ, whereas a continuous decrease in weight due to degradation of the surface-bound O−CD_3 group and additional condensation between silanols is observed for **2′K**.

temperature from 50 °C to room temperature and on decreasing the amount of the catalyst from 10 to 5 mol % (entry K). After the monolith was washed with THF and *n*-hexane and dried in a vacuum for 1 h, the infrared spectrum of the material (**2K**) revealed the presence of CD_3O groups by showing their characteristic CD_3 stretching vibration band at 2077 cm^{-1} (Figure 2a). After the reaction, however, the presence of unreacted Si−H was observed. This remaining Si−H was then catalytically decomposed to Si−O~ by reacting the resulting material with deionized water in the presence of $Zn(2\text{-}EH)_2$ (5 mol %), yielding pure silica immobilized with CD_3O (**2′K**, Figure 2a). No Zn species were detected by elemental analysis in the resultant material after washing. The higher polarity, smaller size, and capability of condensation of as-formed product **2** make water much more prone to dehydrogenative addition than organic alcohols. Catalytic hydrolysis of Si−H to Si−OH/Si−O~ is thermodynamically more favorable than hydrolysis of Si−O−C under neutral

aqueous conditions, since one of the products is hydrogen, which leaves the system to promote the reaction further, and hydrolysis of Si−O−C bonds under neutral aqueous conditions is less favorable. Since the Si−O−C bonds are immobilized on the solid surface, moreover, hydrolysis becomes more difficult than when it is present in the liquid precursor, resulting in very slow decomposition.[40] Complete decomposition of the Si−H moiety was therefore observed with preservation of the Si−O−CD_3 bonds that formed in the first step.[31−33]
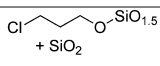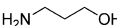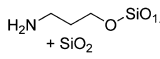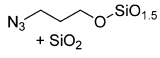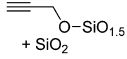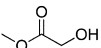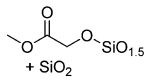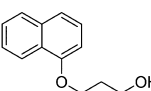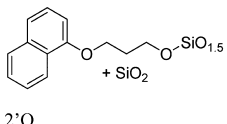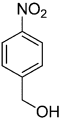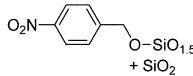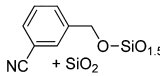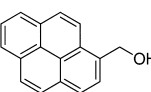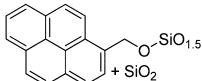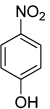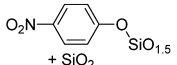
The ^{29}Si solid-state NMR of these materials gives vivid insight into the environment of the silicon atoms in the materials (Figure 2b). The ^{29}Si NMR of the initial monolithic HSQ material shows T^2 (12.7%) and T^3 (87.3%) signals, thus indicating the presence of $HSi(OH)(OSi)_2$ and $HSi(OSi)_3$ species.[41] It is also worth mentioning that most of the silicon nuclei are present as T^3 species. After reaction with CD_3OD in the presence of $Zn(2\text{-}EH)_2$ as a catalyst (**2K**), Q signals appear in the material, indicating the presence of SiX_4 units (X = OSi,

OH, or OR).[42] The appearance of the Q^3 signal (10.7%) is related to the reaction between T^3 Si−H and alcohol. A larger decrease in the intensity of the T^2 signal (from 12.7% in HSQ to 3.8% in **2K**) compared to the T^3 signal (from 87.3% in HSQ to 77.1% in **2K**) is observed, moreover, along with the appearance of the Q^4 signal (8.4%). This can be explained by the dehydrogenative addition of neighboring silanols (T^2) to silanes (T^3) to form siloxane bonds, yielding Q^4 species. Thus, 10.7% of the Si−H (originally 18.9 mmol/g) was converted to a Si−$OCHD_3$ moiety in the first step, indicating a loading of 1.92 mmol/g. Total decomposition of the Si−H moiety is observed in the final material (**2′K**), as no T^3 or T^2 signal is detected. The ^{13}C solid-state NMR of the material also indicates the presence of CD_3 by showing the characteristic signal (Figure 2c). Thermal analysis of **2′K** and its mother material HSQ reveals valuable information on the successful loading and total decomposition of the Si−H moiety (Figure 2d). Oxidation of HSQ yields pure silica with an increase in weight, whereas decomposition of **2′K** to silica results in a decrease in weight due to the loss of the CD_3 group and to additional condensation into siloxane bonds. In addition, nitrogen adsorption−desorption measurement of **2′K** (Supporting Information, S4) reveals reasonable decreases in both the specific surface area and the BJH pore size distribution, results attributable to the increase in specific weight and coverage of the pore surface by covalently attached O−CD_3 groups.

These spectroscopic analyses of **2K** and **2′K** describe the immobilization and stability of $CD_3O\sim$ in the HSQ and the final silica monoliths. The extension of this two-step methodology to primary alcohols containing various functional groups such as chloro (Table 3, entry L), azido (entry N, Figure 3a for FT-IR), alkyne (entry O), and ester (entry P) shows comparable loadings (Table 3 and Figure 3b), indicating analogous reactivity to dehydrogenative addition with HSQ. Although esters are reported to be reduced by silanes in homogeneous media in the copresence of Lewis acid catalysts,[36,43] preservation of the ester moiety was observed in this case (entry P, Figure 3a for FT-IR). This explains the high functional group tolerance of this methodology. In the case of 3-naphthoxy-1-propanol (entry Q), however, a decrease in loading of the organic moiety was observed. This is due to the larger size of the naphthyl group compared to chloro and azide. Interestingly, 3-amino-1-propanol (entry M) reacted relatively faster with the HSQ monolith, and high loading was observed by elemental analysis in this case. Total decomposition of the Si−H moiety was observed just after treatment with 3-amino-1-propanol (see Supporting Information S4 for FT-IR). This can be attributed to the basicity of the amino group and its high affinity toward Si−H bonds, as verified on the hydrogen-terminated silicon surface,[44] which is responsible for decomposition of the Si−H bonds in the first step. In addition, the affinity of amines for a hydrogen-terminated silicon surface for the formation of Si−N bonds has already been reported, and this is one of the key possible factors in this case as well. Reductions in mesopore size and volume and in the BET surface area (Figure 3b, shown together with the original HSQ and "blank" silica gel after the second step without any loading in the first step) were accordingly observed in all loaded samples, as described in detail later.

The possibility of immobilization of benzyl alcohols was also examined using this methodology: p-nitrobenzylalcohol (entry R) and 3-cyanobenzyl alcohol (entry S) reacted with the HSQ monolith in a similar fashion. No reduction of the nitro or

Table 3. Results of Dehydrogenative Addition Reaction between HSQ and Various Alcohols[a]

Entry	Alcohol	Product	Loading amount [mmol/g][b]
L		2'L	0.93
M		2'M	3.41
N		2'N	0.90
O		2'O	0.95
P		2'P	0.97
Q		2'Q	0.35
R		2'R	0.66
S		2'S	0.92
T		2'T	0.21
U		2'U	0.00

[a]Reaction conditions: Step 1: alcohol (1 mmol), HSQ (53 mg, ∼ 1 mmol), THF 2 mL, 17.6 mg of Zn(2-EH)₂ (5 mol %) under a nitrogen atmosphere at room temperature for 3 h. Step 2: treatment with 10 mL of 5 mM aqueous solution of Zn(2-EH)₂ (5 mol %) at room temperature for 1 h (see Supporting Information S4 for details). [b]Loadings were determined by elemental analysis of the final product (**2′**).

cyano groups was observed in this case, either.[45] The bulkiness of 1-pyrenemethanol yields a material with relatively lower loading of the desired organic moiety (entry T). Remarkably, p-nitrophenol also reacted with the HSQ monolith, giving loading of 0.34 mol % (entry U, sample **2U**). In this case, however, total decomposition of the Si−O−Ar bond was observed during the
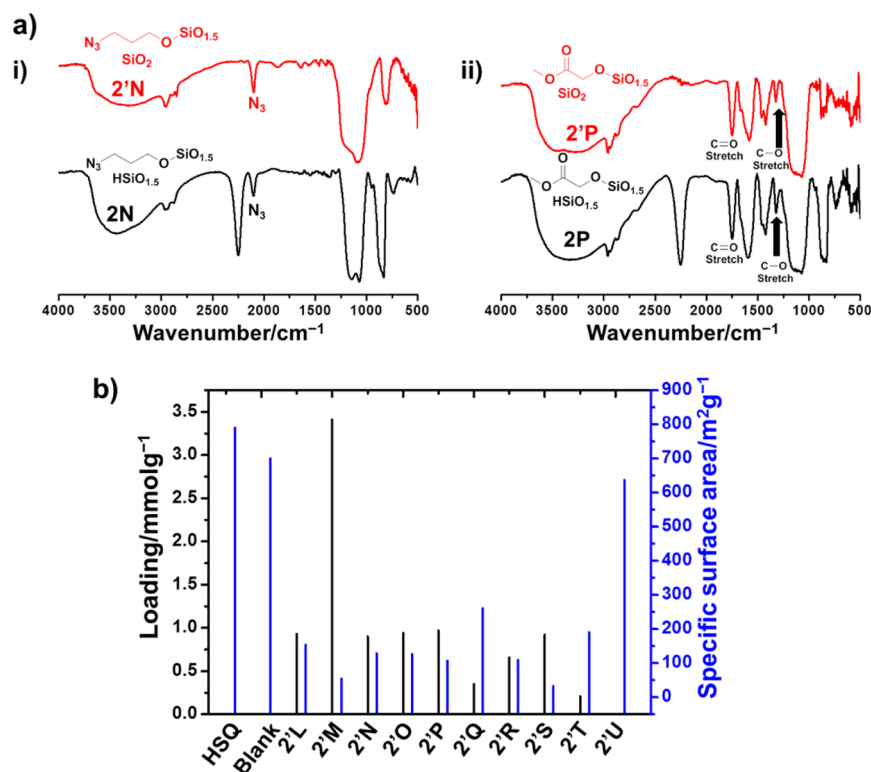
Figure 3. (a) Representative FT-IR spectra of the immobilization of 3-azido-1-propanol (**2N** after step 1 and **2′N** after step 2, in part i) and methyl glycolate (**2P** and **2′P**, in part ii) showing preservation of the functional groups after immobilization. (b) Graphical representation of the relationships between the loading amount and BET specific surface area of HSQ and the "blank" sample and final products (**2′**). The blank sample was obtained after reaction of HSQ with pure water in the presence of Zn(2-EH)₂ as a catalyst, yielding pure silica gel. The decrease in the surface area is related to the loading of alcohols in the materials; as the loading increases, the specific surface area decreases. The decrease in the specific surface area can also be attributed to the increase in specific weight and the additional condensation of as-formed silanols.

Scheme 3. Procedures for Conducting CuAAC Click Reactions on Alcohol-Immobilized Silica Surfaces
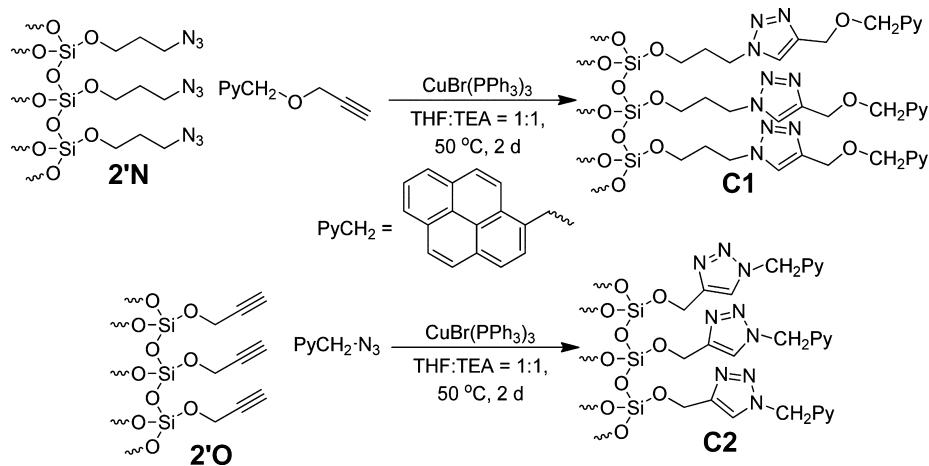
catalytic decomposition of the remaining Si—H moiety (**2′U**, see also Supporting Information S4 for FT-IR).

Thermogravimetric analysis confirms the loading of alcohols via covalent bonds and gives insight into these materials with respect to thermal stability. Weight loss upon heat treatment was observed in every case. The weight loss of these materials at temperatures up to 300 °C is mainly attributed to noncovalently adsorbed alcohol and moisture and to additional condensation in the networks. The weight loss at temperatures above 300 °C is ascribed to covalently anchored alcohols (Supporting Information S4), and the decreases are well correlated with the loading amount obtained by elemental analysis (Table 3). None of the materials shows significant weight loss at below 300 °C, indicating high thermal stability of alcohols covalently anchored via Si—O—C bonds.

Decreases in the BET specific surface area due to the blocking of meso- and micropores by organic molecules were observed in every case (Figure 3b and Supporting Information S4). The decreases in surface area are in accordance with the loading amount in the cases of **2′L**, **2′N**, **2′O**, and **2′P**. The significant decreases in surface area for **2′M** and **2′S** are attributed to the high loading and rigidity of the organic moiety,
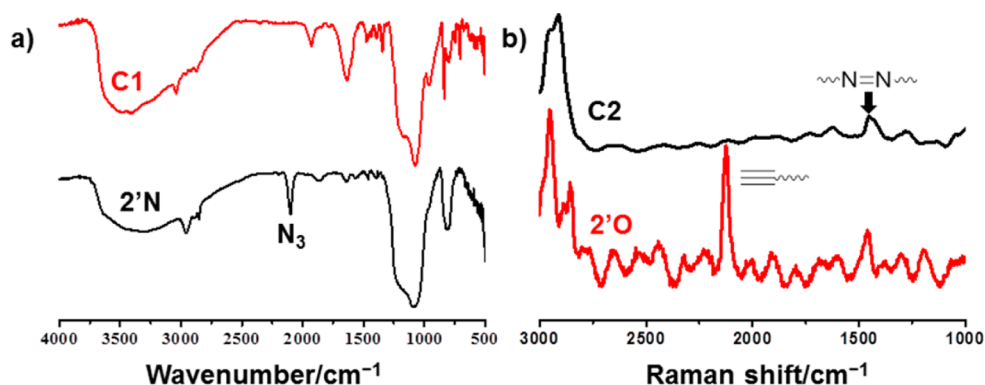
Figure 4. (a) FT-IR spectra of the azide-functionalized material (**2′N**) before and after the click reaction, demonstrating the complete conversion of the azide group and appearance of pyrene absorption after the click (**C1**). b) Raman spectra of the alkyne-functionalized material (**2′O**) before and after the click reaction, showing the disappearance of the alkyne vibration and appearance of a weak N═N vibration in the resulting triazole moiety after the click (**C2**).
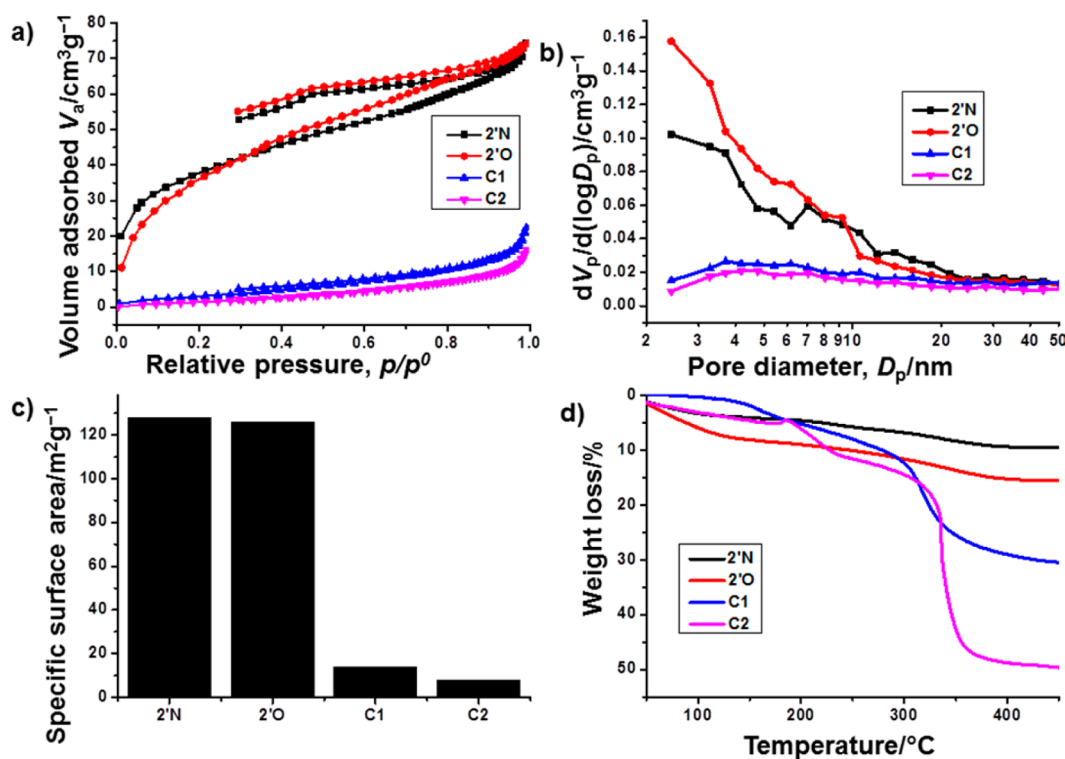

Figure 5. (a) Nitrogen adsorption−desorption isotherms of the materials before and after the click reactions. (b) BJH pore size distribution curves derived from the adsorption branch of the isotherms showing a decrease in pore sizes after the click reactions. (c) Decreases in the specific surface areas of the materials after the click reactions. (d) Thermogravimetric analysis results of the materials showing increased weight loss after the click reactions.

respectively. The relatively lower loadings in **2′Q** and **2′T** retain the high specific surface area of the original HSQ. In the case of **2′U**, no incorporation of organics and a slight decrease in surface area are observed, the latter of which may be due to siloxane bond formation by the hydrolysis and condensation reactions of Si−H in water and which is comparable to that of the blank material.

2.3. CuAAC "Click" Reaction on the Immobilized Silica Surface. The preservation of the reactivity and stability of organic fragments and the possibility of further modification of the functionalized monoliths were investigated by performing CuAAC on **2′N** and **2′O**. In general, CuAAC click reactions are carried out under aqueous conditions in the presence of CuSO$_4$ and sodium ascorbate as catalysts. Upon performance of click

reactions on **2′N** and **2′O** under aqueous conditions, however, total hydrolysis of the Si−O−C bond was observed. The low pH due to the presence of sodium ascorbate catalyzes the Si−O−C hydrolysis, and furthermore, the mildly elevated temperature (50 °C) of the reaction medium also increases the hydrolysis rate. Thus, the reaction medium for click reactions was changed from an aqueous to a nonaqueous medium. Herein, CuBr(PPh$_3$)$_3$ was employed as a catalyst and a THF and triethylamine (TEA) mixture was used as the solvent (Scheme 3). The reaction was monitored by FT-IR and Raman spectroscopy. Total conversion of azides and alkynes was observed after 2 days in the presence of 10 mol % of the catalyst at 50 °C (Figure 4).

In the case of **2′N**, the total conversion of the N_3 group was determined by FT-IR (Figure 4a), with the disappearance of the N_3 vibration band at 2098 cm^{-1} and the appearance of characteristic aromatic pyrene fragment vibrations at 1340 and 1640 cm^{-1}. The band appearing at 1930 cm^{-1} is attributed to overtones of monosubstituted pyrene. For the alkyne-functionalized monolith, Raman spectra were acquired before and after the reaction of **2′O** with 3-azido-1-propanol (Figure 4b) because an overlap of absorptions by N_3 and alkyne was expected in the case of FT-IR. In addition to the disappearance of the alkyne peak at 2125 cm^{-1}, the appearance of a weak N=N peak within the triazole ring is observed at 1460 cm^{-1}.

After the click reaction, some textural changes can be observed in the final material (**C1**, **C2**), which also confirm the success of the click reaction on the surface. With the increase in the size of the organic pendant group in the pores resulting from the click, the pore sizes are expected to decrease. In fact, the nitrogen adsorption–desorption isotherms of **2′N** and **2′O** show the presence of small meso- and micropores in the material; after the CuAAC click reaction, however, the amount of nitrogen adsorbed at each relative pressure decreased drastically, indicating that most of the pores had been filled (Figure 5a). The BJH pore size distribution curves obtained using an adsorption branch indicate the total blocking of meso- and micropores in the material after the click reaction (Figure 5b). A drastic decrease in the specific surface area was also observed after the click reaction (Figure 5c). The origin of these results lies in the inaccessibility of gaseous nitrogen in the pores and an increase in the mass of the material due to the incorporation of pyrene derivatives. Thermogravimetric analysis of **C1** and **C2** (Figure 5d) shows a higher percentage of weight loss at above 300 °C compared to the original materials before the click (**2′N**, **2′O**), moreover, indicating their stability and the incorporation of high amount of organics in the materials, which is the sole reason for the decrease in surface area and pore blocking in the resulting materials.

The fluorescence spectra of these pyrene-immobilized materials (**C1**, **C2**) give insight into the distribution of the organic functions in the materials (Figure 6). Because of the absence of any periodic porous structure in the monolith, the organic part is randomly distributed in the materials. Two distinctive emissions from both monomers and excimers were observed when they were excited at 330 nm as a result. Because of different linkage lengths between the pyrene moiety and
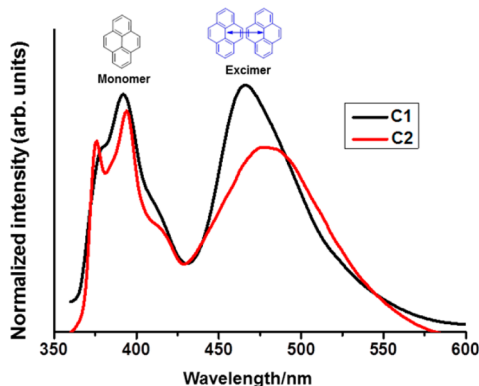
solid surface, packing and interaction of the pyrenes are slightly different between **C1** and **C2** (Scheme 3). The red-shift of excimer emission due to more proximal packing of the pyrenes has also been observed in pyrenes attached on oligonucleotides by the CuAAC click reaction.[46] In addition, since the pyrene groups are connected with the triazole unit by Py–CH$_2$–O– (**C1**) and Py–CH$_2$– (**C2**), the distribution of π electrons is somewhat different. These factors may have an impact on the excimer emissions.

In all the above cases, the cocontinuous macroporous structure of the monolith was preserved, even after several modifications of the HSQ monolith, indicating the tolerence of this HSQ monolith for modification (Supporting Information S4). These characteristics should prove important in practical usage of the present surface modification method of silica for catalytic, separation, adsorption, and optical applications.

2.4. Detachment of Functional Groups from Silica for Recycling/Reuse. The traditional functionalization of silica with silylating agent involves highly stable Si–C bonds, which are rather difficult to extract from a solid matrix for further application or reuse. Functionalization based on Si–O–C bonding is comparatively weak, however, and is theoretically prone to hydrolysis under basic and acidic conditions. In fact, decomposition of the pendent organic group was observed in the case of **2′N** (0.1 g) when subjected to acidic aqueous conditions (0.5 M HCl, 10 mL) after 5 h at room temperature. After the reaction, the recovered solid reveals no incorporation of azides in the material (Figure 7), indicating the complete
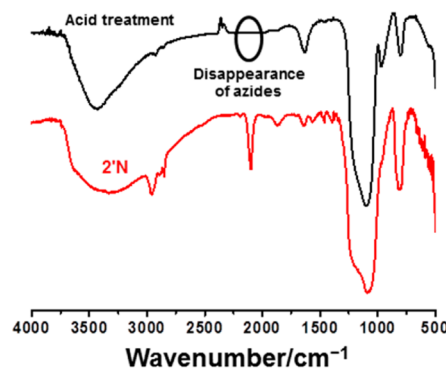
Figure 7. Demonstration of degrafting of an as-immobilized 3-azidopreopyl group in **2′N** when subjected to aqueous acidic conditions. The FT-IR spectrum of the acid-treated sample shows the disappearance of the azide stretching vibration which was present in the original **2′N**. An increase in Si–OH absorbance (940 cm^{-1}) is also observed in the acid-treated sample.

removal of alcohol and formation of pure silica gel. The organic fragment, which had initially been immobilized on the solid matrix, was fully recovered from the acid by means of extraction with ether. This reversible attachment-detachment is particularly important for the refinement and reuse of expensive organic moieties.

3. CONCLUSIONS

Herein, we have successfully demonstrated a two-step methodology for surface modification of silica based on Zn(II)-catalyzed dehydrogenative addition of organic alcohols to recently developed hydrogen silsesquioxane (HSiO$_{1.5}$, HSQ) monoliths. Organic alcohols are generally stable in air, which makes them attractive candidates for effective surface

Figure 6. Fluorescence spectra of the materials after the click reactions, revealing the presence of monomer and excimer pyrene species.

modification of silica. When starting from functionalized alkoxysilanes, which can be prepared by Lewis acid-catalyzed addition of alcohols to silanes with an Si−H moiety such as trimethoxysilane ($HSi(OCH_3)_3$, HTMS), it is fairly difficult to maintain the introduced organic functionality in the final solid product because the functional groups are also hydrolyzed during the hydrolysis−polycondensation-based sol−gel reaction. We have used an HTMS-derived HSQ material containing abundant, inherent, and highly reactive Si−H sites as a solid-state substrate for the surface modification. After the Zn(II)-catalyzed dehydrogenative addition of alcohols to HSQ and subsequent transformation into silica in water, the product contains an immobilized organic moiety with no detectable remaining Si−H. Although the removal of organic moieties from traditional class II hybrid silica is difficult due to the highly stable Si−C bond of the immobilized functionality, we succeeded in decomposing the as-formed Si−O−C bonds using an acidic or basic aqueous condition to transform them into pure silica. Facile recycling/reuse of organic alcohols is possible, which is particularly desirable for expensive organic functional materials.

In addition, preservation of the reactivity of immobilized alcohols bearing functional moieties has been successfully demonstrated using copper-catalyzed azide−alkyne cyclo-addition (CuAAC) reactions of azide- and alkyne-function-alized materials with organic molecules bearing alkynes and azides, respectively. Total conversion of azide and alkyne moieties was verified by spectroscopic analysis of the product materials.

Preservation of the well-defined macroporous structures of the parent HSQ monoliths, which continue to allow easy liquid and gas transport after several modifications, has also been verified. The present methodology of surface modification of porous monolithic materials should lead to a novel method of obtaining hybrid silica with a variety of surface functionalities and should extend its application to heterogeneous catalysts, as it is easier to separate them from reaction mixtures than their particle analogues. Extension of this methodology can be developed to construct a flow-through reaction-separation/purification system, moreover, which would offer considerable advantages for easy, effective, and ecological organic synthesis.

4. EXPERIMENTAL SECTION

Dehydrogenative addition of alcohols to monomeric HTMS: First, 2 mmol of HTMS and 2 mmol of alcohol were entered into a Schlenk tube under a nitrogen atmosphere, to which 1.8 mg of $Zn(OAc)_2$ (0.01 mmol) was added. Immediate evolution of hydrogen gas was observed, and the gas evolution stopped after 1 h. At this point, it was assumed that the reaction was complete. The mixture was then filtered under a nitrogen atmosphere to yield entitled compounds (Table 1).

Synthesis of the HSQ monolith: In a typical synthetic procedure, 1.05 g of PEO was dissolved in 25 mL of a 1:1 (by volume) mixture of 50 mM HNO_3(aq) and methanol. To this solution, 10.5 mL of HTMS was added. This mixture was stirred at room temperature for 2 min, after which the stirring was stopped and the solution was left standing at room temperature. Gelation occurred within 15 min. The resulting gel was aged at room temperature for 2 days, followed by washing with methanol and then drying at 40 °C for 2 days.

General procedure for alcohol immobilization on HSQ: Step 1: typically, 53 mg (~1 mmol) of dried HSQ monolith was soaked in 2 mL of dry THF under a nitrogen atmosphere. To this solution 1 mmol of alcohol was added, followed by the addition of 17.6 mg (0.05 mmol) of Zn(2-EH)$_2$. Instantaneous evolution of hydrogen was observed after the addition of Zn(2-EH)$_2$. The hydrogen evolution continued for 3 h, and the monolith was then removed from the

solution and washed 3 times with each of THF, *n*-hexane, and acetone. After washing, the monolith was dried under a vacuum for 2−3 h. Step 2: the resulting monolith was then soaked in 10 mL of 5 mM aqueous solution of Zn(2-EH)$_2$ and left at room temperature for 2 h. This water-treated monolith was then washed 3 times with each of THF, *n*-hexane, and acetone and dried under a vacuum for 3 h.

CuAAC "click" reaction on functionalized silica: The clickable monoliths (**2′N** and **2′O**) (0.05 mmol of clickable functional groups) were incubated with the corresponding organic counterpart (0.20 mmol) in 5 mL of 1:1 (by volume) THF/triethylamine (Et$_3$N) mixture. To this mixture, CuBr(PPh$_3$)$_3$ (46.5 mg, 0.05 mmol) was added, and the mixture was stirred for 2 days at 50 °C. The monolith was then separated and washed with ethanol and acetone (with each washing repeated 5 times). It was then solvent-exchanged with THF for 2 days (repeated 3 times) in order to eliminate all nonclicked organic parts. The resulting monolith was dried at room temperature for 3 days and recovered with no cracks.

Characterizations: The microstructures of the HSQ monolith were characterized with a scanning electron microscope (JSM-6060S, JEOL Ltd. (Japan)). The meso- and micropores present in the samples were characterized by nitrogen adsorption−desorption measurement (BELSORP-mini II, BEL Japan, Inc. (Japan)). The sample monolith was degassed at 200 °C for 6 h before nitrogen adsorption−desorption measurement. The BET method was used for surface area characterization and the BJH method on the adsorption branch for mesopore size distribution. The FT-IR spectra of the samples were recorded with a FT-IR spectrometer (FT/IR-4100, JASCO Corp. (Japan)) using ground samples that were mixed with KBr, and the Raman spectra were recorded using a confocal Raman spectrometer (Xplora, Horiba, Ltd. (Japan)). Solid-state $^1H−^{13}C/^1H−^{29}Si$ CPMAS experiments were performed in a magnetic field of 7 T using an OPENCORE NMR spectrometer and a 5 mm MAS probe. The carrier frequencies were 299.52, 75.323, and 59.507 MHz for ^1H, ^{13}C, and ^{29}Si, respectively. The contact times and spinning frequencies were 10 ms and 5 kHz for ^{29}Si and 1 ms and 8 kHz for ^{13}C, respectively. Liquid-state ^1H and ^{13}C NMR measurements were performed using an ECX-400 spectrometer (JEOL Ltd. (Japan)) in CDCl$_3$. Thermogravimery−differential thermal analysis (TG-DTA) measurements were performed with a Thermo plus EVO (Rigaku Corp. (Japan)) at a heating rate of 5 °C min^{-1} with air supplied continuously at 100 mL min^{-1}. Elemental analyses were performed at the Center for Organic Elemental Microanalysis of Kyoto University using YANACO MT-3 and MT-6 analyzers. Fluorescence spectra were obtained using an FP-6200 fluorometer (JASCO Corp. (Japan)). Emission spectra were recorded with an excitation wavelength of 330 nm. The samples were ground and dispersed in methanol before each measurement.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H, ^{13}C liquid-state NMR, characterization of HSQ monolith, FT-IR, Raman, nitrogen adsorption−desorption, and thermal and microscopic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: kanamori@kuchem.kyoto-u.ac.jp, Fax +81-75-753-7673.
*E-mail: kazuki@kuchem.kyoto-u.ac.jp, Fax +81-75-753-2925.
*E-mail: shimada@chem.nara-k.ac.jp, Fax +81-743-55-6154.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

(ALCA) from the Japan Science and Technology Agency (JST).

■ ABBREVIATIONS

THF, tetrahydrofuran; BET, Brunauer−Emmett−Teller; BJH, Barrett−Joyner−Halenda; FT-IR, Fourier transform infrared spectroscopy; NMR, nuclear magnetic resonance.

■ REFERENCES

(1) Zamboulis, A.; Moitra, N.; Moreau, J. J. E.; Cattoen, X.; Man, M. W. C. Hybrid materials: versatile matrices for supporting homogeneous catalysts. *J. Mater. Chem.* **2010**, *20*, 9322−9338.

(2) Coti, K. K.; Belowich, M. E.; Liong, M.; Ambrogio, M. W.; Lau, Y. A.; Khatib, H. A.; Zink, J. I.; Khashab, N. M.; Stoddart, J. F. Mechanised nanoparticles for drug delivery. *Nanoscale* **2009**, *1*, 16−39.

(3) Carlos, L. D.; Ferreira, R. A. S.; Bermudez, V. d. Z.; Ribeiro, S. J. L. Lanthanide-containing light-emitting organic-inorganic hybrids: A bet on the future. *Adv. Mater.* **2009**, *21*, 509−534.

(4) Corriu, R. J. P.; Leclercq, D. Recent developments of molecular chemistry for sol-gel processes. *Angew. Chem., Int. Ed.* **1996**, *35*, 1420−1436.

(5) Kapoor, M. P.; Inagaki, S.; Ikeda, S.; Kakiuchi, K.; Suda, M.; Shimada, T. An alternate route for the synthesis of hybrid mesoporous organosilica with crystal-like pore walls from allylorganosilane precursors. *J. Am. Chem. Soc.* **2005**, *127*, 8174−8178.

(6) Hoffmann, F.; Cornelius, M.; Morell, J.; Froba, M. Silica-based mesoporous organic-inorganic hybrid materials. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216−3251.

(7) Aoki, K.; Shimada, T.; Hayashi, T. Immobilization of chiral phosphine ligands on silica gel by means of the allylsilane method and their use for catalytic asymmetric reactions. *Tetrahedron: Asymmetry* **2004**, *15*, 1771−1777.

(8) Fukaya, N.; Haga, H.; Tsuchimoto, T.; Onozawa, S.-y.; Sakakura, T.; Yasuda, H. Organic functionalization of the surface of silica with arylsilanes. A new method for synthesizing organic-inorganic hybrid materials. *J. Organomet. Chem.* **2010**, *695*, 2540−2542.

(9) Shimada, T.; Aoki, K.; Shinoda, Y.; Nakamura, T.; Tokunaga, N.; Inagaki, S.; Hayashi, T. Functionalization on silica gel with allylsilanes. A new method of covalent attachment of organic functional groups on silica gel. *J. Am. Chem. Soc.* **2003**, *125*, 4688−4689.

(10) Yeon, Y.-R.; Park, Y. J.; Lee, J.-S.; Park, J.-W.; Kang, S.-G.; Jun, C.-H. Sc(OTf)₃-mediated silylation of hydroxy functional groups on a solid surface: A catalytic grafting method operating at room temperature. *Angew. Chem., Int. Ed.* **2008**, *47*, 109−112.

(11) Park, J.-W.; Jun, C.-H. Transition-metal-catalyzed immobilization of organic functional groups onto solid supports through vinylsilane coupling reactions. *J. Am. Chem. Soc.* **2010**, *132*, 7268−7269.

(12) Brethon, A.; Hesemann, P.; Rejaud, L.; Moreau, J. J. E.; Man, M. W. C. Functional chiral hybrid silica gels prepared from (R)- or (S)-binaphthol derivatives. *J. Organomet. Chem.* **2001**, *627*, 239−248.

(13) Mizoshita, N.; Goto, Y.; Maegawa, Y.; Tani, T.; Inagaki, S. Tetraphenylpyrene-bridged periodic mesostructured organosilica films with efficient visible-light emission. *Chem. Mater.* **2010**, *22*, 2548−2554.

(14) Moreau, J. J. E.; Vellutini, L.; Man, M. W. C.; Bied, C.; Dieudonne, P.; Bantignies, J. L.; Sauvajol, J. L. Lamellar bridged silsesquioxanes: Self-assembly through a combination of hydrogen bonding and hydrophobic-interactions. *Chem.—Eur. J.* **2005**, *11*, 1527−1537.

(15) Nguyen, T. P.; Hesemann, P.; Tran, T. M. L.; Moreau, J. J. E. Nanostructured polysilsesquioxanes bearing amine and ammonium groups by micelle templating using anionic surfactants. *J. Mater. Chem.* **2010**, *20*, 3910−3917.

(16) Moitra, N.; Moreau, J. J. E.; Cattoen, X.; Man, M. W. C. Convenient route to water-sensitive sol-gel precursors using click chemistry. *Chem. Commun.* **2010**, *46*, 8416−8418.

(17) Burglova, K.; Moitra, N.; Hodacova, J.; Cattoen, X.; Man, M. W. C. Click approaches to functional water-sensitive organotriethoxysilanes. *J. Org. Chem.* **2011**, *76*, 7326−7333.

(18) Yan, J. C.; Wang, L. Asymmetric Aldol reactions catalyzed by efficient and recyclable silica-supported proline-based peptides. *Chirality* **2009**, *21*, 413−420.

(19) Maishal, T. K.; Alauzun, J.; Basset, J. M.; Coperet, C.; Corriu, R. J. P.; Jeanneau, E.; Mehdi, A.; Reye, C.; Veyre, L.; Thieuleux, C. A Tailored organometallic-inorganic hybrid mesostructured material: A route to a well-defined, active, and reusable heterogeneous iridium-NHC catalyst for H/D exchange. *Angew. Chem., Int. Ed.* **2008**, *47*, 8654−8656.

(20) Nakazawa, J.; Stack, T. D. P. Controlled loadings in a mesoporous material: click-on silica. *J. Am. Chem. Soc.* **2008**, *130*, 14360−14361.

(21) Malvi, B.; Sarkar, B. R.; Pati, D.; Mathew, R.; Ajithkumar, T. G.; Sen Gupta, S. "Clickable" SBA-15 mesoporous materials: synthesis, characterization and their reaction with alkynes. *J. Mater. Chem.* **2009**, *19*, 1409−1416.

(22) Moitra, N.; Trens, P.; Raehm, L.; Durand, J. O.; Cattoen, X.; Man, M. W. C. Facile route to functionalized mesoporous silica nanoparticles by click chemistry. *J. Mater. Chem.* **2011**, *21*, 13476−13482.

(23) Yu, P.; He, J.; Guo, C. X. 9-Thiourea Cinchona alkaloid supported on mesoporous silica as a highly enantioselective, recyclable heterogeneous asymmetric catalyst. *Chem. Commun.* **2008**, 2355−2357.

(24) Pini, D.; Mandoli, A.; Orlandi, S.; Salvadori, P. First example of a silica gel-supported optically active Mn(III)-salen complex as a heterogeneous asymmetric catalyst in the epoxidation of olefins. *Tetrahedron: Asymmetry* **1999**, *10*, 3883−3886.

(25) Yu, K.; Gu, Z.; Ji, R.; Lou, L.-L.; Liu, S. Heterogeneous chiral Mn(III) salen catalysts for the epoxidation of unfunctionalized olefins immobilized on mesoporous materials with different pore sizes. *Tetrahedron* **2009**, *65*, 305−311.

(26) Fabre, B. Ferrocene-terminated monolayers covalently bound to hydrogen-terminated silicon surfaces. Toward the development of charge storage and communication devices. *Acc. Chem. Res.* **2010**, *43*, 1509−1518.

(27) Ciampi, S.; Boecking, T.; Kilian, K. A.; James, M.; Harper, J. B.; Gooding, J. J. Functionalization of acetylene-terminated monolayers on Si(100) surfaces: A click chemistry approach. *Langmuir* **2007**, *23*, 9320−9329.

(28) Cummings, S. P.; Savchenko, J.; Ren, T. Functionalization of flat Si surfaces with inorganic compounds-Towards molecular CMOS hybrid devices. *Coord. Chem. Rev.* **2011**, *255*, 1587−1602.

(29) Bocking, T.; James, M.; Coster, H. G. L.; Chilcott, T. C.; Barrow, K. D. Structural characterization of organic multilayers on silicon(111) formed by immobilization of molecular films on functionalized Si-C linked monolayers. *Langmuir* **2004**, *20*, 9227−9235.

(30) Tian, F.; Teplyakov, A. V. Silicon surface functionalization targeting Si-N linkages. *Langmuir* **2013**, *29*, 13−28.

(31) Boukherroub, R.; Morin, S.; Sharpe, P.; Wayner, D. D. M.; Allongue, P. Insights into the formation mechanisms of Si-OR monolayers from the thermal reactions of alcohols and aldehydes with Si(111)-H. *Langmuir* **2000**, *16*, 7429−7434.

(32) Sieval, A. B.; Linke, R.; Heij, G.; Meijer, G.; Zuilhof, H.; Sudholter, E. J. R. Amino-terminated organic monolayers on hydrogen-terminated silicon surfaces. *Langmuir* **2001**, *17*, 7554−7559.

(33) Cecchet, F.; De Meersman, B.; Demoustier-Champagne, S.; Nysten, B.; Jonas, A. M. One step growth of protein antifouling surfaces: Monolayers of poly(ethylene oxide) (PEO) derivatives on oxidized and hydrogen-passivated silicon surfaces. *Langmuir* **2006**, *22*, 1173−1181.

(34) Ciampi, S.; Harper, J. B.; Gooding, J. J. Wet chemical routes to the assembly of organic monolayers on silicon surfaces via the formation of Si-C bonds: surface preparation, passivation and functionalization. *Chem. Soc. Rev.* **2010**, *39*, 2158−2183.

(35) Sattler, W.; Parkin, G. Zinc catalysts for on-demand hydrogen generation and carbon dioxide functionalization. *J. Am. Chem. Soc.* **2012**, *134*, 17462−17465.

(36) Mimoun, H. Selective reduction of carbonyl compounds by polymethylhydrosiloxane in the presence of metal hydride catalysts. *J. Org. Chem.* **1999**, *64*, 2582−2589.

(37) Chauhan, B. P. S.; Rathore, J. S.; Chauhan, M.; Krawicz, A. Synthesis of polysiloxane stabilized palladium colloids and evidence of their participation in silaesterification reactions. *J. Am. Chem. Soc.* **2003**, *125*, 2876−2877.

(38) Xie, Z. Y.; Henderson, E. J.; Dag, O.; Wang, W.; Lofgreen, J. E.; Kubel, C.; Scherer, T.; Brodersen, P. M.; Gu, Z. Z.; Ozin, G. A. Periodic mesoporous hydridosilica - synthesis of an "impossible" material and its thermal transformation into brightly photoluminescent periodic mesoporous nanocrystal silicon-silica composite. *J. Am. Chem. Soc.* **2011**, *133*, 5094−5102.

(39) Moitra, N.; Kanamori, K.; Shimada, T.; Takeda, K.; Ikuhara, Y. H.; Gao, X.; Nakanishi, K. Synthesis of hierarchically porous hydrogen silsesquioxane monoliths and embedding of metal nanoparticles by on-site reduction. *Adv. Funct. Mater.* **2013**, *23*, 2714−2722.

(40) Sano, H.; Maeda, H.; Ichii, T.; Murase, K.; Noda, K.; Matsushige, K.; Sugimura, H. Alkyl and alkoxyl monolayers directly attached to silicon: Chemical durability in aqueous solutions. *Langmuir* **2009**, *25*, 5516−5525.

(41) Loy, D. A.; Baugher, B. M.; Baugher, C. R.; Schneider, D. A.; Rahimian, K. Substituent effects on the sol-gel chemistry of organotrialkoxysilanes. *Chem. Mater.* **2000**, *12*, 3624−3632.

(42) Hook, R. J. A Si-29 NMR study of the sol-gel polymerisation rates of substituted ethoxysilanes. *J. Non-Cryst. Solids* **1996**, *195*, 1−15.

(43) Sakai, N.; Moriya, T.; Konakahara, T. An efficient one-pot synthesis of unsymmetrical ethers: A directly reductive deoxygenation of esters using an InBr$_3$/Et$_3$SiH catalytic system. *J. Org. Chem.* **2007**, *72*, 5920−5922.

(44) Eves, B. J.; Fan, C.; Lopinski, G. P. Sequential reactions with amine-terminated monolayers and isolated molecules on H/Si(111). *Small* **2006**, *2*, 1379−1384.

(45) Addis, D.; Das, S.; Junge, K.; Beller, M. Selective reduction of carboxylic acid derivatives by catalytic hydrosilylation. *Angew. Chem., Int. Ed.* **2011**, *50*, 6004−6011.

(46) Kumar, P.; Shaikh, K. I.; Jørgensen, A. S.; Kumar, S.; Nielsen, P. *J. Org. Chem.* **2012**, *77*, 9562−9573.