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COMMUNICATION

Efficient Mukaiyama Aldol Reaction in Water with TiO₄ Tetrahedra on Hydrophobic Mesoporous Silica Surface

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AcceptedHiroshi Shintaku,^a Kiyotaka Nakajima,^{a,b} Masaaki Kitano^c and Michikazu Hara^{*a,d}

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A new heterogeneous catalyst, hydrophobic TiO₄-deposited mesoporous silica, has been designed for the efficient Mukaiyama-aldol condensation, a water-participating Lewis acid-catalyzed reaction between hydrophobic carbonyl compound and silyl enol ether. Prepared catalyst suspended in water exhibited high catalytic performance as a reusable catalyst for the reaction without a surfactant.

The Mukaiyama-aldol condensation is an essential reaction for the chemoselective synthesis of β -hydroxycarbonyl compounds, and adopts stable and isolable enol ethers as enolizable carbonyl compounds.¹ Enol ethers with at least one acidic hydrogen atom in the α -position act as nucleophiles and react with activated carbonyl compounds (aldehydes or ketones) in the presence of a Lewis acid/base.^{1,2} A variety of homogeneous and heterogeneous catalysts have been investigated for this reaction.¹⁻³ Kobayashi et al. reported that some metal triflates, such as Sc(OTf)₃, can act as Lewis acids in water to promote the Mukaiyama-aldol reaction of silyl enol ethers with aldehydes and ketones in an organic solvent-water mixture or pure water containing an appropriate surfactant.⁴ However, the low solubility of the hydrophobic reactant in pure water necessitates the addition of large amounts of surfactant to enhance the accessibility of hydrophobic reactant molecules to the homogeneous Lewis acid in solution. It has already been reported that resins used to immobilize metal triflates can function as heterogeneous Lewis acid catalysts that are workable even in water,⁵ and homogeneous catalysts composed of Lewis acids and surfactants are effective for reactions of hydrophobic molecules in water.^{4b,c} However, heterogeneous catalysts available for the reaction without surfactants have not been devised to date. Any heterogeneous Lewis acid catalysts derived from ubiquitous, abundant starting materials that efficiently promote such a reaction in water without the addition of surfactants would be applicable to the environmentally benign production of various chemicals on a large scale.

Recently, some unsaturated metal species, such as Sn,^{6a-e} Zr,^{6e,f} Ta,^{6e,f} Nb,^{6e,f,g} and Ti,^{6e,h,i} formed on oxide surfaces have been reported to act as water-tolerant Lewis acid sites to promote various organic reactions in water or organic solvent-water mixtures. We have reported that unsaturated titanium species, tetrahedral TiO₄, formed on mesoporous silica are active Lewis acid sites for the

Mukaiyama-aldol reaction of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene in a water-surfactant system.⁶ⁱ The mesoporous structure of TiO₄-deposited mesoporous silica (TDMS) effectively enhances the access of reactant molecules to TiO₄ Lewis acid sites which exhibit high catalytic activity for the reaction, comparable to that of Sc(OTf)₃. However, sodium dodecyl sulfate (SDS) is necessary in the reaction system to disperse the hydrophobic substrates in water: both Sc(OTf)₃ and TDMS have poor catalytic activity for the reaction in the absence of SDS. Here, the introduction of various hydrophobic organic functional groups was examined on TDMS to realize a surfactant-free aqueous reaction system for the reaction.

TDMS was prepared by a simple impregnation procedure with titanium isopropoxide and acetylacetone (see ESI†).^{6i,7} The catalytic activity of TDMS depends largely on Ti content.⁶ⁱ In this study, TDMS (Ti/Si=0.018) was adopted because it exhibits high catalytic performance for the Mukaiyama-aldol reaction in SDS-water system among tested TDMS samples.⁶ⁱ The density of TiO₄ tetrahedra on the TDMS was estimated to be 0.44 TiO₄ nm⁻² which is smaller than monolayer coverage. Surface modification with hydrophobic organic groups bonded to TDMS through surface silanol groups was conducted using (CH₃(CH₂)₂Si(OCH₃)₃) (propyltrimethoxysilane; Propyl), CH₃(CH₂)₁₁Si(OCH₃)₃ (dodecyltrimethoxysilane; Dodecyl), C₆H₅CH₂Si(OCH₃)₃ (benzyltrimethoxysilane, Benzyl), and CF₃(CF₂)₅(CH₂)₂Si(OCH₃)₃ ((1H,1H,2H,2H-tridecafluoro-n-octyl)trichlorosilane, Tridecafluoro) (see ESI†). The TDMS samples with propyl, benzyl, dodecyl, and tridecafluoro-n-octyl groups are denoted as Propyl-TDMS, Benzyl-TDMS, Dodecyl-TDMS, and Tridecafluoro-TDMS, respectively.

Figure S1 shows small and wide angle X-ray diffraction (XRD) patterns of the samples. All samples have three intense peaks at around 0.9, 1.5, and 1.8° in the small angle region (Figure S1(A)), which are assignable to (100), (110), and (200) diffractions, respectively, of a two-dimensional hexagonal (*P6mm*) symmetry structure.^{6i,7,8} No diffractions were observed in the large angle region (Figure S1(B)), which indicates the absence of large crystalline TiO₂ domains on mesoporous silica. N₂ adsorption-desorption measurements of the samples in Figure S2 show typical type-IV isotherms with an H1-type hysteresis loop that is characteristic of a mesoporous solid with uniform and cylindrical mesopores.^{6i,7,8} Immobilization of organic functional groups (ca. 0.3 nm⁻² for each

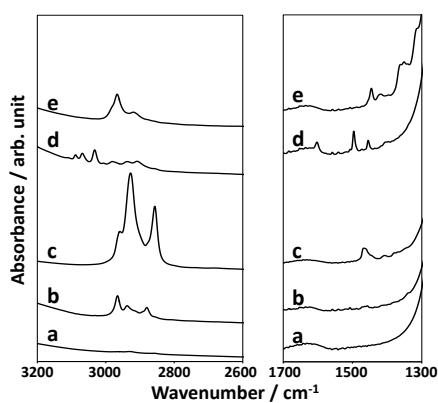


Figure 1. FTIR spectra for (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS.

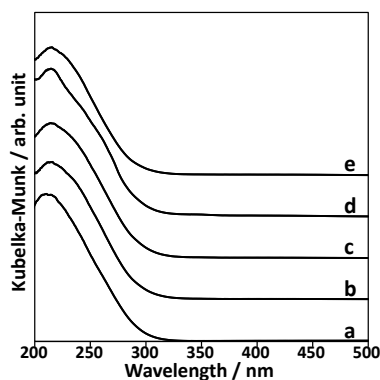


Figure 2. UV-Vis DRS spectra for (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS.

sample) on a mesoporous surface results in a slight decrease in the original Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore size (Table S1). There is no significant differences in the XRD patterns and N_2 adsorption isotherms between the bare and modified TDMS samples, which suggests that the original mesoporosity and periodic mesoporous structure remain intact even after the introduction of various organic functionalities by a simple surface modification technique.

TDMS samples were also evaluated using Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of the modified TDMS samples are shown in Figure 1. Prior to measurement, the samples were heated at 473 K for 1 h to remove physisorbed water. Propyl and Dodecyl-TDMS have several bands for the CH stretching mode ($2820\text{--}3000\text{ cm}^{-1}$) and one band for the CH asymmetric bending mode (1465 cm^{-1}) that are due to methylene and methyl moieties of the propyl and dodecyl groups on the silica surface (Figures 1(b) and 1(c)). Benzyl-TDMS has specific bands for the methylene group (several bands at $2820\text{--}3000\text{ cm}^{-1}$: CH stretching mode) and benzene ring (several bands at $3000\text{--}3095\text{ cm}^{-1}$: CH stretching mode, three bands at 1605 , 1495 , and 1453 cm^{-1} : C=C stretching mode), which indicates the successful introduction of the benzyl group onto the silica surface. A CF stretching band at 1350 cm^{-1} is observed as a shoulder peak for Tridecafluoro-TDMS, in addition to bands for the CH stretching ($2820\text{--}3000\text{ cm}^{-1}$) and bending (1445 cm^{-1}) modes. These results clearly indicate that certain amounts of organic functional groups are successfully embedded on the silica surface. The densities of organic functional groups for Propyl-, Dodecyl-, Benzyl-, and Tridecafluoro-TDMS were estimated to be 0.28 , 0.32 , 0.31 , and 0.33 nm^{-2} , respectively (Table S1), from BET surface area measurements and CHNS elemental analysis. The modified TDMS

samples still have large amounts of silanol group on the surface, due to low organic functional group densities.

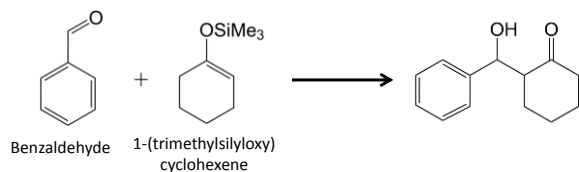
The coordination environment of the titanium species was investigated using ultraviolet-visible diffusive reflectance spectroscopy (UV-Vis DRS).^{6i,7,9} Figure 2 shows UV-Vis DRS spectra for the TDMS samples. TDMS has a narrow absorption band centered at ca. 210 nm, which is assigned to the charge transfer of isolated TiO_4 tetrahedra on the silica framework. The surface-modified TDMS samples also have a similar absorption band, which indicates that TiO_4 tetrahedra on the silica surface remain intact after surface modification, i.e., the introduction of hydrophobic groups onto TDMS does not affect the TiO_4 Lewis acid sites. In the case of Benzyl-TDMS, a shoulder band also appears at around 250 nm, which is attributed to the $\pi\rightarrow\pi^*$ transition of the benzene ring. As a result, TiO_4 tetrahedra on the modified TDMS are expected to function as Lewis acid sites in water.⁶ⁱ

The Lewis acidity of the modified TDMS samples was examined using CO adsorption measurements with FTIR spectroscopy. Figure S3 shows difference FTIR spectra for the CO adsorbed TDMS samples. Prior to measurement, the samples were exposed to saturated water vapor to introduce an excess amount of physisorbed water onto the surface. All modified samples have a band at 2182 cm^{-1} due to CO coordinated on Lewis acid sites.⁶ⁱ This band is not present in the spectrum for bare mesoporous silica (SBA-15) without TiO_4 deposition, which indicates that the TiO_4 tetrahedra function as Lewis acid sites and bond to CO even in the presence of water.

The Lewis acid site densities for the samples were estimated from NH_3 temperature-programmed desorption (TPD) measurements. There were no significant differences in the effective Lewis acid densities of TDMS and the modified TDMS samples (Table S1). Therefore, water-tolerant Lewis acid sites on TDMS are considered to be preserved, even after the introduction of various organic functional groups.

The TDMS samples were applied as catalysts to the Mukaiyama-aldol condensation of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene in water in the absence of a surfactant. The catalytic activities of the tested catalysts are summarized in Table 1. HCl, a homogeneous liquid acid does not catalyze the reaction at all due to rapid hydrolysis of 1-(trimethylsilyloxy)cyclohexene by the Brønsted acid. $Sc(OTf)_3$ has a high catalytic activity for the reaction in the presence of sodium dodecyl sulfate (SDS) as a surfactant, and the yield of 2-(hydroxy(phenyl)methyl)cyclohexanone reaches 83% after 2 h. However, $Sc(OTf)_3$ is not an effective catalyst for the reaction without SDS, as shown in Table 1. TDMS without surface modification also has high catalytic activity in the presence of SDS with a product yield comparable to that for $Sc(OTf)_3$. However, the catalytic activity of TDMS in the absence of SDS is significantly decreased in the same manner as that for $Sc(OTf)_3$ without SDS. Propyl- and Benzyl-TDMS have similar catalytic activity to bare TDMS, whereas Dodecyl- and Tridecafluoro-TDMS work as effective catalysts for the reaction, even in the absence of SDS. In particular, Tridecafluoro-TDMS has the highest catalytic performance without SDS among the tested catalysts. After the reaction, the TDMS catalysts could be readily separated from the reaction solution by filtration. The results of catalyst reuse experiment for Tridecafluoro-TDMS are presented in Figure S4. No decrease in activity was observed even after two reuses of the sample, and it was confirmed that there was no elution of Ti species or hydrophobic functional groups from TDMS. Therefore, Tridecafluoro-TDMS is a stable, reusable, and highly active solid Lewis acid catalyst for SDS-free Mukaiyama-aldol condensation.

Table 1 Catalytic activities of the TDMS samples and reference catalysts for the Mukaiyama-aldol reaction of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene in water



Catalyst	Lewis acid site density ^a / mmol g ⁻¹	Yield ^b (%)
1 mol/L HCl	-	0
Sc(OTf) ₃	2.0	19
Sc(OTf) ₃ -SDS ^c	2.0	83
TDMS	0.16	7
TDMS-SDS ^c	0.16	87
Propyl-TDMS	0.17	3
Dodecyl-TDMS	0.16	35
Benzyl-TDMS	0.16	3
Tridecafluoro-TDMS	0.17	85

Reagents and conditions: benzaldehyde, 0.4 mmol; 1-(trimethylsilyloxy)cyclohexene, 0.6 mmol; water, 3 mL; catalyst, 0.1 g; temperature, 298 K; time, 2 h. ^a Determined by NH₃-TPD measurement. ^b Syn/anti ratio for all tested catalysts was estimated to be ca. 7/3. ^c Reaction in the presence of SDS (0.023 g).

While both Dodecyl and Tridecafluoro-TDMS samples have hydrophobic surfaces that are suitable for adsorption of hydrophobic reactant in water, Tridecafluoro-TDMS shows higher catalytic performance for the SDS-free reaction system than Dodecyl-TDMS (Table 1). It was confirmed that this difference in activity between Dodecyl and Tridecafluoro-TDMS remains unaltered even when the density of dodecyl groups is increased. Dodecyl-TDMS with a higher density of dodecyl groups (0.44 nm⁻²) gave a yield of 44%. Although this value is larger than that (35%) of Dodecyl-TDMS in Table 1 (dodecyl density: 0.32 nm⁻²), Dodecyl-TDMS sample is still inferior to Tridecafluoro-TDMS (0.33 nm⁻²) in activity.

The prepared TDMS catalysts can be classified into two groups with respect to the catalytic activity of the SDS-free system; Dodecyl- and Tridecafluoro-TDMS are distinct from bare, Propyl-, and Benzyl-TDMS. The high catalytic performance of the former SDS-free systems can be attributed to the hydrophobic organic layer formed on the silica surface, which enhances the accessibility of hydrophobic reactants to the TiO₄ Lewis acid sites. The hydrophobicity and hydrophilicity of the TDMS samples were examined using a simple method. Figure 3 shows a photograph of the TDMS samples suspended in a water-benzene (1:1 vol%) mixture. Most of the Propyl-, and Benzyl-TDMS particles are present in the lower water phase. In contrast, the Dodecyl- and Tridecafluoro-TDMS particles are observed in the upper benzene phase, which indicates that Dodecyl- and Tridecafluoro-TDMS are more hydrophobic than the other TDMS samples. Water vapor adsorption-desorption isotherms were measured to determine the hydrophobic characteristics of the TDMS samples and the results are shown in Figure S5. In the case of the SBA-15 silica support, the adsorption of water vapor starts at P/P₀=0.78. Although water adsorption on bare, Propyl-, and Benzyl-TDMS is accelerated at ca. P/P₀=0.78, steep water uptake is not observed up to P/P₀=0.85 in Dodecyl-

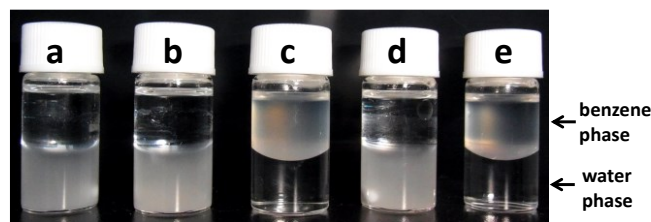


Figure 3. Photograph of TDMS samples dispersed in water-benzene (1:1 vol%) solution. (a) TDMS, (b) Propyl-TDMS, (c) Dodecyl-TDMS, (d) Benzyl-TDMS, and (e) Tridecafluoro-TDMS.

and Tridecafluoro-TDMS. The large shift in P/P₀ indicates that Dodecyl- and Tridecafluoro-TDMS are more hydrophobic than bare, Propyl-, and Benzyl-TDMS, which results in the higher catalytic activity of Dodecyl- and Tridecafluoro-TDMS. Both TiO₄ Lewis acid sites and SBA-15 as a support are primarily hydrophilic materials because of Lewis acidity and silanol groups. As a result, strong hydrophobic functional groups such as dodecyl and tridecafluoro groups are required to enhance the hydrophobicity of TDMS. The difference in catalytic performance between Dodecyl-TDMS and Tridecafluoro-TDMS can be also attributed to surface hydrophobicity. Figure S6 shows a photograph of the Dodecyl- and Tridecafluoro-TDMS suspended in a water-ethanol (4:1 vol%) mixture. Although most of Tridecafluoro-TDMS particles float on the liquid level, Dodecyl-TDMS particles were dispersed in the solution, suggesting that Tridecafluoro-TDMS is more hydrophobic than Dodecyl-TDMS. It has been reported that fluorocarbon moiety is more hydrophobic than normal hydrocarbon chains such as dodecyl group.¹⁰

It should be noted that water is essential for the Mukaiyama-aldol condensation of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene.^{5a,11} This reaction is regarded as a Lewis acid-catalyzed reaction of hydrophobic molecules requiring water and is therefore largely enhanced by the addition of a surfactant. Table S2 shows the catalytic activities of bare dehydrated TDMS for the Mukaiyama-aldol condensation at 1 h conducted in various solvents. The SDS-water system is the most suitable for the reaction. While hydrophobic reactants are readily dissolved in polar (tetrahydrofuran and acetonitrile), nonpolar (dichloromethane and toluene), and protonic (ethanol) solvents, bare TDMS has only moderate catalytic activity in these solvents. The effect of water in the Mukaiyama-aldol reaction was further examined through the reaction for bare TDMS in various aqueous THF solutions. The results are shown in Figure S7. Bare TDMS shows no catalysis in pure THF without water. However, the product yield increases with increasing water content, reaching a maximum at 17 vol%. Further increase of water content decreases product yield, due to phase separation: hydrophilic TDMS and hydrophobic reactants are preferentially dispersed in water and THF phase, respectively, which prevent access of reactant molecules with TiO₄ tetrahedra on TDMS. This means that a certain amount of water is indispensable for the efficient Mukaiyama-aldol reaction. Recently, Hatanaka et al. reported that water molecules contribute largely to the stabilization of a transition state formed between activated aldehyde with a Lewis acid and silyl enol ether and the dissociation of trimethylsilyl groups, which results in an increase of the overall reaction rate.¹² Reactions of hydrophobic molecules that require water, in addition to the Mukaiyama-aldol condensation, have often been reported, and such reactions increase in importance.¹³ Lewis acids that are workable in the presence of water and surfactants are indispensable for such reactions. The

results presented in this study suggest that heterogeneous catalysts prepared from abundant and ubiquitous starting materials could be applied to such complex reactions.

In conclusion, TDMS catalysts modified with various organic functional groups were investigated as a new type of heterogeneous catalyst for efficient Mukaiyama-aldol condensation of benzaldehyde with 1-(trimethylsilyloxy)cyclohexene. The introduction of dodecyl- and tridecafluoro-groups onto TDMS induced strong hydrophobicity to the material, which resulted in high catalytic activity for the reaction without the addition of SDS as a surfactant. For Tridecafluoro-TDMS, the yield of 2-(hydroxy(phenyl)methyl)cyclohexanone reached 85% after 2 h, even without SDS, which is comparable to that for bare TDMS and Sc(OTf)₃ with SDS. The high catalytic performance of hydrophobic TDMS can be attributed to both TiO₄ tetrahedra Lewis acid sites that are workable in water and a highly hydrophobic organic layer that facilitates access of the reactant and water molecules to the Lewis acid sites.

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Notes and references

^a *Materials and Structures Laboratory, Tokyo Institute of Technology, 4259-R3-33 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.*

E-mail: mhara@mssl.titech.ac.jp

^b *Japan Science and Technology (JST) agency, PRESTO, 4-1-8 Honcho, Kawaguchi 332-0012, Japan.*

^c *Materials Research Center for Elemental Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.*

^d *Japan Science and Technology (JST) agency, ALCA, 4-1-8 Honcho, Kawaguchi 332-0012, Japan.*

† Electronic Supplementary Information (ESI) available: Experimental details, physicochemical properties, catalytic activities for the Mukaiyama-aldol reaction in various solvents, XRD patterns, N₂ adsorption-desorption isotherms, CO adsorption FT-IR spectra, catalyst reuse experiment, H₂O adsorption isotherms, Photograph of Dodecyl and Tridecafluoro-TDMS suspended in ethanol-water mixture, Effect of H₂O for the Mukaiyama-aldol reaction in organic solvent. See DOI: 10.1039/c000000x/

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