Supporting information

Effect of immobilized amine structure on the formation and catalysis of Pd nanoparticles for oxidation of alcohols

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Materials and Methods

Materials

Aerosil® 300 (NIPPON AEROSIL Co.) was used as the nonporous silica (SiO_2). $CDCl_3$ for NMR measurements was purchased from Kanto Kagaku Co. Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc. and used without further purification.

Preparation of SiO_2/NR^1R^2

Immobilization of amines on silica was carried out by the silane coupling reaction of precursor molecules and silica supports. (*N*,*N*-diethyl-3-aminopropyl)trimethoxysilane, (*N*,*N*-dimethxyl-3-aminopropyl)trimethoxysilane, (*N*-methyl-3-aminopropyl)trimethoxy silane, (3-aminopropyl)trimethoxysilane, and (diethylaminomethyl)triethoxysilane were used as the precursor for SiO_2/NEt_2, SiO_2/NMe_2, $SiO_2/NHMe$, SiO_2/NH_2, and $SiO_2/NEt_2(C1)$ respectively. To 50 mL Schlenk tube, 0.64 g of nonporous silica was added, followed by vacuum drying at 120 °C for 3 h. After naturally cooling the silica to room temperature, Ar was introduced into the Schlenk tube. Toluene solution of the precursor (1.6 mmol in 15.0 mL) was added to the silica and the mixture was stirred at 40 °C for 1 h under Ar. In the case of $SiO_2/NEt_2(C1)$, temperature and reaction time was set to 50 °C and 2 h, respectively. The removal of solvent by vacuum drying afforded SiO_2/NR^1R^2.

Preparation of $PdCl_2(PhCN)_2$

$PdCl_2$ (0.50 g) was added to the benzonitrile (15 mL) in 50 mL round-bottom flask. The mixture was magnetically stirred at 100 °C for 20 min and filtrated. $PdCl_2(PhCN)_2$ was precipitated by the addition of filtrate into the hexane (90 mL) and obtained as yellow powder after vacuum drying.

Preparation of $SiO_2/NR^1R^2/Pd$

To SiO_2/NR^1R^2 (0.70 g) contained in 50 mL Schlenk tube, isopropanol solution of $PdCl_2(PhCN)_2$ (0.2 mmol in 9.5 mL) was added, followed by stirring at room temperature for 4 h under Ar. The resulting solid was washed by centrifugation using isopropanol and dichloromethane as washing solvent. After vacuum drying, $SiO_2/NR^1R^2/Pd$ was obtained.

Preparation of $SiO_2/NEt_2/Pd$-NPs

To SiO_2/NR^1R^2 (0.70 g) contained in 50 mL Schlenk tube, isopropanol solution of $PdCl_2(PhCN)_2$ (0.2 mmol in 9.5 mL) was added, followed by stirring at 82 °C for 4 h under Ar. The resulting solid was washed by centrifugation using isopropanol and dichloromethane as washing solvent. After vacuum drying, SiO_2/NEt_2/Pd-NPs was obtained.

Preparation of SiO_2/Pd-NPs

To 500 mL round-bottom flask, were added H_2PdCl_4 aq (50 mM, 1.8 mL), polyvinylpyrrolidone (9.9 mg), H_2O (118.2 mL), and EtOH 30 mL. The reaction solution was refluxed for 3 h under air to form polymer-stabilized Pd nanoparticles. After cooling the colloidal solution to room temperature, SiO_2 (0.64 g) was added to the solution, followed by stirring at room temperature for 16 h. The resulting solid was washed by centrifugation using water as washing solvent and dried under vacuum to afford SiO_2/Pd-NPs.

Elemental analysis

The content of C, H, and N in prepared catalysts were determined by a CHN analyzer, UNICUBE (Elementar). The Pd content was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a spectrometer, ICPE-9000 (Shimadzu).

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR spectra of the reaction solution were recorded by a spectrometer, ECA 500 (JEOL) or ECX 400 (JEOL). $CDCl_3$ was used as solvent.

Solid state ^{29}Si, and ^{13}C NMR of SiO_2/NEt_2/Pd was conducted by Avance NEO spectrometer (400 MHz for ^{1}H nuclei) using 4 mm MAS probe (rotation rate: 12.5 kHz). Standard ramped cross polarization (CP) was used to transfer polarization from the ^{1}H nuclei to the nucleus of interest (^{13}C, ^{29}Si). CP contact time was set as 2 ms for ^{13}C and 5 ms for ^{29}Si. SPINAL-64 ^{1}H heteronuclear decoupling was applied during acquisition. ^{13}C and ^{29}Si chemical shifts were referenced to tetramethylsilane at 0 ppm using adamantane (38.52 ppm) and hexamethylcyclotrisiloxane (-9.66 ppm) as an external standard, respectively.. For ^{15}N measurement, Bruker Avance NEO 400 MHz/263 GHz 9.4 T DNP system was used. The sample was prepared by the incipient wetness impregnation method using TEKPol/TCE (16 mM) solution as a polarizing agent. 8.6 mg of SiO_2/NEt_2/Pd was mixed with 20 μL of TEKPol/TCE in Ar-purged glovebox, and the sample was packed into 3.2 mm sapphire rotor and sealed with a Teflon insert and a zirconia cap. The sample was frozen at ca. 100 K inside the precooled low temperature 3.2 mm MAS probe head. A relaxation delay was set as 2.96 s, which was 1.3 times DNP-buildup time (T_{DNP}). Standard ramped CP was used to transfer polarization from the ^{1}H nuclei to ^{15}N nuclei with 3 ms of CP contact time. SPINAL-64 ^{1}H heteronuclear decoupling was applied during acquisition. 3050 scans were accumulated under microwave on conditions at 110.6 K. $^{15}NH_4Cl$ (39.27 ppm) were used as the reference for ^{15}N chemical shift.

X-ray absorption spectroscopy (XAS)

XAS was carried out in the NW10A beamline at PF-AR of High Energy Accelerator Research Organization (proposal Nos. 2022G033 and 2024G054). The electron storage ring was operated at 6.5 GeV and 60 mA. Synchrotron X-ray from the storage ring was monochromatized by Si(311) crystal monochromator. Pd K-edge X-ray absorption fine structures (XAFS) were measured in transmission mode at room temperature by using ionization chambers. The acquired data were analyzed by a REX2000 program (Rigaku).

X-ray photoelectron spectroscopy (XPS)

XPS was carried out by using a spectrometer, PHI Quantera-SXM (ULVAC-PHI), with an energy resolution of 0.125 eV. Electron binding energy was calibrated by setting the Si 2p peak to 103.3 eV.

Powder X-ray diffraction (PXRD)

PXRD pattern was obtained by using a diffractometer, Ultima IV, with Cu Kα radiation (40 kV, 40 mA). The scan rate was set to 0.5 degree/min.

Transmission electron microscopy (TEM)

TEM was conducted by using an electron microscope (JEM-2100F, Jeol) operated at the acceleration voltage of 200 kV. The specimens for the TEM measurements were drop-casting the methanol dispersion of catalysts onto TEM microgrid (NS-C15, Okenshoji Co., Ltd.)

Aerobic oxidation of alcohols

Procedures for the reduction of 1-phenylethanol are described as a representative example. Catalyst (Pd: 3 μmol), toluene (1.5 mL), and 1-phenylethanol (1.0 mmol) were charged in a 20 mL Schlenk tube and the mixture was magnetically stirred at 100 °C for 1 h under air. The reaction products were quantified by ^{1}H NMR or GC-FID using 1,3,5-triisopropylbenzene as an internal standard. The specimens were also analyzed by GC-MS.

Gas chromatography (GC)

GC for quantitative analysis was carried out by a GC with flame ion detector, GC-2025 (Shimadzu, column: DB-WAX), whereas a GC with a mass spectrometer, GCMS-QP2010SE (Shimadzu, column: DB-1), was used for qualitative analysis.

Table S1. Elemental analysis results

Catalyst	Pd (mmol g^{-1})	N (mmol g^{-1})	C (mmol g^{-1})
SiO_2/NEt_2/Pd	0.16	0.85	7.1
SiO_2/NMe_2/Pd	0.15	0.93	6.0
SiO_2/NHMe/Pd	0.14	1.02	5.5
SiO_2/NH_2/Pd	0.11	1.28	6.0
SiO_2/NEt_2/Pd-NPs	0.17	0.93	8.1

Table S2. Curve-fitting results

Sample	Shell	CN [a]	r (Å) [b]	σ (Å) [c]	R (%) [d]
SiO_2/NEt_2/Pd	Pd–O/N	2.1(9)	2.05(5)	0.074(43)	11
	Pd–Cl	1.8(8)	2.29(1)	0.056(30)	
SiO_2/NMe_2/Pd	Pd–O/N	2.1(1.4)	2.07(6)	0.065(48)	9.9
	Pd–Cl	1.9(1.0)	2.28(2)	0.045(43)	
SiO_2/NHMe/Pd	Pd–O/N	2.4(1.2)	2.04(4)	0.059(41)	14
	Pd–Cl	2.1(9)	2.28(2)	0.053(35)	
SiO_2/NH_2/Pd	Pd–O/N	3.8(3)	2.062(7)	0.081(9)	16

[a]Coordination number. [b]Interatomic distance. [c]Debye-Waller factor. [d]R factor calculated by following equation: $R = [\Sigma\{k^3\chi^{\mathrm{data}}(k) - k^3\chi^{\mathrm{fit}}(k)\}^2]^{1/2}/[\Sigma\{k^3\chi^{\mathrm{data}}(k)\}^2]^{1/2}$

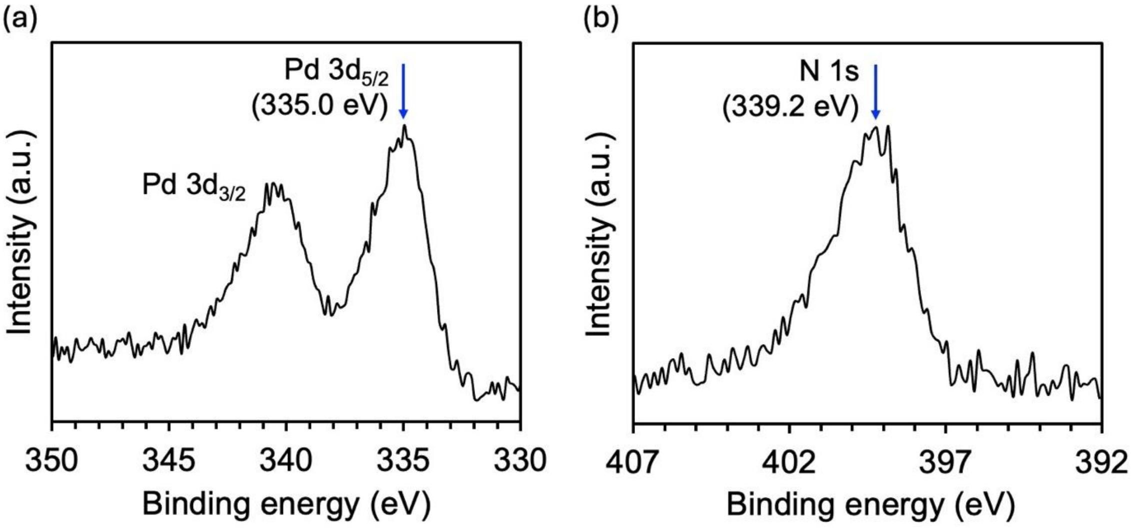


Figure S1 XPS of SiO_2/NEt_2/Pd after the aerobic oxidation of 1-phenylethanol.

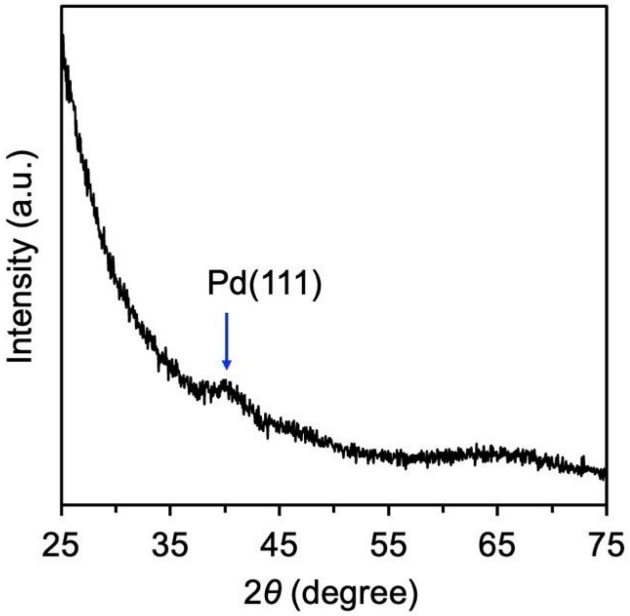


Figure S2 PXRD pattern of SiO_2/NEt_2/Pd after the aerobic oxidation of 1-phenylethanol.

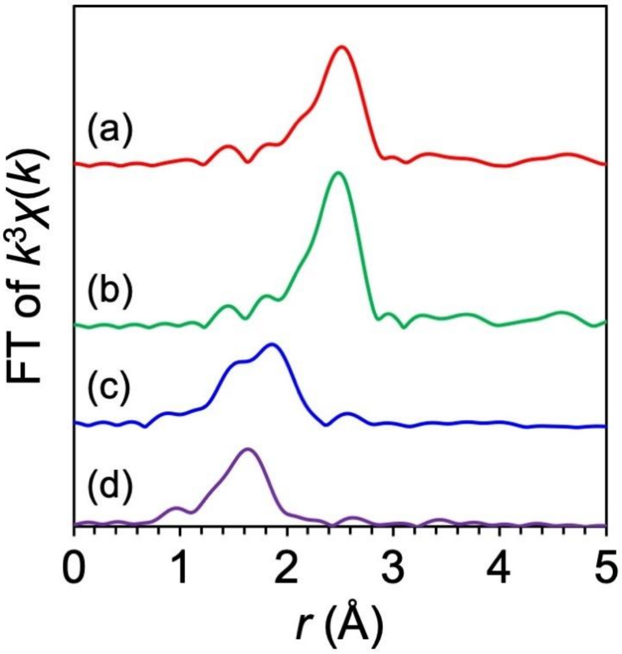
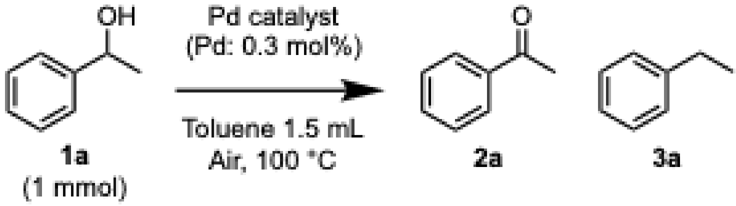


Figure S3 FT-EXAFS spectra of (a) SiO_2/NEt_2/Pd, (b) SiO_2/NMe_2/Pd, (c) SiO_2/NHMe/Pd, and (d) SiO_2/NH_2/Pd after heating in isopropanol at 82 °C for 4 h under Ar.

Table S3. Catalytic reaction with $SiO_2/NR^1R^2/Pd$ after reductive treatment in isopropanol at 82 °C for 4 h under Ar



Catalyst	Time (h)	Yield of **2a**	Yield of **3a**
$SiO_2/NEt_2/Pd$	1	41	<1
$SiO_2/NMe_2/Pd$		40	1
$SiO_2/NHMe/Pd$		1	<1
$SiO_2/NH_2/Pd$		1	<1
$SiO_2/NEt_2/Pd$	16	97	<1
$SiO_2/NMe_2/Pd$		92	3

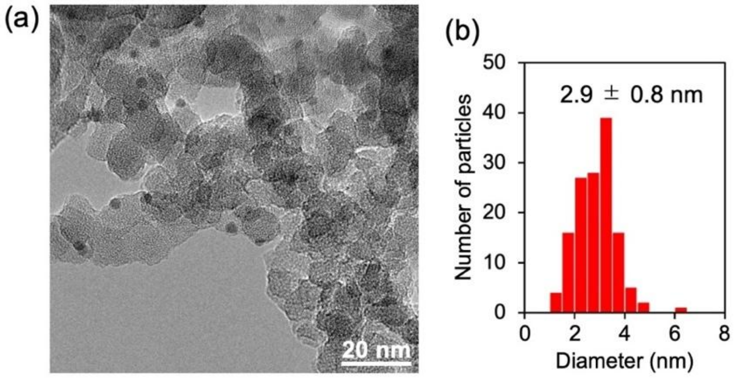


Figure S4 (a) TEM image and (b) size distribution of $SiO_2/NEt_2/Pd$-NPs, which was obtained by heating $SiO_2/NEt_2/Pd$ in isopropanol at 82 °C for 4 h under Ar.

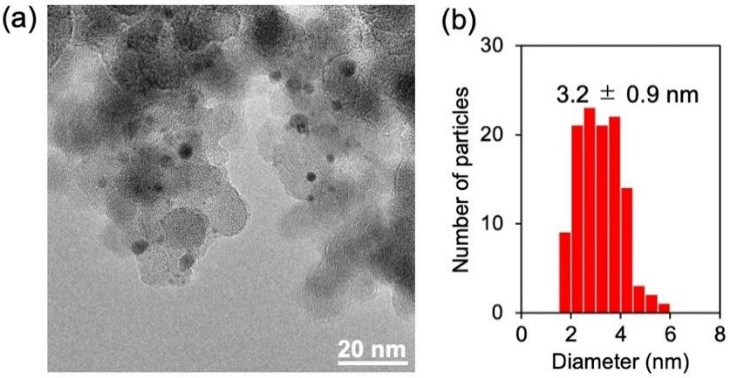


Figure S5. (a) TEM image and (b) size distribution of SiO_2/Pd-NPs.

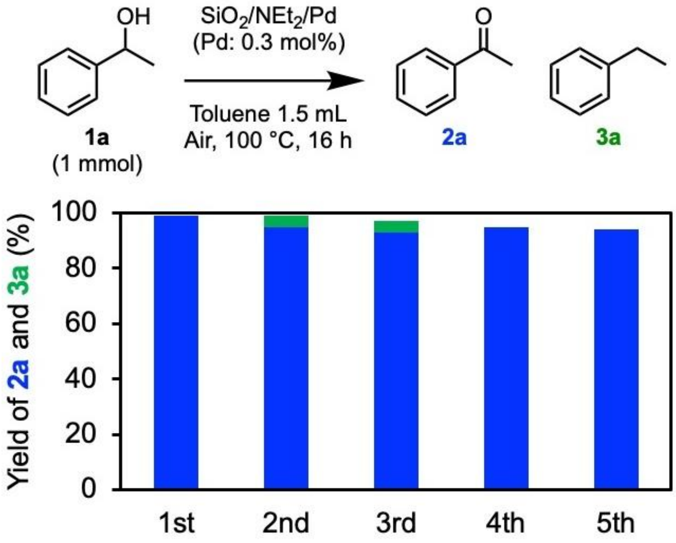


Figure S6. Recyclability of $SiO_2/NEt_2/Pd$.

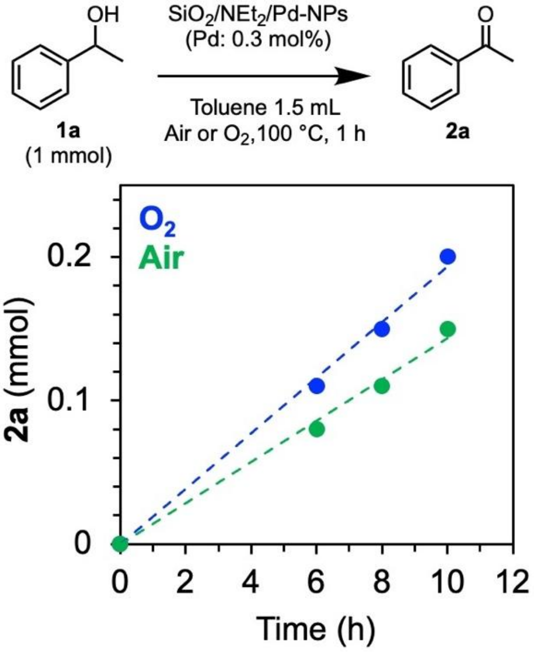


Figure S7. Effect of O_2 pressure.

Table S4 Coordinates of the points plotted in **Figure 5**

Figure 5b

ln([**1a**]/M)	ln{r_0/(mmol min^{-1})}
-1.10	-4.76
-0.405	-4.27
0.288	-3.51

Figure 5c

Time (h)	ln([**1a**]/[**1a**]$_0$)
0	0
0.0500	-0.00401
0.0833	-0.0202
0.167	-0.0834
0.333	-0.198
1	-0.478

Time (h)	ln([**1a-*d***]/[**1a-*d***]$_0$)
0	0
2	-0.145
4	-0.331

Figure 5d

σ_p	log(k_R/k_H)
-0.16 (*p*-OMe)	-0.672
-0.11 (*p*-Me)	-0.828
0 (H)	0
0.17 (*p*-F)	-2.31
0.27 (*p*-Cl)	-2.76

Figure 5e

1/T (K^{-1})	ln(k/min^{-1})
0.00268	-4.38
0.00275	-4.79
0.00283	-6.03
0.00291	-6.68
0.00300	-7.99

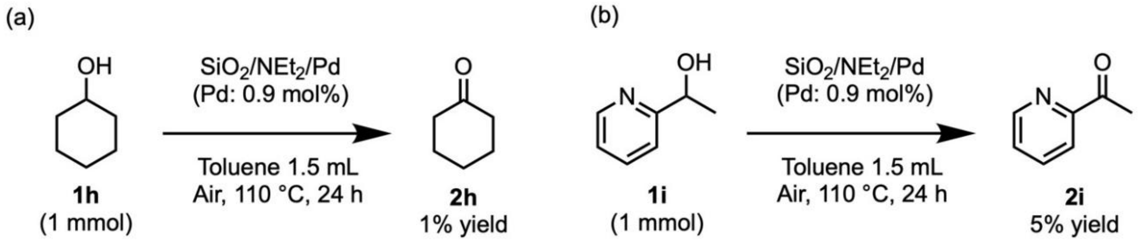


Figure S8. Results of (a) cyclohexanol and (b) 1-(pyridin-2-yl)ethan-1-ol.

Table S5. Representative Pd catalysts for the oxidation of 1-phenylethanol

Catalyst	Temp. (°C)	Time (h)	TON	TOF (h^{-1})	Ref.
SiO$_2$/NEt$_2$/Pd	100	1		177	This work
SiO$_2$/NEt$_2$/Pd	100	24 ×5	1,587		This work
PdHAP-0	160	24	236,000	9,800	Kaneda (2004)[1]
Au-Pd/TiO$_2$	160	0.5		269,000	Hutchings (2006)[2]
Au$_{60}$Pd$_{40}$-PVP/HT	150	24	>682,300	119,260	Ebitani (2013)[3]
Au$_{87}$Pd$_{13}$/LDH	80	1	6,810	6,810	Zhang (2019)[4]
Pd/LDH	80	1	260	260	

[1] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657.

[2] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362.

[3] S. Nishimura, Y. Yakita, M. Katayama, K. Higashimine, K. Ebitani, *Catal. Sci. Technol.* **2013**, *3*, 351.

[4] J. Li, Y. Xu, S. Wang, H. Zhang, *J. Phys. Chem. C* **2019**, *123*, 15483.