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Preparation and the catalytic activity of novel Pd nanocluster catalysts utilizing an oligosilsesquioxane ligand

Kenji Wada,* Kousuke Yano, Teruyuki Kondo, and Take-aki Mitsudo

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 615-8510, Japan

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Palladium acetate together with a newly synthesized silsesquioxane- pyridyl ligand showed excellent catalytic activity towards the aerobic oxidation of benzyl alcohol to benzaldehyde. TEM measurements revealed the *in situ* formation of Pd nanoclusters during the reaction period.

KEY WORDS: silsesquioxane; pyridyl ligand; palladium; nanoclusters; aerobic oxidation; benzyl alcohol.

1. Introduction

Recently, oxidation of alcohols with air or molecular oxygen has been extensively studied from the viewpoint of green chemistry [1–3], and a number of homogeneous and heterogeneous palladium catalysts [4–21] have been explored. However, the precipitation of a palladium(0) species during the reaction in the homogeneous catalytic systems and the resulting loss of the activity were often observed, especially in the case with low oxygen partial pressure and low substrate to catalyst molar ratio [21,22]. The stabilization of palladium species as nanoclusters instead of the formation of palladium black would be very advantageous, since nanoclusters often show excellent catalytic activity towards this type of reactions [13–20,23–25].

One can expect that the use of a caged silsesquioxane-containing ligand would suppress the formation of large aggregates and promote the formation of nanoclusters. Caged oligosilsesquioxanes have attracted attention mainly as building blocks of novel organic-inorganic hybrid materials as well as soluble analogue of siliceous catalysts or zeolites [26–35]. In addition, several ligands bearing a silsesquioxane moiety have been synthesized and utilized for the preparation of transition metal complexes by us [36] and others [37–42]. The use of silsesquioxanes bearing peripheral alkyl substituents as protecting groups of nanoclusters is expected to suppress the aggregation and improve the dispersion of nanoclusters because their steric hindrance and high hydrophobicity compared to conventional ligands [26–34,37,38].

In the present study, we have synthesized a novel silsesquioxane pyridine ligand, and found that palladium acetate together with this ligand acts as an excellent catalyst for the aerobic oxidation of benzyl alcohol to benzaldehyde. In situ formation of palladium nanoclusters during the reaction period was observed, which would prevent the formation of palladium black.

2. Experimental

2.1. Materials and methods

All reactions and subsequent manipulations were carried out under unaerobic and anhydrous conditions either under high vacuum or an atmosphere of argon using standard Schlenk technique. Organic solvents and triethylamine were dried and distilled under argon with appropriate drying agents (sodium, calcium chloride, calcium hydride) [43] just before use. Dehydrated acetonitrile , dimethylethoxyethynylsilane, *p*-toluenesulfonic acid, CuI, $PdCl_2(PPh_3)_2$, 2-bromopyridine, and $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ (**1**) were obtained commercially and used without further purification.

2.2. Physical and analytical measurements

Solution-phase NMR spectra were recorded on JEOL JNM-EX-400 instruments. ^1H and ^{13}C spectra were referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for the ^{29}Si nuclei were referenced to external $SiMe_4$ resonance. Fast atomic bombardment (FAB) mass spectra were recorded using JEOL SX-102A mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Note that microanalyses of **3** was hampered by the inevitable formation of carbidic species. XPS (X-ray photoelectron spectra) of the catalysts were acquired using an ULVAC-PHI 5500MT system equipped with a hemispherical energy analyzer. Samples

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*To whom correspondence should be addressed.
E-mail: wadaken@scl.kyoto-u.ac.jp

were mounted on indium foil and then transferred to an XPS analyzer chamber. The residual gas pressure in the chamber during data acquisition was less than 1×10^{-8} Torr (1 Torr = 133.3 N m^{-2}). The spectra were measured at room temperature using Mg $K\alpha_{1,2}$ radiation (15 kV, 400 W). The electron take-off angle was set at 45 deg. Binding energies were referenced to Si 2p level [44]. The TEM observation was performed using a Hitachi H-9000 transmission electron microscope (300 kV). The oxidation products were analyzed by GC-MS (Shimadzu QP 5000, CBP10-S25-050 capillary column, i.d. 0.33 mm, length 25 m, o.d. 0.43 mm at 323–473 K) and gas chromatography (SE-30, i.d. 3.0 mm, length 3.0 m at 323–473 K).

2.3. Synthesis of 2

A mixture of **1** (0.92 g, 1.0 mmol), dimethylethoxyethynylsilane (0.50 cm^3, 3.5 mmol), and *p*-toluenesulfonic acid (0.050 g, 0.26 mmol) in toluene (20 cm^3) was stirred at 80 °C for 20 h in an Ar atmosphere. The reprecipitation by slow diffusion of acetonitrile into the toluene solution followed by the vacuum drying gave $(c\text{-}C_5H_9)_7Si_8O_{12}(OSiMe_2CCH))$ (**2**) as an off-white powder. Yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.28 (s, 1H, SiCC*H*), 1.85–1.40 (br m, 56H), 1.05–0.93 (br m, 7H, C*H* of Cy), 0.31 (s, 6H, $Si(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ 92.06 (SiC*C*H), 88.48 (Si*C*CH), 27.34, 27.07, 27.04 (CH_2 of Cy), 22.31, 22.26, 22.19 (1 : 3 : 3 for CH of Cy), 1.67 ($Si(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C) $\delta - 15.79, -65.58, -66.24, -108.13$ (1:3:4:1). IR (KBr): 3583, 2048 cm^{-1}. Anal. Calcd for $C_{39}H_{70}O_{13}Si_9$ (999.76): C, 46.85; H, 7.06. Found C, 46.63; H, 6.83. MS (FAB-NPOE) m/z : 973 ($[M - C_2H + H]^+$), 929 ($[M - C_5H_9]^+$), 861.

2.4. Synthesis of 3

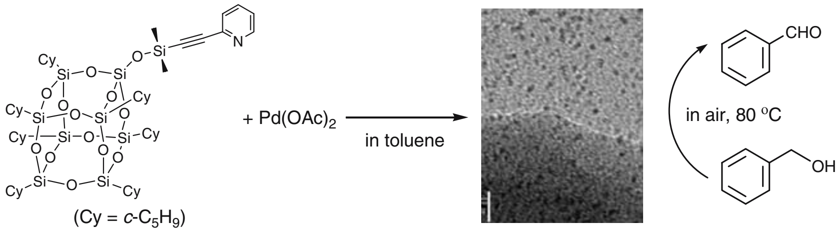
In the presence of CuI (0.035 g, 0.22 mmol) and $PdCl_2(PPh_3)_2$ (0.066 mg, 0.094 mmol), a mixture of $(c\text{-}C_5H_9)_7Si_8O_{12}(OSiMe_2CCH))$ (**2**, 0.80 g, 0.80 mmol), and 2-bromopyridine (0.25 cm^3, 2.5 mmol) in triethylamine (20 cm^3) was stirred at room temperature for 20 h in an Ar atmosphere. To the resulting dark brown solution added *ca.* 50 cm^3 of diethyl ether. The organic layer was washed with water (*ca.* 30 $cm^3 \times 3$), followed by drying by unhydrous Na_2SO_4. After removal of the solvent by the rotary evaporation the crude product was separated by column chromatography (Florisil, 1.5 cmφ × 25 cm, in $CHCl_3$ solution). The solvent was evaporated, and then the reprecipitation by slow diffusion of acetonitrile into the toluene solution followed by the vacuum drying gave **3** as a white powder. Yield 54%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.57 (d, J = 5.6 Hz, 1H, Py), 7.63 (dt, J = 10.2, 2.2 Hz, 1H, Py), 7.46 (d, J = 10.3 Hz, 1H, Py), 7.22 (m, 1H, Py), 1.78–1.48 (br m, 56H, C*H*$_2$ of Cy), 1.03–0.94 (br m, 7H, C*H* of Cy), 0.39 (s, 6H, $Si(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ 149.96, 142.90, 135.90, 127.41, 123.13 (Py), 27.28, 27.00, 26.94 (CH_2 of Cy), 22.23, 22.19, 22.12 (1 : 3 : 3 for *C*H of Cy), 1.62 ($Si(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C) $\delta - 15.12, -65.58, -66.27, -108.18$ (1:3:4:1). Anal. Calcd for $C_{44}H_{73}NO_{13}Si_9$ (1076.8): C, 49.08; H, 6.83. Found C, 48.48; H, 6.70. HR-MS (FAB-NPOE). Calcd for $C_{44}H_{74}NO_{13}Si_9$. 1076.3084. Found 1076.3064 ($[M + H]^+$).

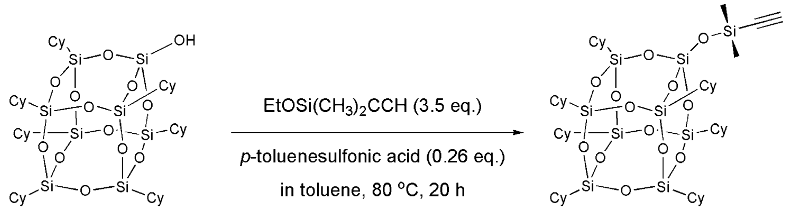
2.5. Typical procedure for the aerobic oxidation of benzyl alcohol

Under air (open), 3.0 cm^3 of a toluene solution containing palladium acetate (0.0050 mmol), **3** or pyridine (0.0050 mmol), and benzylic alcohol (5.0 mmol) were added to a 10 cm^3 Schlenk tube together with a Teflon-coated stirbar. The mixture was stirred at 80 °C for 2–20 h by the use of a hot stirrer equipped with stainless steal cooling blocks.

3. Results and discussion

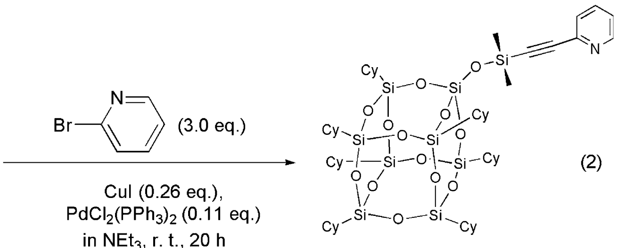
A silsesquioxane-pyridine ligand (**3**) was newly synthesized via a silsesquioxane with an ethynylsilyl group (**2**). The reaction of $(c\text{-}C_5H_9)_7Si_8O_{12}OH$ (**1**) with 3.5 equivalent of dimethylethoxyethynylsilane in the presence of 3 mol% of *p*-toluenesulfonic acid in toluene at 80 °C for 20 h, followed by reprecipitation, quantitatively afforded a silsesquioxane with one ethynylsilyl group **2**. The Sonogashira-coupling reaction of **2** with 2-bromopyridine in the presence of 27.5 mol % of CuI and 12.5 mol % of $[(C_6H_5)_3P]_2PdCl_2$ for 20 h afforded a novel silsesquioxane-pyridine ligand **3** (54%). These products were fully characterized by NMR, IR, FAB-MASS and elemental analysis.



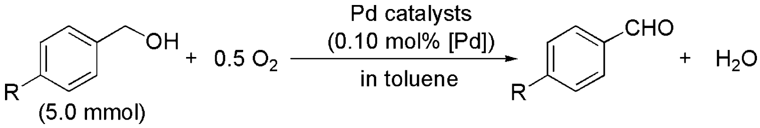


1 (Cy = c-C_5H_9) **2** (yield 99 %) (1)

2



3 (yield 54 %) (2)



(3)

The catalytic activity of the 1:1 mixture of silsesquioxane-pyridine ligand (**3**) and $Pd(OAc)_2$ for the aerobic oxidation of benzylic alcohols was examined. This catalyst (Pd 0.10 mol %) was added to the toluene solution of benzyl alcohol (5.0 mmol) and stirred in air at 80 °C for 20 h (table 1). For comparison, the activity of palladium acetate combined with 1 eq. of pyridine was also examined. Although the initial activity of $Pd(OAc)_2$/**3** was relatively low, after 20 h benzaldehyde was selectively obtained in higher yield (97%) than that in the case with $Pd(OAc)_2$/pyridine. Note that just after the reaction started, the solution turned from clear yellow to be clear red brown without the formation of precipitates. On the other hand, in the case of $Pd(OAc)_2$ with pyridine severe formation of palladium black was observed within 15 min of the reaction, and the color of the solution, initially yellow, turned to be colorless [21]. The trend is also true for the oxidation of *p*-methylbenzyl alcohol in O_2 for 20 h. The $Pd(OAc)_2$/**3** catalyst afforded corresponding aldehyde in the yield of 20% without the formation of other products. Again, just after the reaction started, the color of the solution turned to transparent red brown without the formation of any precipitates, while palladium black was formed from $Pd(OAc)_2$/pyridine.

Table 1
Catalytic activity of the silsesquioxane-Pd catalysts

Run	Catalysts[a]	R	Conditions	Yield (%)[b]
1	$Pd(OAc)_2$ + **3**	H	80 °C, 2 h, in air	6
2		H	80 °C, 20 h, in air	97
3	$Pd(OAc)_2$ + pyridine	H	80 °C, 2 h, in air	19
4		H	80 °C, 20 h, in air	86
5	$Pd(OAc)_2$ + **3**	Me	80 °C, 20 h, in O_2	20
6		Me	100 °C, 20 h, in O_2	27
7	$Pd(OAc)_2$ + pyridine	Me	80 °C, 20 h, in O_2	13

[a] Molar ratio Pd:ligand = 1:1.
[b] Determined by GLC.

The TEM photographs of the contents of the red brown mixture after the reaction for 10 min show the formation of monodispersed nanoclusters with a mean diameter just less than 2 nm, as shown in figure 1(a). Each particle was well separated, probably because of the steric hindrance of the protecting silsesquioxane shell. After the reaction for 2 h (figure 1(b)), the size of each particle was almost unchanged. After 10 h mean size of nanoclusters slightly increased to be 3–4 nm (figure 1(c)), but formation of large aggregates was not observed. These results indicate that these nanoclusters were stable even at the reaction conditions.

The XPS analysis of the contents of the mixture after 10 min reaction revealed that palladium species was composed of 57% of Pd(0) and 43% of Pd(II) (see figure 2). This indicates that at the initial stage of the reaction a major part of palladium(II) acetate was reduced to be Pd(0) without the formation of palladium black.

In conclusion, palladium acetate with a newly synthesized silsesquioxane-pyridyl ligand showed excellent catalytic activity towards the aerobic oxidation of benzylic alcohols. The use of **3** was found to be very effective to suppress the formation of large aggregates of Pd(0) species. Instead, it is considered to stabilize in situ formed nanoclusters. Although we should be very

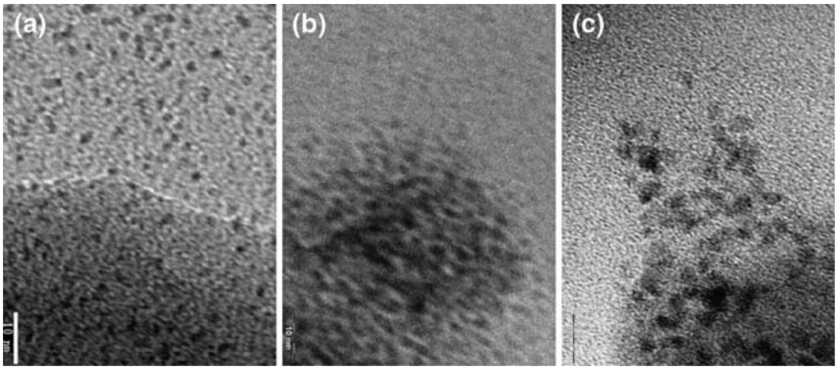


Figure 1. TEM photographs of the contents of the reaction mixture. (a) After 10 min (b) 2 h, and (c) 10 h of the reaction.

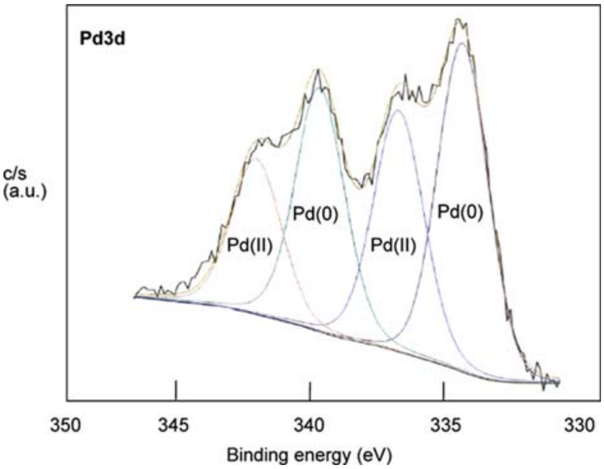


Figure 2. XPS spectrum of the contents of the reaction mixture after 10 min of the reaction at the Pd 3d region.

careful to conclude the true catalytically active species, the results shown above suggest that palladium nanoclusters is responsible for high activity. Note that very high turnover numbers for this type of the reactions have been often recorded for palladium nanocluster catalysts.^{6} The induction period going with formation of palladium nanoparticles as well as large steric hinderance of **3** could be one reason for relatively low initial activity of Pd(OAc)$_2$/**3**. Now, the examination on effects of various silsesquioxane ligands as well as more detailed studies on the catalytically active species was on going, and the results will be reported in due course.

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