

Supplementary Information

Supported Silver Nanoparticle Catalyst for Selective Hydration of Nitriles to Amides in Water

1) General

All organic reagents were purified before use. AgNO₃ and HAP were purchased from Wako Pure Chemical Industries, Ltd. Activated carbon (Shirasagi C) was obtained from Japan EnviroChemicals, Ltd. MgO (MgO #1000) was purchased from Tateho Chemical Industries Co., Ltd. SiO₂ (JRC-SIO-6) and TiO₂ (JRC-TIO-4) were obtained from the Catalysis Society of Japan as reference catalysts. Powder X-ray diffraction (XRD) was measured using an X'pert diffractometer (Philips Co. Ltd.). Inductively coupled plasma (ICP) spectroscopy was performed using a Nippon Jarrell-Ash ICAP-575 Mark II. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-AL400. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum One spectrometer. Gas chromatography (GC-FID) was performed on a Shimadzu GC-2014 equipped with a KOCL-3000T column (3 m). High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-10ADvp: STR ODS-II (150×4 mm). Dielectric absorption curves were recorded on an 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, Japan Atomic Energy Research Institute (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 extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function.

2) Characterization of AgHAP

Elemental analysis showed that the Ca/P ratio of AgHAP remained at 1.68 and the Ag loading was 3.3 wt%. The UV-vis analysis revealed a plasmon peak at 414 nm, indicating that the diameter of the Ag NPs was in the range of 6-8 nm. Ag K-edge X-ray absorption spectra and transmission electron microscopy (TEM) showed that Ag nanoparticles with a mean diameter of 7.6 nm and a narrow size distribution with a standard deviation of 1.8 nm were formed on the surface of the HAP support. Other Ag solid catalysts were synthesized by impregnating solids with an aqueous solution of silver nitrate followed by evaporation to dryness at 110 °C and by calcination in air at 500 °C for 4 h. The obtained powders were treated with an aqueous solution of KBH_4 , filtered, washed with deionized water, and dried at room temperature *in vacuo* to provide solid-supported Ag nanoparticles. The mean diameters (d) and standard deviations (σ) of Ag particles of Ag/C, Ag/MgO, Ag/SiO₂, and Ag/TiO₂ were $d = 43 \text{ \AA}$ ($\sigma = 28.5 \text{ \AA}$), 31 \AA ($\sigma = 24 \text{ \AA}$), 16 \AA ($\sigma = 5.9 \text{ \AA}$), and 13 \AA ($\sigma = 4.9 \text{ \AA}$), respectively.

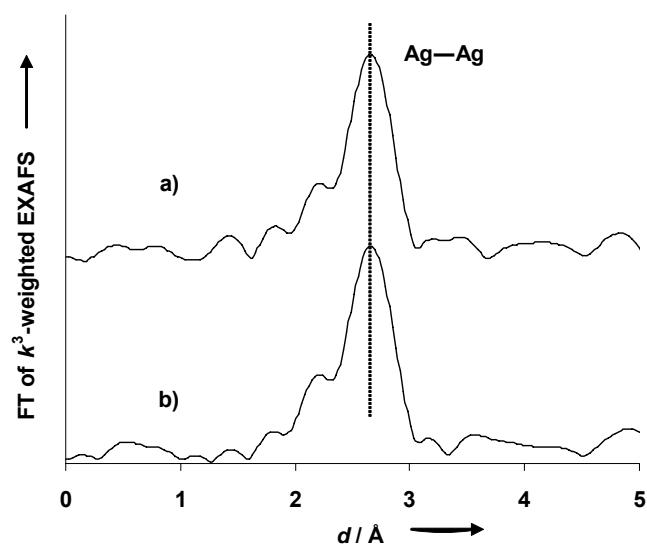


Figure 1S. Fourier transforms of k^3 -weighted Ag K-edge EXAFS experimental data for a) AgHAP and b) Ag foil.

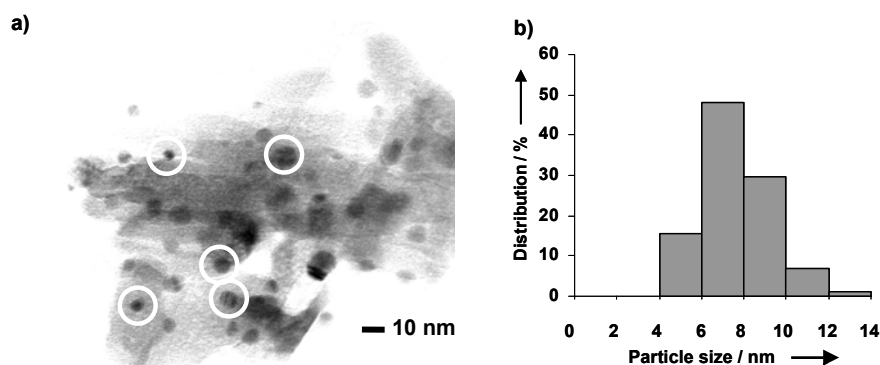


Figure 2S. a) TEM image of AgHAP, and b) size distribution diagram of the Ag nanoparticles of AgHAP.

3) General reaction procedures

A typical procedure for the hydration of **1** using the AgHAP catalyst was as follows: AgHAP (0.10 g, 0.03 mmol Ag) was placed in a heavy-wall pressure tube (ACE GLASS, ϕ 25 mm, 10 cm), followed by the addition of water (3 mL) and **1** (1 mmol), and the reaction mixture was vigorously stirred at 140 °C for 3 h under Ar. After the hydration reaction, AgHAP was removed by filtration at 90 °C, and the filtrate was cooled to 0 °C, and white crystals were precipitated from the filtrate. The crystalline product was obtained by simple filtration and dried *in vacuo* at room temperature to give analytically pure benzamide in a 94% yield.

4) Recycle experiments of pyrazinecarbonitrile

The first run was carried out under the identical conditions as described in Table 2, entry 8. After the hydration, the spent AgHAP could be easily separated from the reaction mixture by a filtration and the isolated AgHAP was washed with deionized water prior to reuse. These recycling procedures were repeated four times in the same manner. Time profile of 4th reuse experiment is shown in Figure 3S.

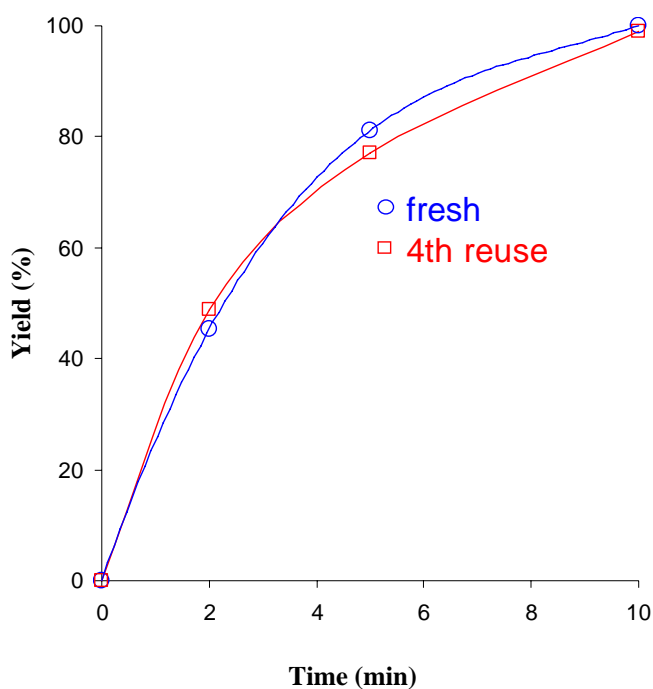


Figure 3S. Time profile of hydration of pyrazinecarbonitrile.

5) Product identification: All products, except for 3-quinolinecarboxamide, were commercially available. The yields of products were determined by HPLC [STR ODS-II (150×4 mm); detection at 254 nm, flow rate 1.0 mL/min, eluent: a mixture of acetonitrile and water (3:7)]. Gas chromatography (GC) and/or LC retention times and ^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) chemical shifts of products were in agreement with those of authentic samples and also with the reported data for 3-quinolinecarboxamide.

Benzamide (Table 1, Entry 1)

CAS registry No. [55-21-0]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

2-Chlorobenzamide (Table 1, Entry 2)

CAS registry No. [609-66-5]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.²

3-Chlorobenzamide (Table 1, Entry 3)

CAS registry No. [618-48-4]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.³

4-Chlorobenzamide (Table 1, Entry 4)

CAS registry No. [619-56-7]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

4-Fluorobenzamide (Table 1, Entry 5)

CAS registry No. [824-75-9]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

4-Nitrobenzamide (Table 1, Entry 6)

CAS registry No. [619-80-7]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

4-Acetylbenzamide (Table 1, Entry 7)

CAS registry No. [67014-02-2]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.⁴

4-Methoxybenzamide (Table 1, Entry 8)

CAS registry No. [3424-93-9]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

3-Methylbenzamide (Table 1, Entry 10)

CAS registry No. [618-47-3]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.⁵

4-Methylbenzamide (Table 1, Entry 11)

CAS registry No. [619-55-6]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

2-Naphthamide (Table 1, Entry 12)

CAS registry No. [2243-82-5]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.⁶

Cinnamamide (Table 1, Entry 13)

CAS registry No. [621-79-4]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

Picolinamide (Table 2, Entry 1)

CAS registry No. [1452-77-3]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.⁴

Nicotinamide (Table 2, Entry 2)

CAS registry No. [98-92-0]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

Isonicotinamide (Table 2, Entry 3)

CAS registry No. [1453-82-3]; ^1H NMR (400 MHz, $\text{d}_6\text{-DMSO}$) δ 8.70 (d, $J = 5.86$ Hz, 2H), 8.21 (bs, 1H), 7.75 (d, $J = 6.10$ Hz, 2H), 7.68 (bs, 1H); ^{13}C NMR (100 MHz, $\text{d}_6\text{-DMSO}$) δ 166.06, 149.94, 141.08, 121.17.

3-Quinolincarboxamide (Table 2, Entry 4)

CAS registry No. [6480-67-7]; melting point 198-199 °C; ^1H NMR were consistent with previously reported values.⁹ ^{13}C NMR (100 MHz, $\text{d}_6\text{-DMSO}$) δ 166.25, 148.92, 148.28, 135.52, 130.90, 128.88, 128.54, 127.10, 126.70, 126.34.

2-Furamide (Table 2, Entry 5)

CAS registry No. [609-38-1]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.¹

5-Methyl-2-furamide (Table 2, Entry 6)

CAS registry No. [99968-74-8]; ^1H NMR (400 MHz, $\text{d}_6\text{-DMSO}$) δ 7.57 (bs, 1H), 7.19 (bs, 1H), 6.97 (d, $J = 3.42$ Hz, 1H), 6.21 (d, $J = 3.42$ Hz, 1H), 2.31 (s, 3H); δ ^{13}C NMR (100 MHz, $\text{d}_6\text{-DMSO}$) δ 159.19, 153.96, 146.31, 114.52, 107.90, 13.40.

2-Thiophenecarboxamide (Table 2, Entry 7)

CAS registry No. [5813-89-8]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.⁴

Pyrazinecarboxamide (Table 2, Entry 8-13)

CAS registry No. [98-96-4]; ^1H NMR, ^{13}C NMR were consistent with previously reported values.⁸

6) Hydration of benzonitrile using Ag catalyst on various supports

Table 1S. Hydration of benzonitrile using Ag catalyst on various supports ^[a]

Entry	Catalyst	Conversion of benzonitrile [%]	Selectivity for benzamide [%]
1	AgHAP	99	>99
2	Ag/TiO ₂	93	72 ^[b]
3	Ag/MgO	59	59
4	Ag/SiO ₂	30	37
5	Ag/C	30	40
6	Ag ⁰ powder	2	>99
7 ^[c]	AgHAP	14	>99
8	HAP	n.r.	-

[a] Reaction conditions: benzonitrile (1 mmol), catalyst (Ag 0.03 mmol), water (3 mL), 140 °C, 3 h. [b] Benzoic acid was formed as a by-product. [c] Unreduced AgHAP was used.

7) Dielectric absorption curves of AgHAP and HAP in water

Microwave dielectric studies on the dynamics of water demonstrated the relaxation peak of water in AgHAP appeared at a lower frequency than that in HAP, providing that H₂O interacts strongly with the surface of the Ag nanoparticles to generate a nucleophilic OH⁻ species.⁹

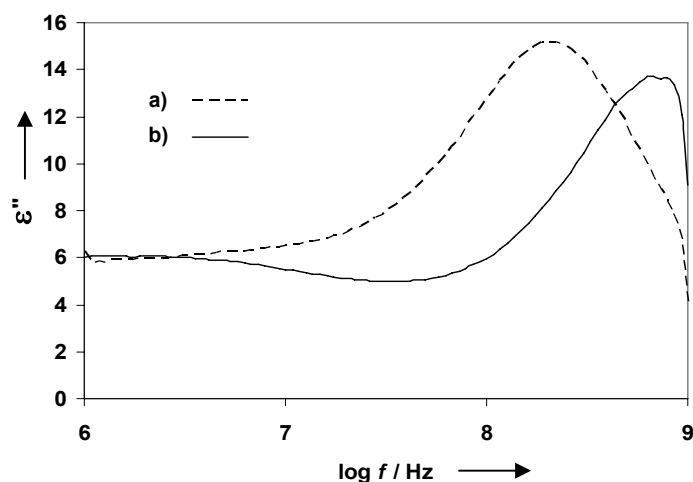


Figure 4S. Dielectric absorption curves of a) AgHAP and b) HAP in water.

8) FTIR spectra of **1**, **3** and **4** adsorbed on AgHAP

The hydrations of **1**, **3**, and **4** using AgHAP were examined using Fourier transform infrared (FTIR) spectroscopy. The bands assigned to C≡N stretching vibrations of **1**, **3**, and **4** shifted from 2230, 2236, and 2247 cm^{-1} to 2247, 2259, and 2261 cm^{-1} , respectively, after the adsorption of them onto AgHAP at 1 Torr. Band-shifts to 1591, 1574, 1490, 1437 cm^{-1} for pyridyl ring skeletal vibrations of **3** were observed with respect to the molecule in the liquid phase.

9) FTIR study of the interaction between the AgHAP and nitriles

During the treatment of the above nitriles **1**, **3**, and **4** onto AgHAP with water vapor at 298 K, time-resolved FTIR spectra was measured every 5 min (Figure 5S-8S).

Decrease of C≡N stretching vibration (2259 cm^{-1})

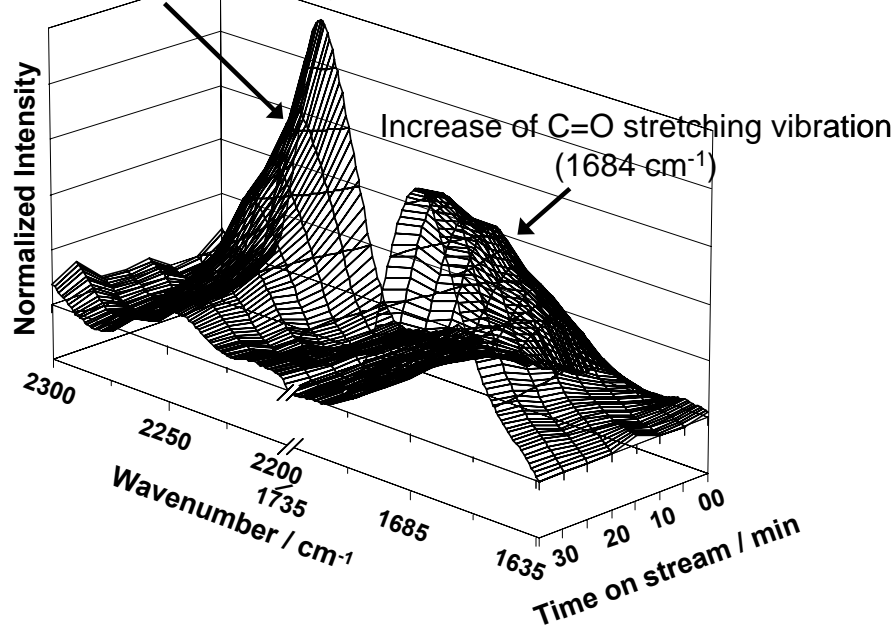


Figure 5S. Time-resolved FTIR spectra of 3 adsorbed on AgHAP.

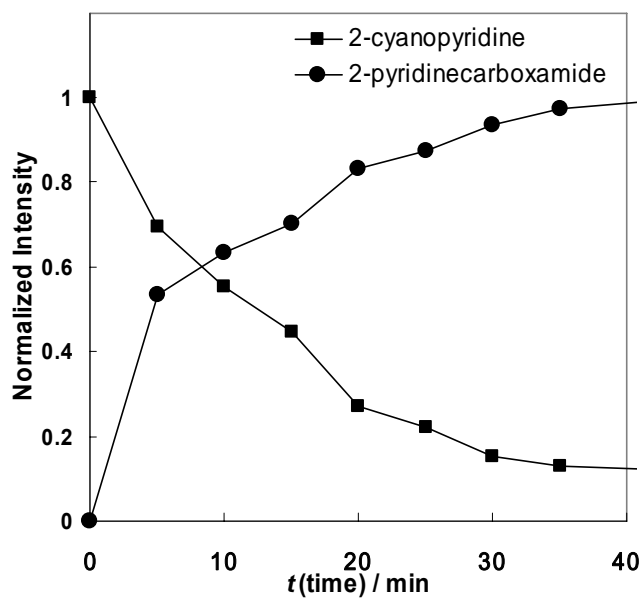


Figure 6S. Decrease of 3 and increase of 2-pyridinecarboxamide adsorbed on AgHAP. For comparison, the bands were normalized using the corresponding calculated intensities.

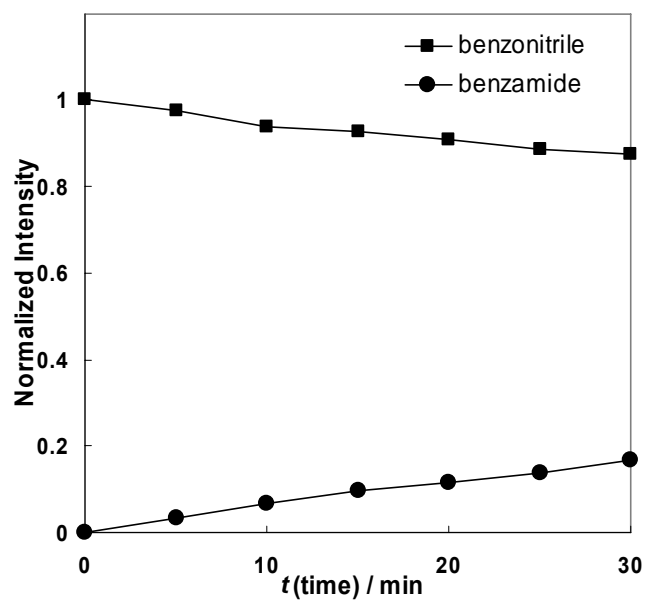


Figure 7S. Decrease of 1 and increase of benzamide adsorbed on AgHAP. For comparison, the bands were normalized using the corresponding calculated intensities.

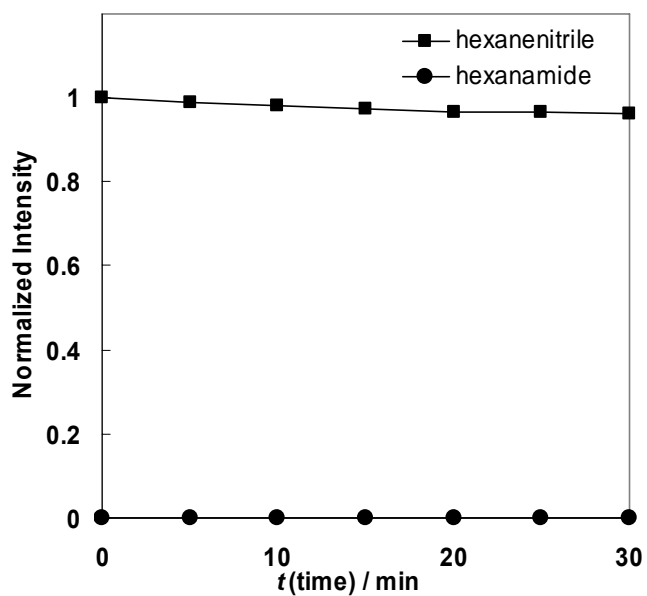


Figure 8S. Decrease of 4 and increase of hexanamide adsorbed on AgHAP. For comparison, the bands were normalized using the corresponding calculated intensities.

10) Hammett plots for the competitive reaction of benzonitrile and *p*-substituted benzonitrile using AgHAP

The effect of the substituent on reactivity; a ρ value of 1.69 in a Hammett plot with σ^+ value, supports the formation of a negatively charged transition state.¹⁰

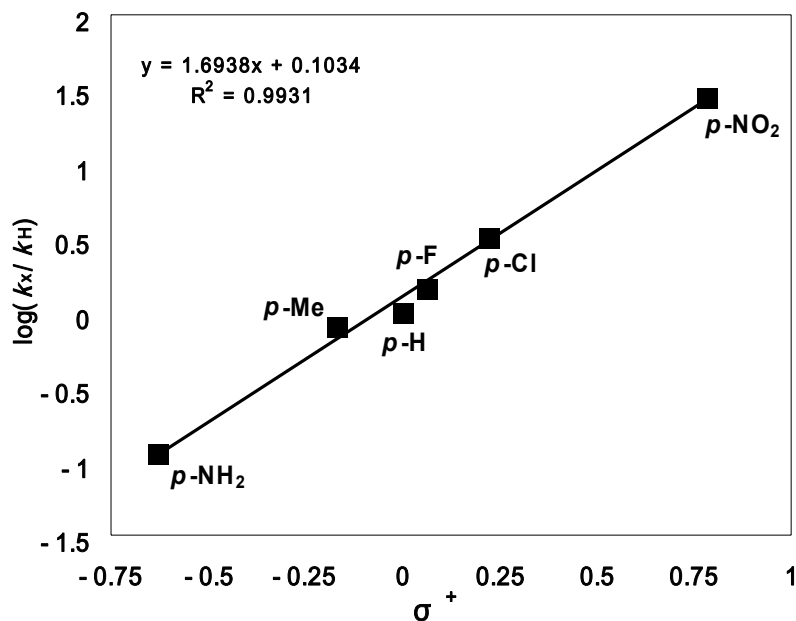


Figure 9S. Hammett plots for the competitive reaction of benzonitrile and *p*-substituted benzonitrile. The reaction conditions were as follows; benzonitrile (0.5 mmol), *p*-substituted benzonitrile (0.5 mmol), AgHAP (Ag:0.03 mmol), water (3 mL), 140 °C.

References

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