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An Immobilized Organocatalyst for Cyanosilylation and Epoxidation

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Abstract: An immobilized organocatalyst has been synthesized by covalently anchoring an *N*-octyldihydroimidazolium hydroxide fragment onto SiO_2 (denoted as **1**-OH/SiO_2). This catalyst exhibits high catalytic performance for the cyanosilylation of various carbonyl compounds with trimethylsilyl cyanide (Me_3SiCN). The effectiveness of the system is evidenced by the high to excellent yields of the corresponding trimethylsilyl ethers under mild reaction conditions, which are superior to those obtained with commercially available MgO and anion exchange resins. This catalyst also acts as a heterogeneous catalyst for the epoxidation of electron-deficient olefins with hydrogen peroxide. Further, the catalyst/product(s) separation can be easily carried out by the simple filtration (or centrifugation) and the reaction is immediately stopped by the removal of the solid catalyst, suggesting that the nature of the observed catalysis is truly heterogeneous.

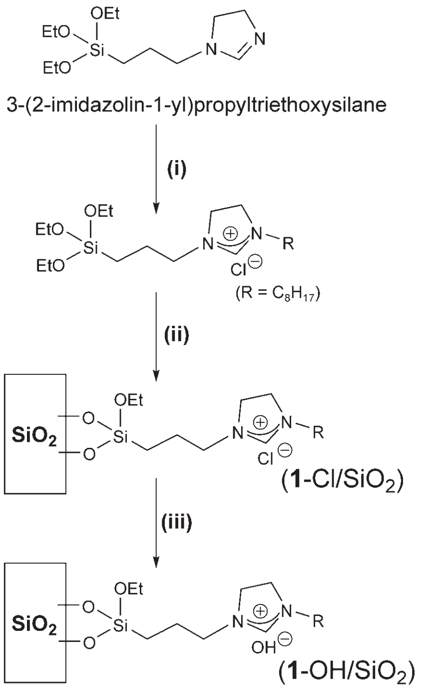
Keywords: cyanosilylation; epoxidation; heterogeneous catalysis; immobilized catalyst

There is an increasing demand for the green and sustainable production of chemicals.[1] For this achievement, catalytic processes with high atom efficiency, simple operations, and simple work-up procedures are desirable and many (transition) metal catalysts have been developed. Organomolecular acid or base catalysts have recently been exclusively studied in the field of organic syntheses, because the efficiency and selectivity are tunable with structural modifications and the catalysts do not involve any (toxic) metals.[2] Many organocatalysts contain heteroatoms such as nitrogen, sulfur, and phosphorus, and tend to act as heteroatom-centered Lewis bases. The recovery and reuse of the organomolecular acid/base catalysts can be achieved by their immobilization onto appropriate solid supports.[3]

In this paper, we report that a solid Brønsted base organocatalyst, which has been synthesized by anchoring an *N*-octyldihydroimidazolium hydroxide fragment onto SiO_2,[4] is active for (i) the cyanosilylation of carbonyl compounds with trimethylsilyl cyanide (Me_3SiCN) and (ii) the epoxidation of electron-deficient olefins with hydrogen peroxide.

The immobilized organocatalyst **1**-OH/SiO_2 has been prepared by the post-modification method[4] according to Scheme 1 (see also Experimental Section). Compound **1**-Cl was synthesized by the *N*-alkylation of 3-(2-imidazolin-1-yl)propyltriethoxysilane with 1-chlorooctane [step (i)]. Then, the pretreated SiO_2 was refluxed in a chloroform solution containing **1**-Cl [step (ii)], giving modified SiO_2 with covalently anchored **1**-Cl (**1**-Cl/SiO_2). The **1**-Cl/SiO_2 was treated with a THF solution containing aqueous NH_3 to afford the **1**-OH/SiO_2 [step (iii)]. The IR spectrum of **1**-OH/SiO_2 showed bands characteristic of the parent dihydroimidazolium skeleton [$\nu = 2959$, 2930, 2860 ν(C–H), 1652 cm^{-1} ν(C=N)]. No bands characteristic of ammonia and ammonium cation were observed. The elemental analysis of **1**-Cl/SiO_2 showed the presence of chlorine (0.76 wt%) whereas no chlorine was detected for **1**-OH/SiO_2, suggesting the progress of complete exchange of Cl^- with OH^- in step (iii). The elemental analysis of **1**-OH/SiO_2 revealed that 186 μmol of dihydroimidazolium fragments existed in one gram of the catalyst. The BET surface area and pore volume of **1**-OH/SiO_2 were 234 m^2g^{-1} and 0.37 cm^3g^{-1}, respectively.

Cyanosilylation of carbonyl compounds with Me_3SiCN is a very important transformation, which allows the formation of C–C bonds and the protection of a hydroxy function.[5] The products (cyanohydrin trimethylsilyl ethers) can be further transformed to a



Scheme 1. Procedures for the preparation of **1**-OH/SiO_2 catalyst. All operations were performed using Schlenk techniques under an argon atmosphere. Reaction conditions; (i) 1-chlorooctane (3 equivs. with respect to starting material), 353 K, 24 h; (ii) SiO_2, chloroform, reflux, 24 h; (iii) NH_3 (28% aqueous solution, 0.5 M in THF), 298 K, 12 h.

Table 1. Cyanosilylation of cyclopentanone with trimethylsilyl cyanide (Me_3SiCN) by various catalysts.[a]

Entry	Catalyst	Yield [%]
1	**1**-OH/SiO_2	91
2	**1**-Cl/SiO_2	3
3	MgO[b]	51
4	Amberlite IRA[c]	41
5	SiO_2[d]	<1
6	SiO_2 treated with NH_3 solution[e]	<1
7	[omim]OH[f]	19
8	No catalyst	<1

[a] *Reaction conditions:* cyclopentanone (0.5 mmol), catalyst (75 mg, **1**: 2.8 mol% with respect to cyclopentanone), Me_3SiCN (2 mmol), CH_2Cl_2 (0.5 mL), 305 K, 1 h. Yields were determined by GC using naphthalene as an internal standard. The corresponding cyanohydrin trimethylsilyl ether was formed as a sole product (>99% selectivity based on cyclopentanone).

[b] 35 mol% with respect to cyclopentanone.

[c] OH^- form. 2.8 mol% with respect to cyclopentanone.

[d] 100 mg.

[e] 100 mg. SiO_2 was pretreated at 393 K for 3 h under the reduced pressure ($<10^{-2}$ torr). Then, the pretreated SiO_2 was added to a THF solution of NH_3 (28% aqueous, 0.5 M) and the resulting mixture was vigorously stirred at room temperature for 12 h.

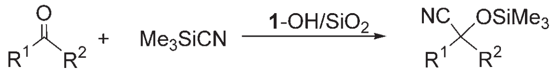
[f] [omim]OH = *N*-methyl-*N'*-octylimidazolium hydroxide (2.8 mol% with respect to cyclopentanone).

wide range of important synthetic intermediates including α-hydroxy acids, α-amino acids, and β-amino alcohols.[5] Therefore, the cyanosilylation process has stimulated considerable interest in the development of efficient catalysts. Many efficient catalysts such as Lewis acids and Lewis bases have been developed.[6,7] However, most of them are homogeneous systems and there are few excellent heterogeneous systems using solid (supported) catalysts[8] in spite of the significant advantages from environmental and economical standpoints.[1]

First, the applicability of **1**-OH/SiO_2 to cyanosilylation was examined. Table 1 shows the results of cyanosilylation of cyclopentanone with Me_3SiCN by various catalysts. The reaction conditions were optimized by changing the reaction temperature, solvent, and scale. No reaction proceeded in the absence of catalyst (entry 8) or in the presence of unmodified SiO_2 (entry 5) or SiO_2 treated with NH_3 (entry 6). The reaction of cyclopentanone with Me_3SiCN in the presence of **1**-OH/SiO_2 (**1**, 2.8 mol%) gave the corresponding cyanohydrin trimethylsilyl ether in 91% yield for 1 h (entry 1).[9] The catalytic activity of chloride form **1**-Cl/SiO_2 was very low (entry 2), indicating that the hydroxy group of **1**-OH/SiO_2 plays an important role in the present cyanosilylation. It is noted that the **1**-OH/SiO_2 catalyst showed a higher catalytic activity than commercially available solid base catalysts such as MgO and the hydroxy form of an ion-exchange resin under the present conditions (entries 3 and 4). Interestingly, the catalytic activity of **1**-OH/SiO_2 was much higher than that of [omim]OH (entry 7). The much higher activity of **1**-OH/SiO_2 than that of [omim]OH is possibly explained by the condensation of OH^- on the catalyst surface.

The results of **1**-OH/SiO_2-catalyzed cyanosilylation of various carbonyl compounds with Me_3SiCN are summarized in Table 2. The **1**-OH/SiO_2 catalyst was applicable to a wide range of aldehydes and ketones. No desilylation products (cyanohydrins) were detected in each case. All benzylic aldehydes and ketones were converted into the corresponding cyanohydrin trimethylsilyl ethers in almost quantitative yields (entries 1, 2, 5–7, 12, and 13). The reaction rates did not change much with the electronic and steric variations due to the substituents on aromatic rings. Not only aromatic carbonyl compounds but also aliphatic ones were selectively converted into the corresponding cyanohydrin trimethylsilyl ethers (entries 11, 14, and 15). The present system was also applicable to sulfur- and nitrogen-containing carbonyl compounds, giving the corresponding cyanohydrin trimethylsilyl ethers in quantitative yields within 0.5 h (entries 9 and 10). Sterically hindered cyclic ketones such as cyclopentanone, cyclooctanone, and 2-adamantanone also react-

Table 2. Cyanosilylation of various carbonyl compounds with trimethylsilyl cyanide (Me_3SiCN) catalyzed by **1**-OH/SiO_2.[a]



Entry	Substrate	Time [h]	Yield [%]
1	$R^1=Ph$, $R^2=H$	0.5	>99
2	$R^1=4\text{-}MeC_6H_4$, $R^2=H$	0.5	99
3[b]	$R^1=4\text{-}MeC_6H_4$, $R^2=H$	0.5	90
4[c]	$R^1=4\text{-}MeC_6H_4$, $R^2=H$	1	99
5	$R^1=2\text{-}MeOC_6H_4$, $R^2=H$	0.5	>99
6	$R^1=4\text{-}MeOC_6H_4$, $R^2=H$	0.5	>99
7	$R^1=4\text{-}ClC_6H_4$, $R^2=H$	0.5	>99
8	$R^1=PhCH{=}CH$, $R^2=H$	0.5	>99
9	$R^1=3$-pyridyl, $R^2=H$	0.5	>99
10	$R^1=2$-thiophenyl, $R^2=H$	0.5	>99
11	$R^1=C_6H_{13}$, $R^2=H$	0.5	91
12	$R^1=Ph$, $R^2=Me$	1	94
13	$R^1=Ph$, $R^2=$cyclopropyl	8	81
14	$R^1=C_3H_7$, $R^2=Me$	1	90
15	$R^1=C_6H_{13}$, $R^2=Me$	1	>99
16	cyclopentanone	1	91
17	cyclooctanone	4	87
18	2-adamantanone	0.5	>99
19	2-cyclohexen-1-one	2	94[d]

[a] *Reaction conditions:* Substrate (0.5 mmol), catalyst (75 mg, **1**: 2.8 mol% with respect to substrate), Me_3SiCN (2 mmol), CH_2Cl_2 (0.5 mL), 305 K. Yields were determined by GC using naphthalene as an internal standard. The corresponding cyanohydrin trimethylsilyl ether was formed as a sole product in each case (>99% selectivity based on starting carbonyl compound).

[b] Recycling experiment.

[c] Me_3SiCN (1 mmol).

[d] The corresponding 1,4-adduct was obtained in 5% yield.

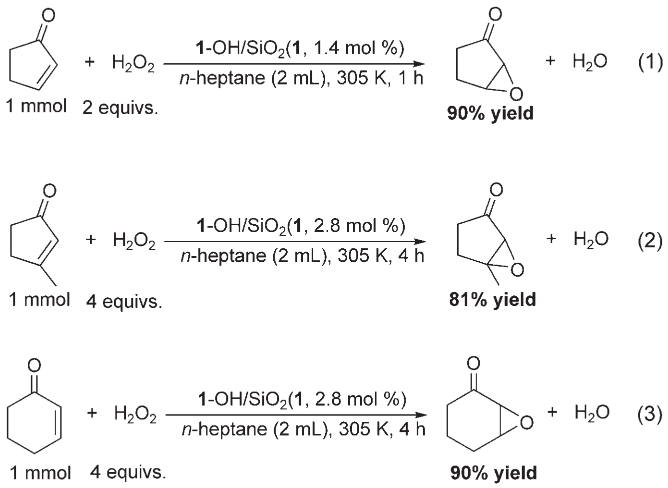
ed with Me_3SiCN to afford the corresponding products in high yields (entries 16–18). In the case of an α,β-unsaturated ketone such as 2-cyclohexen-1-one, 1,2-addition of Me_3SiCN mainly occurred to give 1-cyano-1-trimethylsilyl-2-cyclohexene in 94% yield and the yield of Michael addition (1,4-addition) product was only 5% (entry 19). These high selectivities to the 1,2-adduct for cyanosilylation of an α,β-unsaturated ketone are very similar to those achieved with solid bases such as MgO and CaO.[8c]

In order to verify whether the observed catalysis is truly heterogeneous or not, the catalytic cyanosilylation of *p*-tolualdehyde with Me_3SiCN was carried out with **1**-OH/SiO_2 under the conditions indicated in Table 2 and the solid **1**-OH/SiO_2 was removed by filtration at around 50% conversion. Then, the filtrate was allowed to react under the same conditions. No increases of conversion and yield were observed. This suggests that the nature of the observed catalysis is truly heterogeneous.[10] The solid **1**-OH/SiO_2 could be easily separated by the simple filtration (or centrifugation) after the reaction. The recovered catalyst could be reused without a significant loss of the catalytic activity and selectivity (entry 3 in Table 2).

The present cyanosilylation possibly proceeds in the following way: the hydroxy group in **1**-OH/SiO_2 acts as a nucleophile to form a hypervalent silicate species.[2d] This species readily reacts with a carbonyl compound to produce the corresponding trimethylsilyl ether with the restoration of the hydroxy group since the nucleophilicity of the cyano group is increased by the electron donation.

The high performance of **1**-OH/SiO_2 as a solid base catalyst was further demonstrated in epoxidation of electron-deficient olefins using hydrogen peroxide as a sole oxidant.[11] Various cyclic α,β-unsaturated ketones could be epoxidized to form the corresponding epoxy ketones in high yield [Scheme 2, Eqs. (1) to (3)]. Under the same conditions, the epoxidation proceeded efficiently with a conventional solid base catalyst of MgO. However, the epoxidation was not completely stopped by the removal of MgO. In contrast, the heterogeneous nature of **1**-OH/SiO_2 was confirmed by the fact that the epoxidation did not proceed after removal of **1**-OH/SiO_2. In the present epoxidation, hydrogen peroxide may react with the hydroxy group in **1**-OH/SiO_2 to form a hydroperoxy anion.[11] The anion nucleophilically attacks the electron-deficient β-carbon of an enone, followed by ring closure to give the corresponding epoxy ketone with the restoration of the hydroxy group.

In summary, the immobilized organocatalyst **1**-OH/SiO_2 was found to be an effective heterogeneous base catalyst for cyanosilylation of a wide variety of carbonyl compounds with Me_3SiCN to give excellent yields of the corresponding cyanohydrin trimethylsilyl ethers. Heterogeneously catalyzed epoxidation of electron-deficient olefins with hydrogen peroxide as a



Scheme 2. Epoxidation of various cyclic α,β-unsaturated ketones to the corresponding epoxy ketones.

sole oxidant also efficiently proceeded with this catalyst. Further studies on the application of this type of the immobilized organocatalyst to enantioselective cyanosilylation and epoxidation are now in progress.

Experimental Section

Instruments and Reagents

GC analyses were performed on Shimadzu GC-2014 with an FID detector equipped with a TC-WAX or TC-5 capillary column. Mass spectra were determined on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, in acetone-d_6 or chloroform-d_1 with TMS as an internal standard. IR spectra were measured on a Jasco FT/IR-460 Plus.

Substrates and solvents were commercially obtained from Tokyo Kasei or Aldrich (reagent grade) and purified prior to the use.[12] 3-(2-Imidazolin-1-yl)propyltriethoxysilane (Fluka) and hydrogen peroxide (Kanto) were of analytical grade and used without the further purification. SiO_2 was obtained from Fuji Silysia Chemical Ltd.(CARiACT Q-10, Lot No. C-0502007, 75–150 μm, BET surface area: 273 $m^2 g^{-1}$, pore volume: 1.23 $cm^3 g^{-1}$). MgO was obtained from Ube Industries Ltd. (500 A, Lot No. P0082, BET surface area: 28 $m^2 g^{-1}$). An anion exchange resin (Amberlite IRA402BL CL, chloride form) was obtained from Organo Co. and chloride ion was exchanged to hydroxide ion using 1 M aqueous NaOH solution.

Synthesis of Compound 1-Cl

All operations were performed using Schlenk techniques under an argon atmosphere. A mixture of 3-(2-imidazolin-1-yl)propyltriethoxysilane (25 mmol) and 1-chlorooctane (75 mmol) was treated at 353 K for 24 h under an argon atmosphere. After the reaction, the mixture was cooled to room temperature and the volatiles were removed by evaporation under reduced pressure. The orange colored viscous liquid was washed with *n*-pentane (50 mL × 3) and dried under vacuum, giving 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (**1**-Cl); yield: 98 %. ^{1}H NMR (270 MHz, acetone-d_6, TMS, 298 K): $\delta = 10.53$ (1 H, s), 4.08–4.10 (4 H, m), 3.80 (6 H, q, $^3J_{H,H} = 6.92$ Hz), 3.63–3.68 (4 H, m), 1.27–1.78 (14 H, m), 1.17 (9 H, t, $^3J_{H,H}) = 6.92$ Hz), 0.83 (3 H, t, $^3J_{H,H} = 6.59$ Hz), 0.60–0.67 (2 H, m); $^{13}C\{^1H\}$ NMR (67.8 MHz, chloroform-d_1, TMS, 298 K): $\delta = 158.90$, 58.40, 50.23, 48.23, 48.09, 47.84, 31.52, 28.93, 28.90, 27.30, 26.24, 22.40, 21.05, 18.15, 13.87, 7.03; ^{29}Si NMR (53.5 MHz, acetone-d_6, TMS, 298 K): $\delta = -45.4$; ESI-MS (positive ion mode): $m/z = 387$ ($[C_{20}H_{43}N_2O_3Si]^+$).

Preparation of 1-OH/SiO_2

All operations were performed using Schlenk techniques under an argon atmosphere. SiO_2 was pretreated at 393 K for 3 h under the reduced pressure ($<10^{-2}$ torr). The TG/DTA analysis revealed that 3.5 silanol groups per nm^2 existed on the surface of pretreated SiO_2.[13] The pretreated SiO_2 (3.0 g) was vigorously stirred with a chloroform solution of **1**-Cl (0.24 M, 50 mL) for 24 h under reflux conditions (bath temperature, 353 K). The solid was separated by the filtration, washed with *n*-heptane (50 mL) and acetonitrile (50 mL), and then dried under vacuum to afford **1**-Cl/SiO_2 as a pale yellow solid.

Then, **1**-Cl/SiO_2 (3 g) was added to a THF solution of NH_3 (28 % aqueous, 0.5 M, 120 mL) and the resulting mixture was vigorously stirred at room temperature for 12 h. The solid was filtered off, washed with a large amount of water, and dried under vacuum at 323 K for 5 h to afford **1**-OH/SiO_2. Elemental analysis: C 3.42 %, H 1.20 %, N 0.52 %, Cl 0 %; IR (KBr disk): $\nu = 2959$, 2930, 2860 ν(C–H), 1652 cm^{-1} ν(C=N); BET surface area: 234 $m^2 g^{-1}$; pore volume: 0.37 $cm^3 g^{-1}$

Synthesis of Compound [omim]OH

N-Methyl-*N'*-octylimidazolium chloride ([omim]Cl) was synthesized by *N*-alkylation of *N*-methylimidazole with 1-chlorooctane according to the same procedure as that for the synthesis of **1**-Cl. Then, [omim]Cl (8.8 mmol) was dissolved in an acetonitrile solution of NH_3 (28 % aqueous, 2.5 M, 36 mL). The resulting mixture was vigorously stirred at room temperature. After 12 h, the volatiles (acetonitrile and NH_3) were evaporated under reduced pressure, followed by extraction of [omim]OH with chloroform. ^{1}H NMR (270 MHz, chloroform-d_1, TMS, 298 K): $\delta = 9.68$ (1 H, s), 7.56 (1 H, s), 7.36 (1 H, s), 4.18 (2 H, t, $^3J_{H,H} = 7.02$ Hz), 3.95 (3 H, s), 1.70–1.82 (2 H, m), 1.14–1.20 (10 H, m), 0.76 (3 H, t, $^3J_{H,H} = 6.75$ Hz); $^{13}C\{^1H\}$ NMR (67.8 MHz, chloroform-d_1, TMS, 298 K): $\delta =$ 136.34, 123.75, 121.71, 49.74, 36.41, 31.52, 30.08, 28.88, 28.84, 26.10, 22.39, 13.87.

Catalytic Reaction

The catalytic reaction was carried out with a glass tube reactor. The reaction solution was periodically sampled and analyzed by GC. The products were identified by comparison of mass and NMR spectra with those of authentic samples. The carbon balance in each experiment was in the range of 95–100 %. After the reaction, the catalyst and reaction solution were separated by the filtration (or centrifugation). The recovered catalyst was washed with appropriate solvents and dried before recycling.

Acknowledgements

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[9] For cyanosilylation of cyclopentanone as a model reaction, the first-order dependence of the initial rate on the amount of catalyst in the range of 50–200 mass% with respect to cyclopentanone was observed. In addition, the quantitative yield of the corresponding cyanohydrin trimethylsilyl ether was obtained with the 50 mass% catalyst (only 0.8 mol% with respect to cyclopentanone) while it required longer reaction time (20 h).

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