Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Conversion of 5-Hydroxymethylfurfural to a Cyclopentanone Derivative by Ring Rearrangement over Supported Au Nanoparticles

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Material.

Nb_2O_5 was obtained by calcination of niobium oxalate supplied from CBMM at 773 K under air. TiO_2 (JRC-TIO-8), Al_2O_3 (JRC-ALO-8), CeO_2 (Rhodia), ZrO_2 (JRC-ZRO-5), and silica-alumina (JRC-SAH-1, denoted as SA) were supplied from the committee of reference catalyst, Catalysis society of Japan. Hydrotalcite (denoted as HT) was obtained from Kyowa Chemical Industry Co. Ltd. La_2O_3, $HAuCl_4$, H_2PtCl_6, $RuCl_3$, and NaOH were purchased from Kishida Chemical Co., Ltd. 2,5-Hydroxymethylfurfural (HMF) was obtained from Tokyo Chemical Industry Co., Ltd.

Catalyst preparation.

Supported Au catalysts were prepared by deposition-precipitation method. A 1 M NaOH aqueous solution was added dropwise to a suspension of supports (0.99 g) in 50 mL of 1 mM $HAuCl_4$ aqueous solution, and the pH of the solution was adjusted to ca. 7. The suspension was stirred at 343 K for 1 h, followed by centrifugation. The resulting residue was washed with ca. 40 mL of water and centrifuged. The washing process was repeated 5 times. The resulting powder was dried at 353 K, and calcined under air at 573 K to prepare various metal oxides supported Au catalysts.

As references, Pt/Nb_2O_5 and Pd/Nb_2O_5 was prepared by impregnation method to be 1wt% of metal loading by using H_2PtCl_6 and $Pd(NO_3)_2$ as metal precursor. After the suspension containing metal precursor and Nb_2O_5 in water was stirred under 343 K for 1h, the suspension was evaporated to dryness. Resulting powder was dried at 353 K, and calcined at 573 K under air. Ru/Nb_2O_5 was prepared in the same method as Au/Nb_2O_5 using $RuCl_3$ as a precursor. To a suspension of Nb_2O_5 (0.99 g) in 50 mL of 2 mM $RuCl_3$ aqueous solution, A 1 M NaOH aqueous solution was added dropwise to adjust the pH of the solution to ca. 7. The suspension was stirred at 343 K for 1 h. After centrifugation, the residue was washed with ca. 40 mL of water. The washing process was repeated 5 times. The resulting powder was dried at 353 K, and then calcined under air at 573 K.

Catalytic test.

In a typical reaction, 3 mL of 0.067 M HMF aqueous solution and 10 mg of a supported catalyst were added to an autoclave with a gas in- and outlet (30mL, Taiatsu Techno Co., TVS-1 type). Prior to the reaction, the catalysts were pretreated under H_2 at 473 K and subsequently under O_2 at 473 K. The reaction was conducted under 8 MPa of H_2 at 413 K, after 5 times of replacement of air in an autoclave by ca. 1 MPa of H_2. Sample analysis was performed using a gas chromatograph (SHIMADZU GC-14A) equipped with FID with Ultra ALLOY$^+$-5 capillary column (Frontier Laboratories Ltd.). Products were identified by using a NMR spectrometer (Varian, INOVA-500, 500 MHz) and GC-MS (SHIMADZU-QP5000). Prior to the NMR analysis, the products were purified by column chromatography on silica gel eluted with ethyl acetate or ethyl acetate/methanol (10:1).

Reaction of BHF under N_2

We checked the reaction of BHF over Au/Nb_2O_5 under N_2 (BHF: 3 mL aqueous solution, 0.067 M; Temp.: 413 K; Time: 4 h). As a result, 63% yield of HCPEN was obtained. This result supports Scheme 1.

Recycle test.

After the reaction using Au/Nb_2O_5, the suspension was filtered off, and the residue was washed with 20 mL of acetone. This washing process was repeated 3 times, and also operated with 20 mL of water. After the dryness at 353 K, the resulting Au/Nb_2O_5 powder was pretreated and applied to the reaction as described above.

Catalyst characterization.

Au L_3 edge XAFS measurement was carried out on the BL9C beamline of the Photon Factory (2.5 GeV) with a Si(111) two-crystal monochromator. The XAFS spectra of supported Au catalysts were recorded in fluorescence mode using a Lytle detector, and those of Au foil and Au_2O_3 references in transmission mode. The X-ray energy was calibrated with a spectrum of Cu foil at 8980 eV. Data reduction of XAFS spectra was performed using REX2000 program Ver. 2.5.9 (Rigaku Co.). Curve-fitting of the Fourier-filtered EXAFS spectra was performed using ab initio-calculated phases and amplitudes from the program FEFF 8.

FT-IR spectra were recorded on a JASCO FT/IR-6100 (JASCO Co.) with a 4 cm^{-1} of resolution. A supported Au catalyst (30-50 mg) was pressed into a wafer with 20 mm diameter. The wafer was pretreated under 10%O_2/Ar flow (100 mL min^{-1}) at 473 K for 30 min, and then exposed to pyridine vapor (12.4 μmol) under Ar flow (90 mL min^{-1}) at 423 K to investigate the acidity of Au catalyst.

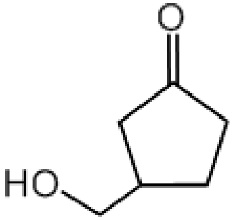
Au/Nb_2O_5 before and after the reaction for 12 h were observed using HITACHI H-800 transmission electron microscope operated at 200 kV.

The loading amount of supported Au catalysts was determined using an inductively-coupled plasma (ICP) spectrometer (Thermo Jarrel Ash IRIS/AP).

Table S1. The Au loading of various supported Au catalysts determined by ICP.

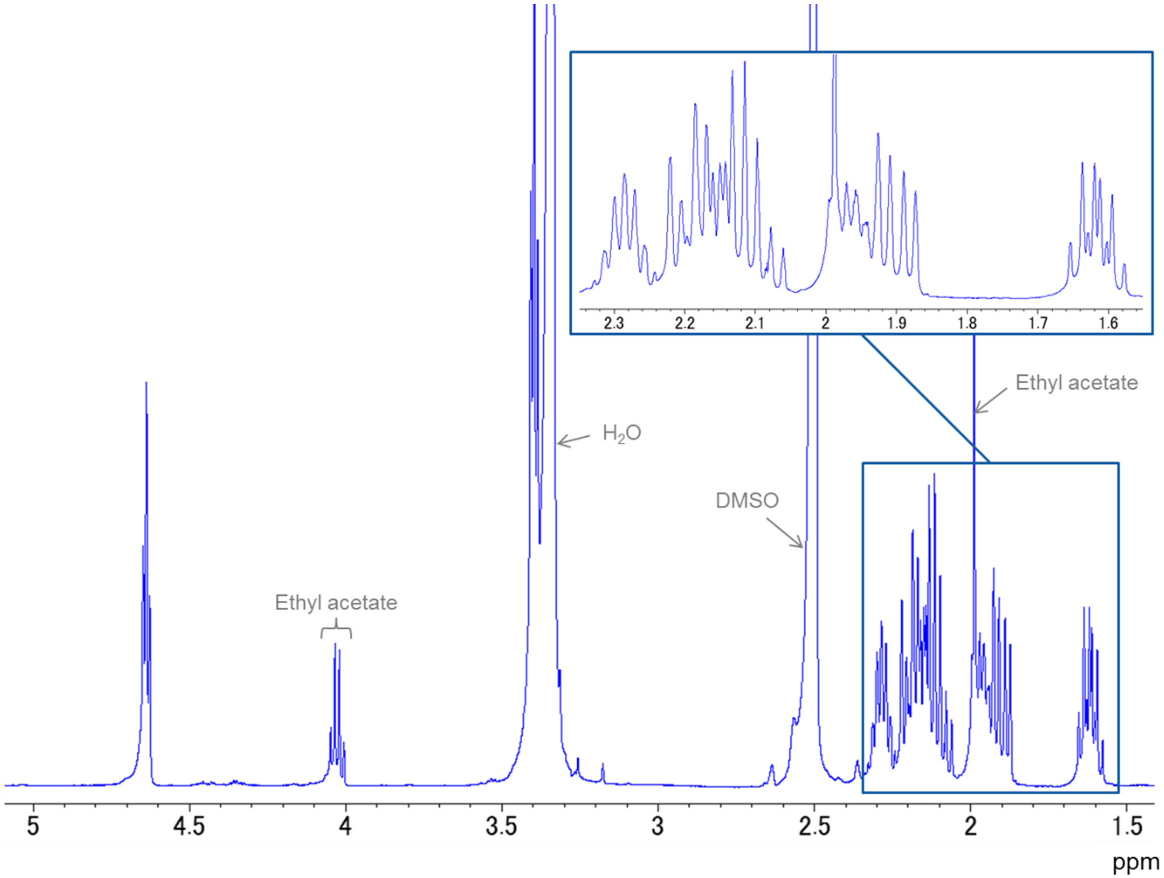
Catalyst	Au loading (wt%)
Au/Nb_2O_5	0.56
Au/ Nb_2O_5 after catalytic test for 12 h	0.56
Au/Al_2O_3	0.60
Au/ZrO_2	0.70
Au/TiO_2	0.77
Au/SA	0.28
Au/La_2O_3	0.70
Au/CeO_2	0.69
Au/HT	0.60

HCPN

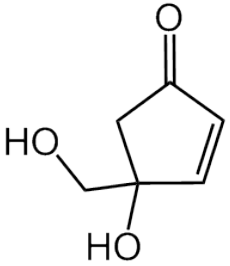


GC-MS: m/z = 114 $[M]^+$

NMR chart (DMSO-d6, 500 MHz)

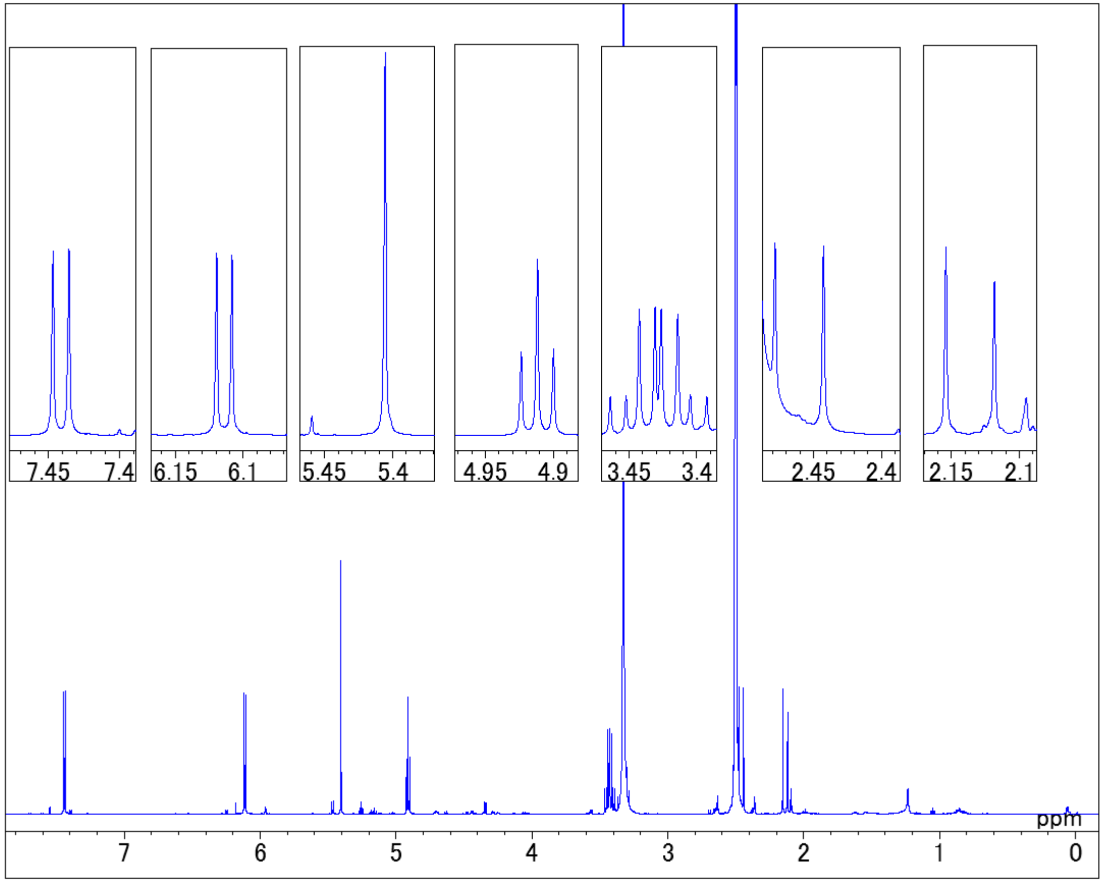


HCPEN

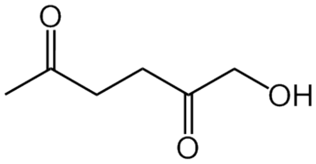


GC-MS: m/z = 128 $[M]^+$

NMR chart (DMSO-d6, 500 MHz)

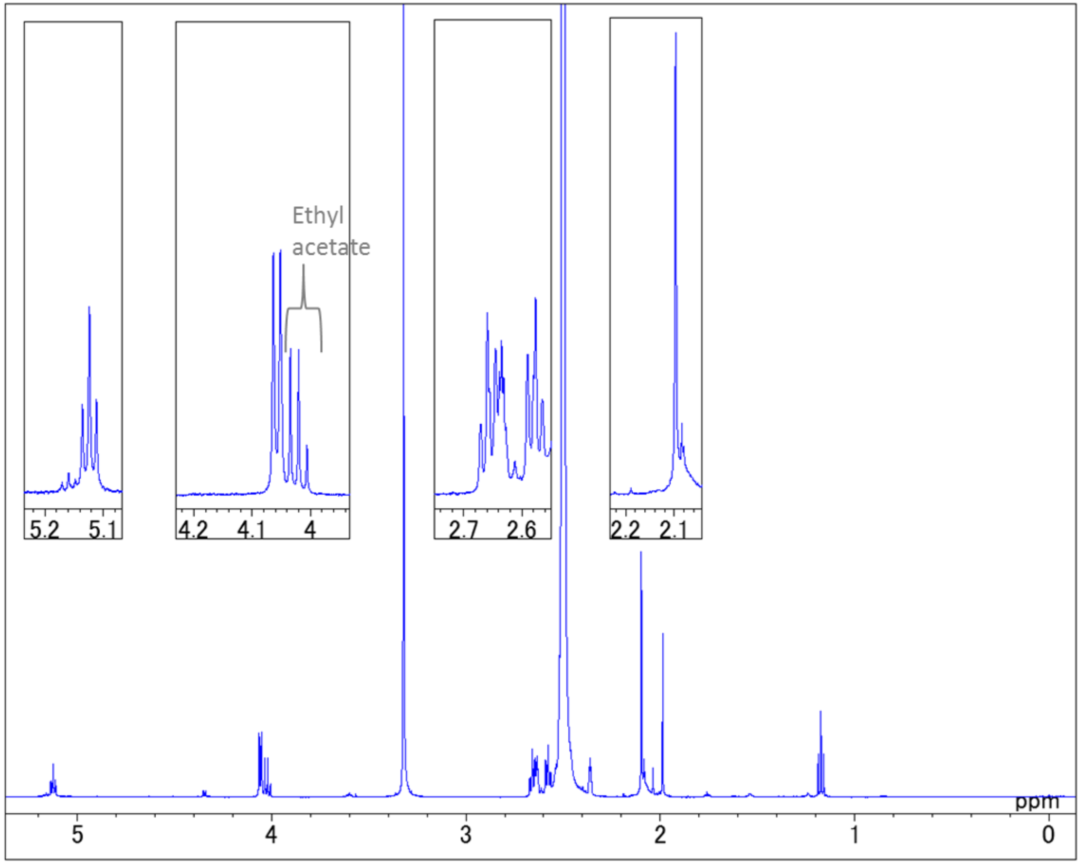


HHD

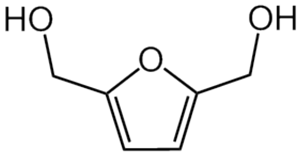


GC-MS: m/z = 131 $[M+H]^+$

NMR chart (DMSO-d6, 500 MHz)

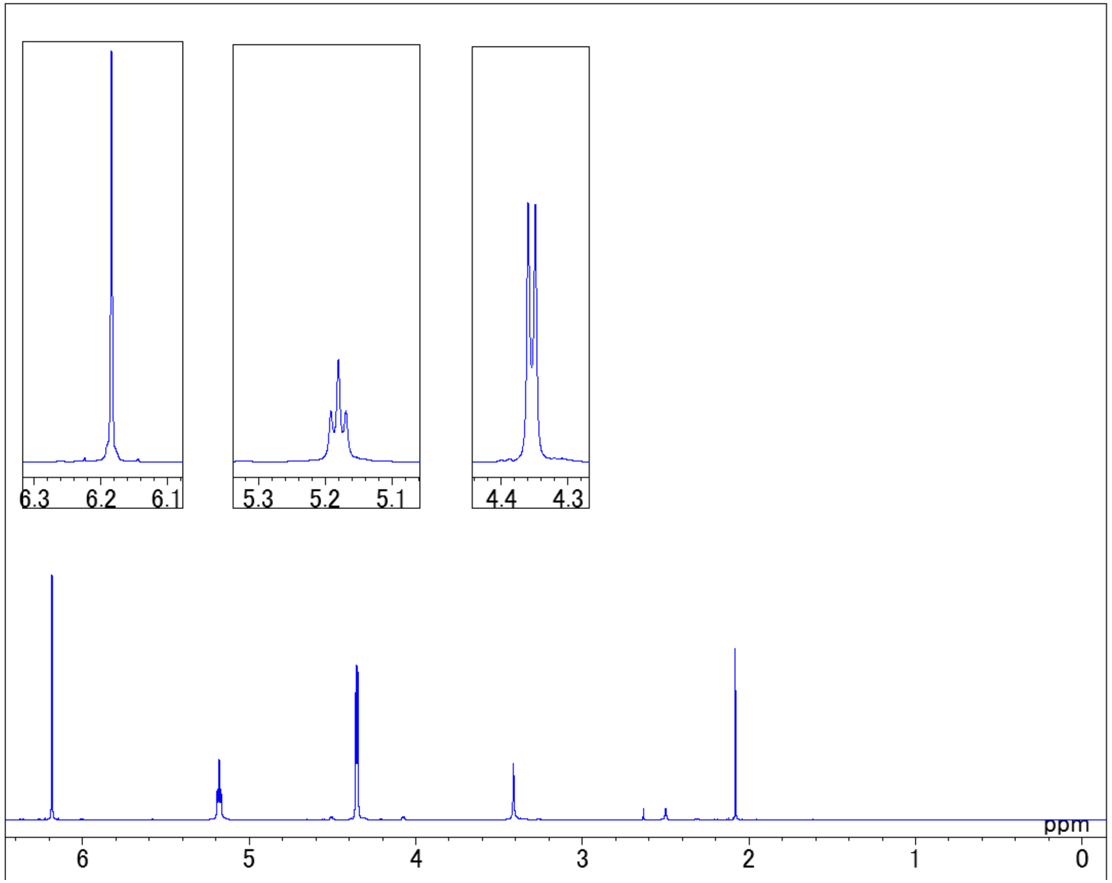


BHF



GC-MS: m/z = 128 $[M]^+$

NMR chart (DMSO-d6, 500 MHz)



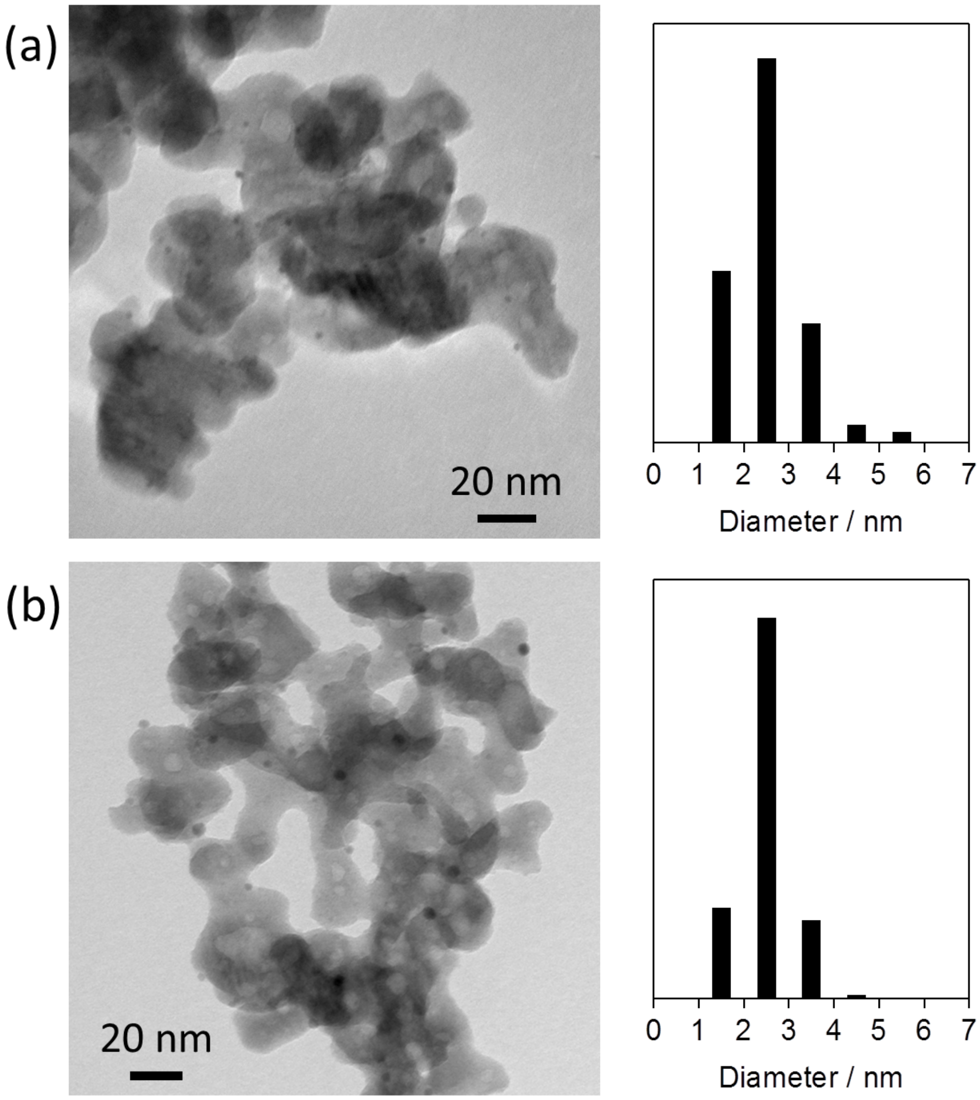


Figure S1. Typical TEM images and histograms of Au/Nb_2O_5 (a) before and (b) after the reaction for 12 h. The size of gold nanoparticles before and after the reaction was 2.5 ± 0.7 nm and 2.5 ± 0.5 nm, respectively.

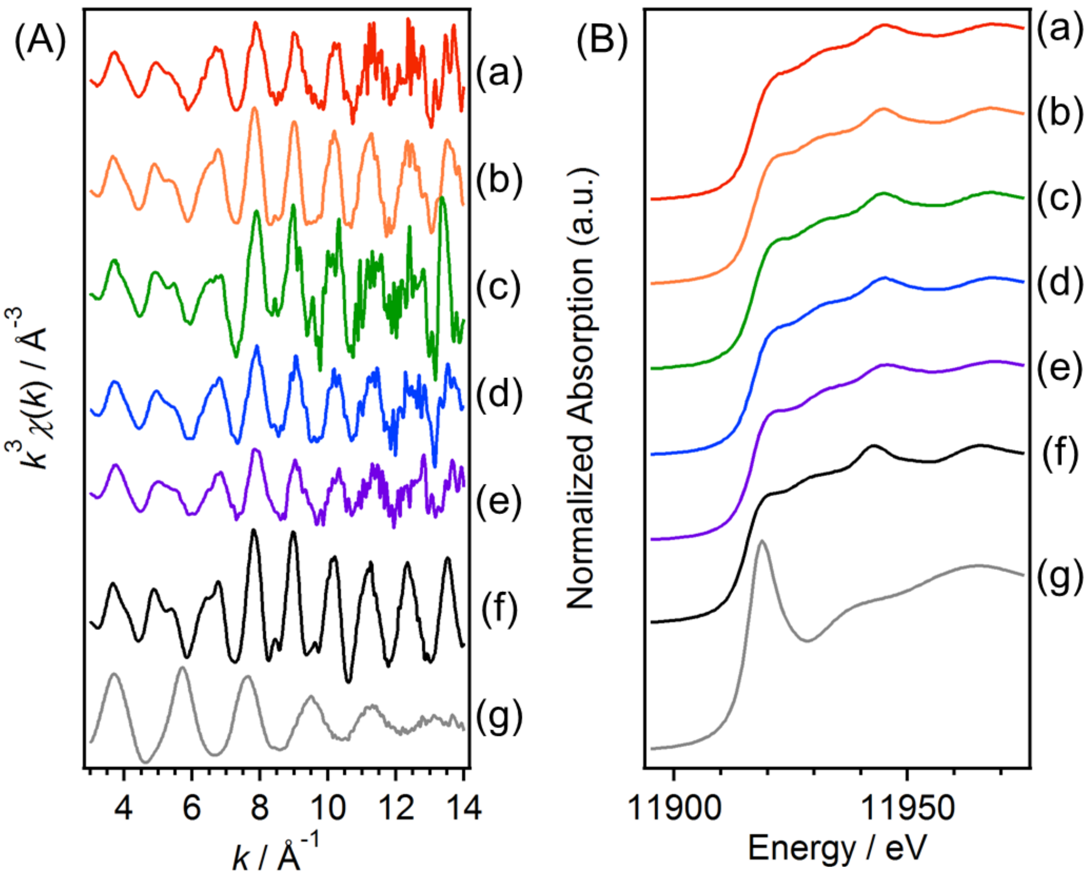


Figure S2. (A) EXAFS spectra and (B) XANES spectra of (a) Au/Nb_2O_5, (b) Au/Al_2O_3 (c) Au/ZrO_2, (d) Au/TiO_2, and (e) Au/SA.

Table S2. Results of curve-fitting analysis of Au-Au scattering of supported Au catalysts.

Catalyst	C.N. [a]	r / Å [b]	σ / Å [c]	R [d]
Au/Nb_2O_5	9.0	2.82	0.100	0.35
Au/Al_2O_3	11.9	2.84	0.096	0.04
Au/ZrO_2	11.6	2.83	0.098	0.35
Au/TiO_2	10.0	2.82	0.100	0.024
Au/SA	8.1	2.80	0.106	0.253

r fitting range: 2.34-3.18 Å. k fitting range: 3.4-14 $Å^{-1}$. [a] Coordination number. [b] Interatomic distance. [c] Debye-Waller factor. [d] So called R factor: $R = \Sigma\{k^3\chi_{obs}(k)-k^3\chi_{cal}(k)\}^2/\Sigma\{k^3\chi_{obs}(k)\}^2$.