Supplementary Information

Selective Hydrogenation of 2,5-Hydroxymethylfurfural to 2,5-Bishydroxymethylfurfural over Supported Gold Subnanocluster

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Materials

Al_2O_3 (JRC-ALO5), TiO_2 (JRC-TIO-1), CeO_2 (JRC-CEO-2), ZrO_2 (JRC-ZO-1), sulfated zirconia (JRC-SZ-1) were supplied from the committee of reference catalyst, Catalysis society of Japan. TiO_2-SiO_2 (3% SiO_2 97% TiO_2) and Ta_2O_5 were obtained from Shokubai Kasei Co. Ltd. and Kojundo Chemical Lab. Co., Ltd., respectively. La_2O_3, $HAuCl_4$, NaOH, and $NaBH_4$ were purchased from Kishida Chemical Co., Ltd. 2,5-Hydroxymethylfurfural (HMF) was obtained from Tokyo Chemical Industry Co., Ltd.

Preparation of Au catalysts.

Supported Au catalysts were prepared by deposition-precipitation method as reported elsewhere. A NaOH aqueous solution (1.0 M) was added dropwise to a 50 mL of $HAuCl_4$ aqueous solution (51 μmol) to adjust the pH of the solution to ca. 7. Metal oxide supports (1.0 g) was added to the solution and stirred at 343 K for 2 h, followed by centrifugation. The resulting residue was washed with ca. 50 mL of water and centrifuged. The washing process was repeated 5 times. The resulting powder was dried at 363 K, then calcinated under air at 573 K to prepare various metal oxides supported Au catalysts. As for Al_2O_3 supported Au catalyst (Au/Al_2O_3), calcination condition was varied to control Au particle size: under air at 573, 773, and 873 K; under 100 mL/min of H_2 flow at 473 and 573 K. The loading amount of Au on Al_2O_3 determined using an inductively-coupled plasma (ICP) spectrometer (Thermo Jarrel Ash IRIS/AP) was 0.83wt%.

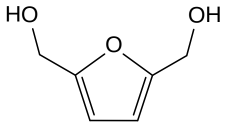
Preparation of Al_2O_3 supported Pt, Pd, Ag, and Cu catalysts

Al_2O_3 supported Pt, Pd, Ag, and Cu catalysts were prepared by impregnation method to be 1wt% of metal loading by using H_2PtCl_6, $Pd(NO_3)_2$, $AgNO_3$, and $Cu(CH_3CO_2)_2$ as metal precursor: After the suspension containing metal precursor and Al_2O_3 (JRC-ALO5) in water was stirred under 343 K for 1h, the suspension was evaporated to dryness; Resulting powder was dried at 353 K overnight; The powders containing Pt, Ag, and Cu were calcined at 573 K under H_2 for 1 h, and that containing Pd was calcined at 773 K under H_2 for 1 h after calcination at 773 K under air for 5 h.

Hydrogenation of HMF.

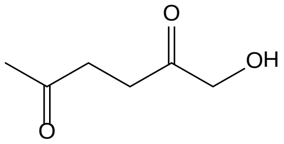
Hydrogenation of HMF was carried out in an autoclave with a gas in- and outlet (30 mL, Taiatsu Techno Co., TVS-1 type). To a 2 mL of HMF aqueous solution (0.2 mol L^{-1}) in an autoclave was added 10 mg of a supported Au catalyst together with a stirrer bar. The experiment were conducted under 3.8-6.5 MPa of H_2 at 403 – 433 K, after 5 times of replacement of air in an autoclave by ca. 1 MPa of H_2. The reaction solution with 1,4-dioxane as an internal standard was analyzed by a gas chromatograph (SHIMADZU GC-14A) equipped with FID using Ultra ALLOY$^+$-5 capillary column (Frontier Laboratories Ltd.). On the other hand, HMF (95 mg in 20 mL of water) was reduced by $NaBH_4$ (201 mg in water) to synthesize BHF. Products were identified by using a NMR spectrometer (Varian, INOVA-500, 500 MHz) and GC-MS (SHIMADZU-QP5000).

BHF



^{1}H NMR (d-DMSO): δ 4.34 (d, 4H), 5.17 (t, 2H), 6.17 (s, 2H).

B1



^{1}H NMR (d-DMSO): δ 2.07 (s, 3H), 2.57 (t, 2H), 2.65 (t, 2H), 4.05 (d, 2H), 5.11 (t, 1H).

Recoverability and reusability of Au/Al_2O_3-473H, and the Au loading after reaction

After HMF hydrogenation reaction using Au/Al_2O_3-473H, the supported Au catalyst was washed with water to test its recoverability and reusability. As a result, the catalyst almost did not work (HMF conversion was 0.6% using 10 mg of the catalyst under 6.5 MPa of H_2 at 393K for 2h.). However, interestingly, the treatment of the catalyst with O_2 and H_2 at 473K reactivated the catalyst (Conversion: 33%). The decrease of the catalytic activity might be due to growth of Au particles and change in their morphology and chemical state, which is now under investigation.

The Au loading amount of Au/Al_2O_3-473H after the HMF hydrogenation reaction was evaluated by using ICP spectrometer. The Au loading was 0.8wt% after the reaction, which was consistent with as-prepared catalyst. It is very likely that the Au ion does not leach under the catalytic reaction.

Table S1. Conversion of HMF and product yields for HMF hydrogenation over various metal supported Al_2O_3.*

Catalyst	Conversion (%)	Yield (%)		
		BHF	B1	Unknown
Pt/Al_2O_3	100	0	28	72
Ag/Al_2O_3	4.5	4.5	0	0
Cu/Al_2O_3	0	0	0	0
Pd/Al_2O_3	100	19	6.1	74

*Reaction was carried out using 10 mg of catalyst at 413 K under 3.8 MPa of H_2 for 4 h.

Table S2. Turnover frequency per all Au atoms for 1, 0.5, and 0.1wt% Au/Al_2O_3.*

Catalyst	Turnover frequency per all Au atoms (h^{-1})
1wt% (Au/Al_2O_3-473H)	574
0.5wt%	106
0.1wt%	49

*Reaction was carried out using 10 mg of catalyst at 393 K under 6.5 MPa of H_2.

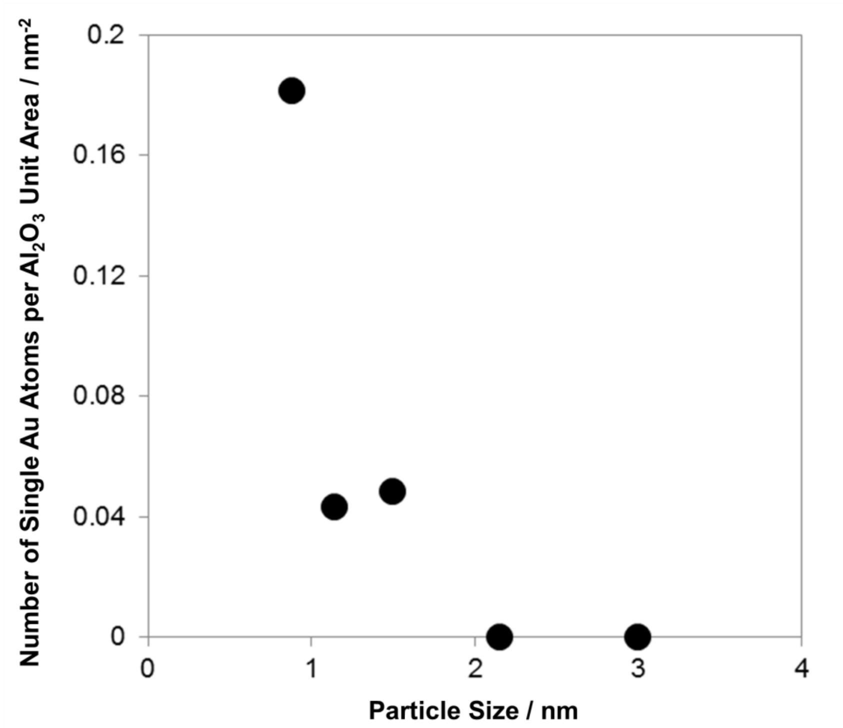


Figure S1. The number of Au atoms per Al_2O_3 unit area plotted against Au particle size. The Au atoms in more than 7500 nm^2 of Al_2O_3 observed on corresponding STEM images were counted.

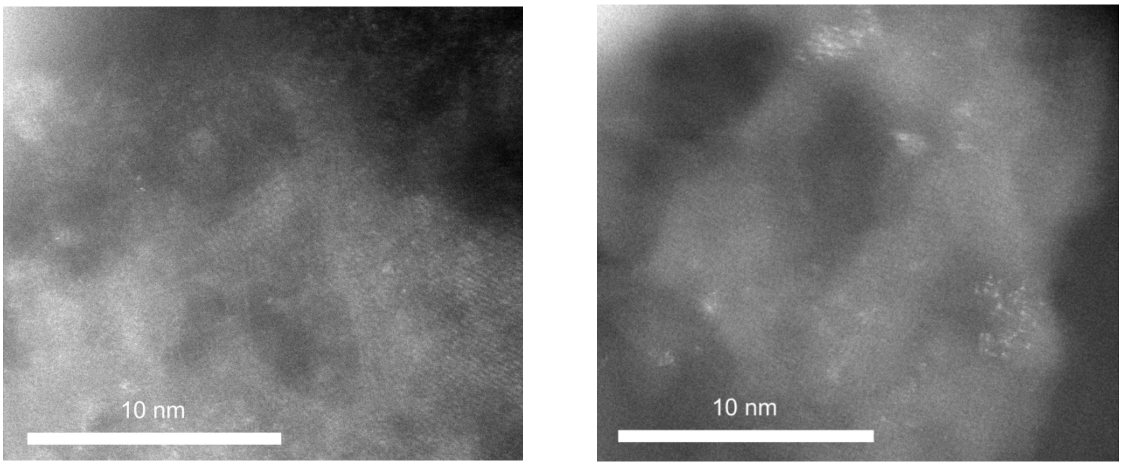


Figure S2. Typical HAADF STEM image of 0.1 (left) and 0.5wt% Au/Al_2O_3 (right) prepared under 100 mL/min of H_2 flow at 473 K.