

Supplementary Information

Supported Gold Nanoparticles Catalyst for the Selective Oxidation of Silanes to Silanols in Water

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Experimental

1) General

All organic reagents were purified before use. $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ was obtained from N. E. Chemcat Co. Ltd.. GC-FID and GC-MS were performed on Shimadzu GC-2014: Silicone OV-17 (2 m) and Shimadzu GC-17A: URBON Capillary Column HR-1 (30 m \times 0.25 mm \times 0.25 μm). LC was performed on Shimadzu LC-10ADvp: STR ODS-II (150mm \times 4 mm). ^1H and ^{13}C NMR spectra were recorded on JNM-AL400 and 270. HRMS spectra of silanols were recorded on JEOL the MStation JMS-700. X-ray diffraction (XRD) was measured using an X'pert diffractometer (Phillips Co. Ltd.). Inductively coupled plasma measurement was performed by Nippon Jarrell-Ash ICAP-575 Mark II. Au L-edge X-ray absorption spectra were recorded at room temperature using a fluorescence-yield collection technique at the beam line 01B1 station attached with Si (111) monochromator at SPring-8, JASRI, Harima, Japan. Details of data analysis were performed using the REX 2000 program ver. 2.0.4 (RIGAKU). Fourier transformation (FT) of k^3 -weighted EXAFS data was performed to obtain the radial structural function.

2) A typical procedure for the oxidation of triethylsilane by AuHAP: AuHAP (0.10 g, 0.0083 mmol Au) was placed in a Schlenk tube equipped with a reflux condenser. Water (3 mL) and triethylsilane (1.0 mmol) were added, and the reaction mixture was vigorously stirred at 80 °C under air for 2 h. After the oxidation reaction, the product was extracted with diethylether. The yield was determined by GC analysis with naphthalene as an internal standard (Shimadzu GC-2014, carrier gas: N_2 (100 kPa), column: Silicone OV-17 (2 m); oven temperature program: from 100 °C, 6 °C/min up to 220 °C, injection and detection temperature: 270 °C, retention time: triethylsilane (2.9 min), triethylsilanol (4.9 min), standard naphthalene (13.2 min), hexaethylidisiloxane (11.4 min)).

3) Product identification: the products except for tripropylsilanol, tributylsilanol, triisobutylsilanol, trihexylsilanol, dimethylpropenylsilanol, 1,1-dimethylphenylmethylsilanol are commercially available. The products (silanols and disiloxanes) were determined by GC [Silicone OV-17 (2 m); oven temperature program: from 100 °C to 220 °C], GC-MS [URBON Capillary Column HR-1(30 m × 0.25 mm × 0.25 μm); 100 °C (5 min) temperature programmed from 100 °C to 250 °C (30 °C/min); He carrier 1.3 mL/min.], LC [STR ODS-II(150 mm × 4 mm); detection at 254 nm, flow rate 1.0 mL/min, eluent: methanol/water (70 / 30)], NMR, and HRMS. GC and/or LC retention times and ¹H and ¹³C NMR chemical shifts of products agreed with those of authentic samples.

4) Reuse experiment for the oxidation of triethylsilane: Fresh oxidation reaction using triethylsilane (1 mmol), water (3 mL), and AuHAP (0.1 g) was carried out at 80 °C under air condition (See A typical procedure for the oxidation of triethylsilane by AuHAP in 2S). After 2 h, the reaction mixture was cooled to room temperature. Next, diethyl ether was added to the reaction mixture and then, the organic phase containing triethylsilanol was decanted (5 mL × 3). The residual aqueous phase containing AuHAP was subjected to the reuse experiment; another portion of triethylsilane (1 mmol) was successively added into the residual aqueous phase containing AuHAP, followed by stirring under identical conditions.

NMR data

triethylsilanol: CAS registry No. [597-52-4] (Table 2, Entry 1)

Products were determined by GC; retention times: $t_R = 4.9$ min for triethylsilanol and $t_R = 11.4$ min for hexaethyldisiloxane. ¹H NMR and ¹³C NMR were consistent with previously reported values.^{1S,}

tert-butyldimethylsilanol: CAS registry No. [18173-64-3] (Entry 2)

Products were determined by GC; retention times: $t_R = 3.6$ min for *tert*-butyldimethylsilanol and $t_R = 10.2$ min for 1,3-bis(*tert*-butyl)-1,1,3,3-tetramethyl-disiloxane. ^1H NMR (270 MHz, CDCl_3) δ 2.25 (bs, 1H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 25.7, 18.1, -3.5.

tributylsilanol: CAS registry No. [18388-85-4] (Entry 3)

Products were determined by GC; retention times: $t_R = 10.8$ min for tributylsilanol and $t_R = 16.0$ min for hexabutyldisiloxane. ^1H NMR(270 MHz, CDCl_3) δ 1.92 (bs, 1H), 1.26-1.42 (m, 12H), 0.89 (t, 9H, $J = 6.6$ Hz), 0.59 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3) δ 26.6, 25.4, 14.9, 13.8. HRMS (EI) exact mass calcd for ($\text{C}_{12}\text{H}_{28}\text{OSi}$) requires m/z 216.1909, found m/z 216.1886.

trihexylsilanol: CAS registry No. [60782-58-3] (Entry 4)

Products were determined by GC; retention times: $t_R = 14.0$ min for trihexylsilanol. ^1H NMR and ^{13}C NMR were consistent with previously reported values.¹⁵ HRMS (EI) exact mass calcd for ($\text{C}_{18}\text{H}_{40}\text{OSi}$) requires m/z 300.2848, found m/z 300.2834.

triisobutylsilanol: CAS registry No. [317374-14-4] (Entry 5)

Products were determined by GC; retention times: $t_R = 10.0$ min for triisobutylsilanol and $t_R = 15.0$ min for hexaisobutyldisiloxane. ^1H NMR and ^{13}C NMR were consistent with previously reported values.²⁵

triisopropylsilanol: CAS registry No. [17877-23-5] (Entry 6)

Products were determined by GC; retention times: $t_R = 7.1$ min for triisopropylsilanol and $t_R = 12.8$ min for hexaisopropyldisiloxane. ^1H NMR and ^{13}C NMR were consistent with previously reported values.¹⁵ HRMS (EI) exact mass calcd for ($\text{C}_9\text{H}_{22}\text{OSi}$) requires m/z 174.1440, found m/z 174.1425.

tripropylsilanol; CAS registry No. [17888-60-7] (Entry 7)

Products were determined by GC; retention times: $t_R = 7.3$ min for tripropylsilanol and $t_R = 13.5$ min for hexapropyldisiloxane. ^1H NMR (270 MHz, CDCl_3) δ 1.32-1.46 (m, 6H), 0.97 (t, $J = 7.2$ Hz, 9H), 0.56-0.62 (m, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 18.3, 18.0, 16.7. HRMS (EI) exact mass calcd for ($\text{C}_9\text{H}_{22}\text{OSi}$) requires m/z 174.1440, found m/z 174.1430.

dimethylpropenylsilanol: CAS registry No. [64185-05-3] (Entry 8)

Product was determined by GC; retention times: $t_R = 3.2$ min for dimethylpropenylsilanol. ^1H NMR (270 MHz, CDCl_3) δ 5.75-5.91 (m, 1H), 4.87-4.96 (m, 2H), 2.02 (bs, 1H), 1.62 (d, $J = 6.9$ Hz, 2H), 0.16 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 134.5, 114.3, 26.4, 0.0.

cyclohexyldimethylsilanol: CAS registry No. [274676-43-6] (Entry 9)

Product was determined by GC; retention times: $t_R = 7.2$ min for cyclohexyldimethylsilanol and $t_R = 13.1$ min for 1,1,3,3-tetramethyl-1,3-dicyclohexyldisiloxane. ^1H NMR (270 MHz, CDCl_3) δ 1.60-1.74 (m, 5H), 1.01-1.13 (m, 5H), 0.55-0.59 (m, 1H), 0.08 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 27.9, 27.5, 27.0, 26.8, -2.2. HRMS (EI) exact mass calcd for ($\text{C}_8\text{H}_{18}\text{OSi}$) requires m/z 158.1127, found m/z 158.1113.

1,1-dimethylphenylmethylsilanol: CAS registry No. [56633-16-0] (Entry 10)

Products were determined by GC; retention times: $t_R = 9.4$ min for 1,1-dimethylphenylmethylsilanol and $t_R = 16.2$ min for 1,1,3,3-tetramethyl-1,3-bis(phenylmethyl) disiloxane. ^1H NMR (270 MHz, CDCl_3) δ 6.99-7.37 (m, 5H), 2.09 (s, 2H), 0.08 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 145.5, 130.0, 129.8, 125.7, 29.6, 0.0. HRMS (EI) exact mass calcd for ($\text{C}_9\text{H}_{14}\text{OSi}$) requires m/z 166.0814, found m/z 166.0795.

dimethylphenylsilanol: CAS registry No. [5272-18-4] (Entry 11)

Products were determined by GC; retention times: $t_R = 5.1$ min for dimethylphenylsilanol and $t_R = 10.2$ min for 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane; CAS registry No. [56-33-7]. ^1H NMR and ^{13}C NMR were consistent with previously reported values.^{3S, 4S}

diphenylmethylsilanol: CAS registry No. [778-25-6] (Entry 12)

Products were determined by GC; retention times: $t_R = 10.0$ min for diphenylmethylsilanol and $t_R = 20.0$ min for 1,1,3,3-tetraphenyl-1,3-dimethyldisiloxane. ^1H NMR, ^{13}C NMR were consistent with previously reported values.^{3S}

triphenylsilanol: CAS registry No. [791-31-1] (Entries 13 and 14)

Products were determined by LC; retention times: $t_R = 1.9$ min for triphenylsilanol and $t_R = 3.5$ min for hexaphenyldisiloxane. ^1H NMR and ^{13}C NMR were consistent with previously reported values.^{3S}

diphenylsilanediol: CAS registry No. [947-42-2] (Entry 15)

Product was determined by LC; retention times: $t_R = 1.6$ min for diphenylsilanediol. ^1H NMR and ^{13}C NMR were consistent with previously reported values.^{3S}

1,4-bis(hydroxydimethylsilyl) benzene: CAS registry No. [2754-32-7] (Entry 16)

Product was determined by LC; retention times: $t_R = 1.7$ min for 1,4-bis(hydroxydimethylsilyl) benzene. ^1H NMR and ^{13}C NMR were consistent with previously reported values.^{5S}

dimethyl(4-methylphenyl) silanol: CAS registry No. [17920-15-9] (Entry 17)

Products were determined by GC; retention times: $t_R = 6.7$ min for dimethyl(4-methylphenyl) silanol

and $t_R = 11.1$ min for 1,1,3,3-tetramethyl-1,3-bis (4-methylphenyl)disiloxane. ^1H NMR, ^{13}C NMR were consistent with previously reported values.^{6S}

dimethyl(4-methoxyphenyl) silanol: CAS registry No. [22868-26-4] (Entry 18)

Products were determined by GC; retention times: $t_R = 8.1$ min for dimethyl(4-methoxyphenyl) silanol and $t_R = 12.9$ min for 1,1,3,3-tetramethyl-1,3-bis (4-methoxyphenyl)disiloxane. ^1H NMR and ^{13}C NMR were consistent with previously reported values.^{2S}

dimethyl(4-chlorophenyl)silanol: CAS registry No. [18246-04-3] (Entry 19)

Products were determined by GC; retention times: $t_R = 7.6$ min for dimethyl(4-chlorophenyl)silanol and $t_R = 12.2$ min for 1,1,3,3-tetramethyl-1,3-bis(4-chlorophenyl) disiloxane. ^1H NMR and ^{13}C NMR were consistent with previously reported values.^{5S}

Reference

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EXAFS

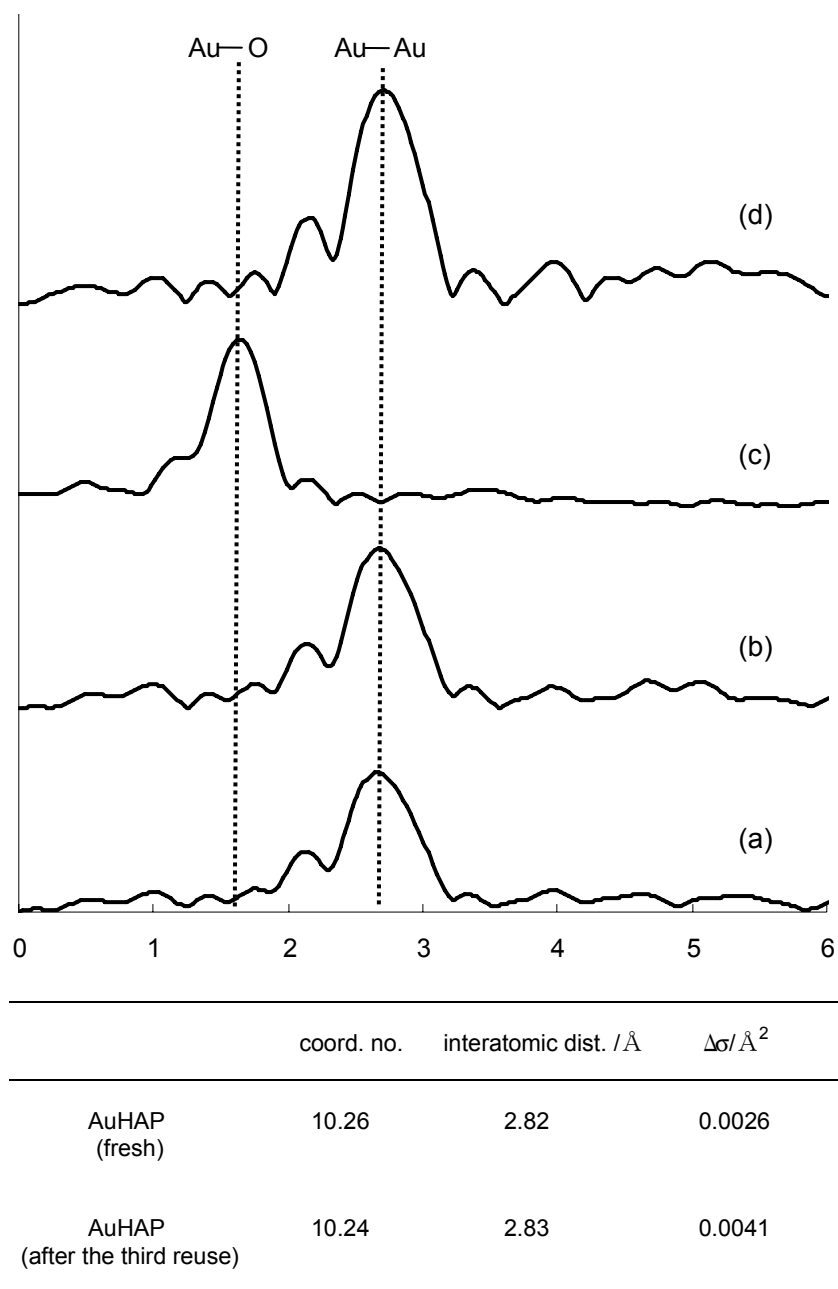


Figure 1S Fourier transformation of k^3 -weighted Au L-edge EXAFS of (a) fresh AuHAP, (b) AuHAP after the third reaction, (c) Au₂O₃, and (d) Au foil.

TEM

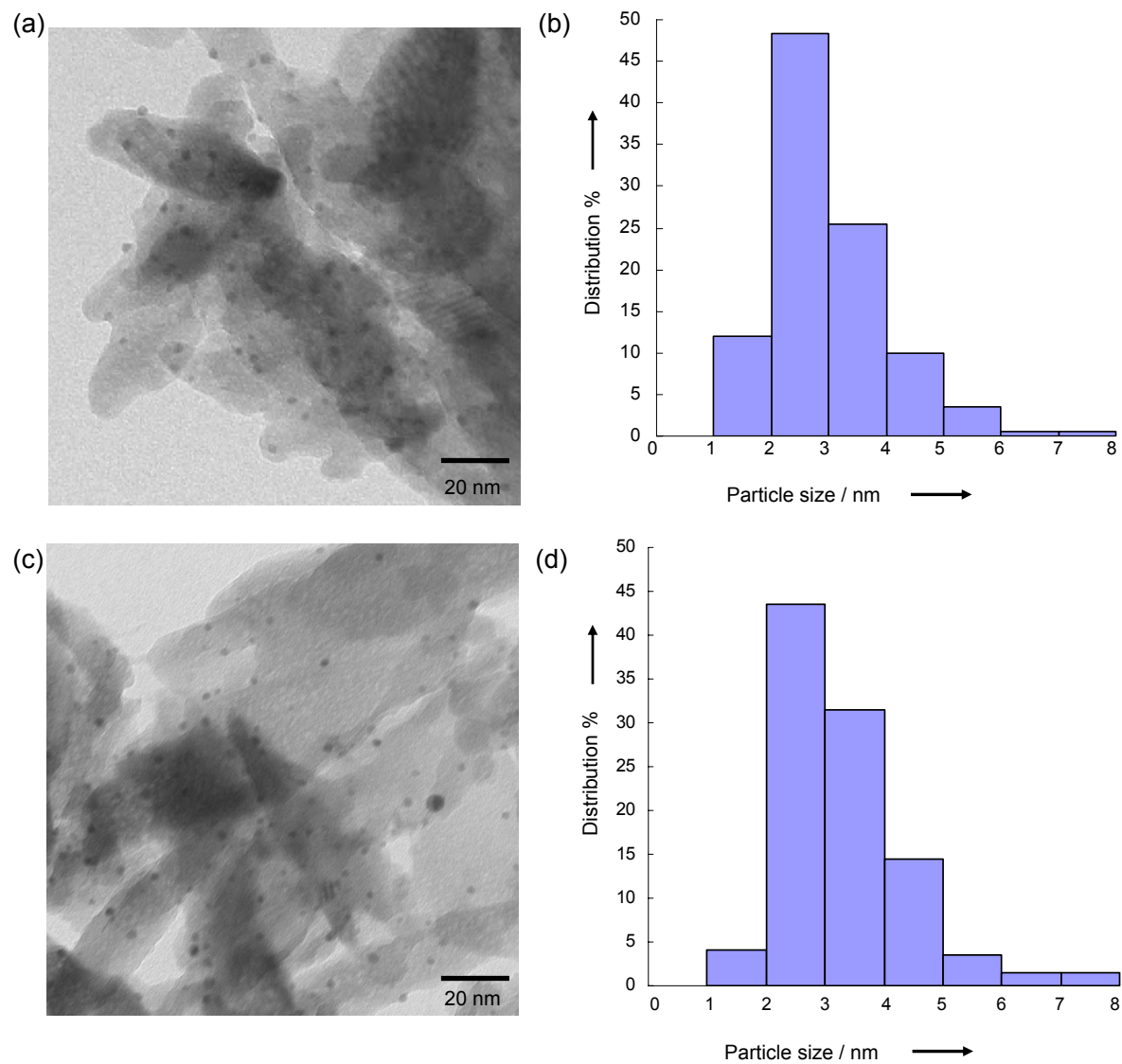


Figure 2S (a) TEM image of AuHAP, and (b) their size distribution diagram.

(c) TEM image of AuHAP after reuse experiment, and (d) their size distribution diagram.