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Supporting Information

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Supported Silver Nanoparticles-Catalyzed Highly Efficient Oxidation of Phenylsilanes to Silanols in Water

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Experimental

1) General

All organic reagents were purified before use. $AgNO_3$ was purchased from Wako Pure Chemical Co. Ltd.. 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. ^{1}H and ^{13}C NMR spectra were recorded on JNM-AL400. IR spectra were recorded on a Horiba FT-720 spectrometer. GC was performed on Shimadzu GC-17A: URBON Capillary Column HR-1 (30 m × 0.25 mm × 0.25 μm). LC was performed on Shimadzu LC-10ADvp: STR ODS-Ⅱ (150 mm × 4 mm). Dielectric absorption curves were recorded on Agilent RF IMPEDANCE/MATERIAL ANALYZER 4291B. Ag K-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) Reaction Procedures

A typical procedure for the oxidation of **1** by the AgHAP catalyst was as follows: AgHAP (0.10 g, 0.03 mmol Ag) was placed in a reaction vessel, followed by addition of water (2 mL) and **1** (1 mmol), and the reaction mixture was vigorously stirred at 80 ^{o}C under Ar for 15 min. After the oxidation reaction, AgHAP was removed by filtration, and the filtrate was concentrated under reduced pressure. The yield was determined by GC analysis with naphthalene as an internal standard (Shimadzu GC-17A, carrier gas: He (100 kPa), column: Shinwa URBON Capillary Column HR-1 (30 m); oven temperature program: from 100 ^{o}C, hold for 5 min, 30 ^{o}C/min up to 250 ^{o}C, hold for 15 min, injection and detection temperature: 320 ^{o}C and 250 ^{o}C, retention time: dimethylphenylsilane (2.9 min), dimethylphenylsilanol (5.1 min), naphthalene (6.3 min), 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (10.2 min)).

Product purification: after the oxidation reaction, AgHAP was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was subjected to silica gel column (Wakogel C-200), and eluted by a mixture of EtOAc and hexane (30:1).

Product identification: the products except for ethenylmethylphenylsilanol are commercially available. The products(monomers and dimmer) were determined by GC-MS [URBON Capillary Column HR-1(30 m × 0.25 mm × 0.25 μm); 100 ^{o}C (5 min) temperature programmed at 100 ^{o}C to 250 ^{o}C (30 ^{o}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: acetonitrile], NMR, and HRMS. GC and/or LC retention times and ^{1}H and ^{13}C NMR chemical shifts of products agreed with those of authentic samples and also with the reported data for ethenylmethylphenylsilanol.

Table 2, Entry 1

Products were determined by GC; retention times: t_R = 5.1 min for dimethylphenylsilanol; CAS registry No. [5272-18-4] and t_R = 10.2 min for 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane; CAS registry No. [56-33-7]. ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[1, 2]

Entry 2

Products were determined by GC; retention times: t_R = 6.7 min for dimethyl (4-methylphenyl)silanol; CAS registry No. [17920-15-9] and t_R = 11.1 min for 1,1,3,3-tetramethyl-1,3-bis (4-methylphenyl)disiloxane. ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[3]

Entry 3

Products were determined by GC; retention times: t_R = 8.1 min for dimethyl (4-methoxyphenyl)silanol; CAS registry No. [22868-26-4] and t_R = 12.9 min for 1,1,3,3-tetramethyl-1,3- bis(4-methoxyphenyl)disiloxane ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[1]

Entry 4

Products were determined by GC; retention times: t_R = 7.6 min for dimethyl(4-chlorophenyl)silanol; CAS registry No. [18246-04-3] and t_R = 12.2 min for 1,1,3,3-tetramethyl-1,3-bis(4-chlorophenyl)disiloxane.dimethyl(4-chlorophenyl)silanol

: ^{1}H NMR (400MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.54 Hz, 2H), 7.35 (d, *J* = 8.54 Hz, 2H), 2.16 (bs, 1H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.50, 136.08, 134.56, 128.26, 0.30.

Entry 5

Products were determined by GC; retention times: t_R = 6.6 min for ethenylmethylphenylsilanol; CAS registry No. [187389-44-2] and t_R = 10.9 min for 1,3-diethenyl-1,3-dimethyl-1,3-diphenyldisiloxane. ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[4]

Entry 6

Products were determined by GC; retention times: t_R = 10.0 min for diphenylmethylsilanol; CAS registry No. [778-25-6] and t_R = 20.0 min for 1,1,3,3-tetraphenyl-1,3-dimethyldisiloxane. ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[1]

Entry 7

Products were determined by LC; retention times: t_R = 1.9 min for triphenylsilanol; CAS registry No. [791-31-1] and t_R = 3.5 min for hexaphenyldisiloxane. ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[1]

Entry 8

Product was determined by LC; retention times: t_R = 1.6 min for diphenylsilanediol; CAS registry No. [947-42-2]; melting point 140 ^{o}C; HRMS(EI) exact mass calcd for ($C_{12}H_{12}O_2Si$) requires *m/z* 216.0607, found *m/z* 216.0593; ^{1}H NMR, ^{13}C NMR were consistent with previously reported values.[1]

Entry 9

Product was determined by LC; retention times: t_R = 1.7 min for 1,4-bis(hydroxydimethylsilyl)benzene; CAS registry No. [2754-32-7]; melting point 137 ^{o}C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.52 (s, 4H), 5.84 (bs, 2H), 0.23 (s, 12H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 141.05, 131.83, 0.50; HRMS(EI) exact mass calcd for ($C_{10}H_{18}O_2Si_2$) requires *m/z* 226.0845, found *m/z* 226.0826.

References

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(3) S. E. Denmark, J. M. Kallemeyn, *Org. Lett.* **2003**, *5*, 3483.
(4) K. Hirabayashi, E. Takahisa, Y. Nishihara, A. Mori, T. Hiyama, *Bull. Chem. Soc. Jpn.*, **1998**, *71*, 1677.

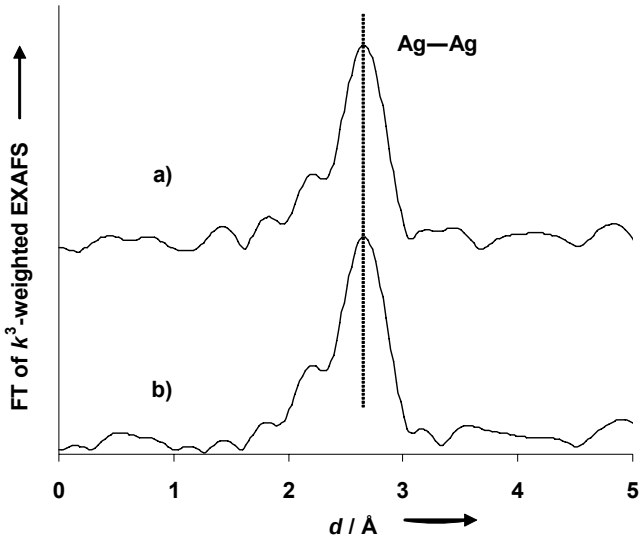

Figure 1S. Fourier transforms of k^3-weighted Ag K-edge EXAFS experimental data for a) AgHAP and b) Ag foil.

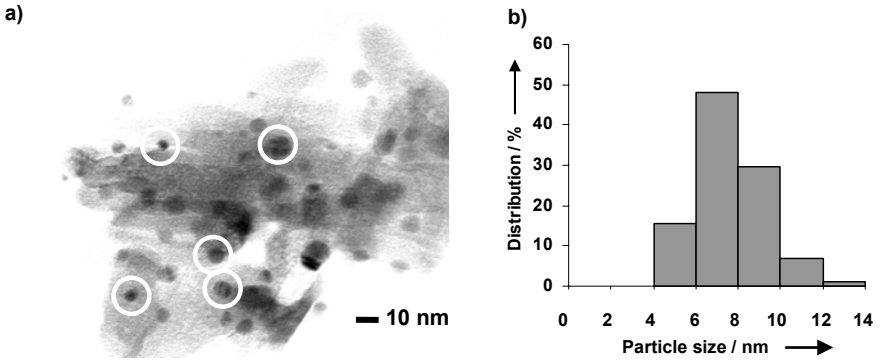

Figure 2S. a) TEM image of AgHAP, b) size distribution diagram of the Ag nanoparticles of AgHAP.

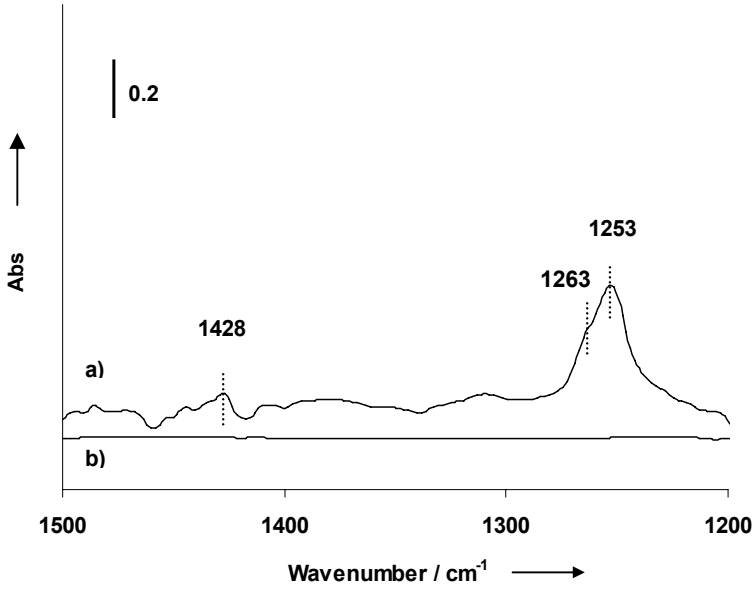

Figure 3S. FTIR spectra of a) **1** and b) **4** adsorbed on AgHAP.

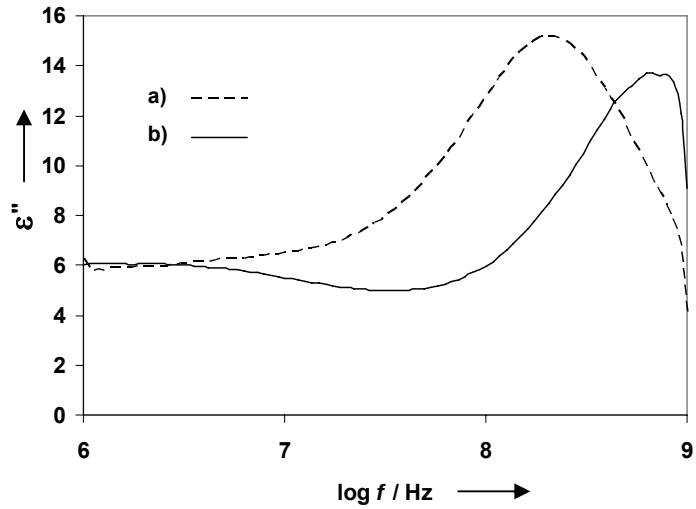

Figure 4S. Dielectric absorption curves of the water mixtures of a) AgHAP and b) HAP.