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Supporting Information

Nanogold supported on manganese oxide doped alumina microspheres as a highly active and selective catalyst for CO oxidation in a H_2-rich stream

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† Electronic Supplementary Information (ESI) available: Details of catalyst preparation, reaction measurements and tests, as well as characterization data of XRD, Raman, BET, EDX, TEM, HAADF-STEM, XPS, CO-DRIFTS and H_2-TPR. See DOI: 10.1039/b000000x/

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1. Catalyst preparation

1.1 Synthesis of MnO_2-Al_2O_3 support

All the chemicals used in the current work were of analytical grade without further purification. The γ-Al_2O_3 support was prepared using a hydrothermal method we reported previously.[1] Manganese doped γ-Al_2O_3 support was prepared by a redox method. Typically, 0.09 g γ-Al_2O_3 and 0.865 g $KMnO_4$ were dissolved in 5 ml of deionized water under vigorous stirring at 25 °C, Then 125 μl of glycol was added and the mixture was stirred continuously at 25 °C for 0.5 h. Afterward, the precipitate was washed, dried, and calcined in muffle oven at 200 °C for 2 h in order to obtain the MnO_2-Al_2O_3 supports (denoted as **MnAl**). For comparison purpose, the pure MnO_2 was made by a redox method following the above procedure, which was not adding the γ-Al_2O_3 at first.

1.2 Synthesis of Au/MnO_2-Al_2O_3 catalyst

All the supported Au catalysts were prepared by a deposition-precipitation (DP) method as described elsewhere.[2,3] In a typical preparation, The required amount of $HAuCl_4$ solution (7.888 g/L) was added into an aqueous suspension of supports (γ-Al_2O_3, MnO_2-Al_2O_3 and MnO_2) and the pH value was adjusted to about 8 by dropwise addition of $(NH_4)_2CO_3$ (0.5 M) solution. Then, the mixture was aged at 60 °C for 2 h. After centrifugation, washing with deionized water for 4 times and drying under vacuum, the Au catalyst was obtained. The Au loading for each catalyst was 1 wt.%. These samples are denoted as **Au/Al**, **Au/MnAl**, and **Au/Mn**, respectively. For comparison, the 3 wt.% Au catalyst was made by the DP method, denoted as **3Au/Al**, **3Au/MnAl**, and **3Au/Mn**. For the preparation of Au/MnO_2-CeO_2 and Au/MnO_2-Al_2O_3 catalysts, the similar processes were used, but replacing Al_2O_3 (microspheres structures) with home-made CeO_2[4] or Al_2O_3[3] (denoted as **3Au/Ce-cube**, **3Au/MnCe-cube**, **3Au/Al-sheet**, and **3Au/MnAl-sheet**).

2. Catalyst tests

The catalysts were heated at 250 °C for 2 h in a muffle oven, and then their activities for CO oxidation were evaluated in a fixed-bed quartz reactor (8 mm i.d.) at atmospheric pressure. The feed gases were consisted of 1 vol.% CO, 1 vol.% O_2, 40 vol.% H_2 (balanced with N_2) and were allowed to pass through 100 mg of catalyst at a flow rate of 67 mL/min (corresponding space velocity was 40,000 mL/h·g_{cat}). The effluent gas compositions were analyzed with an on-line gas chromatograph (Tianmei GC-7890) equipped with a TCD detector and a 5A molecular sieve column. The temperature range of catalyst tests was from 30 to 150 °C, where the water gas shift (WGS) reaction is negligible. The conversion and the selectivity of CO were estimated according to the following equation:

$$X_{CO}(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\%$$

$$X_{O_2}(\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100\%$$

$$S_{CO_2}(\%) = \frac{0.5 \times \{[CO]_{in} - [CO]_{out}\}}{[O_2]_{in} - [O_2]_{out}} \times 100\%$$

Where X and S are the conversion of CO or O_2 and the selectivity of O_2 to oxidize CO, respectively.

3. Catalyst characterization

The actual loadings of gold and manganese were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on the Optima 2000 DV. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-2400 diffractometer (Cu Kα radiation, λ = 1.54056 Å). The nitrogen adsorption measurements were performed on a Micromeritics Tristar 3000 instrument at -196 ^{o}C. Raman spectra were recorded with a Thermo DXR Raman Microscope using a laser excitation wavelength of 532 nm. The morphologies of MnAl support was carried out with a FEI Quanta 450 scanning electron microscope (SEM). Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) were carried out using a FEI Tecnai F30 electron microscope at an accelerating voltage of 300 kV. Hydrogen temperature-programmed reduction (H_2-TPR) experiments were measured by a Micromeritics Autochem II 2920 instrument equipped with a thermal conductivity detector (TCD). The catalyst was pretreated in Ar flow at 150 ^{o}C for 30 min. After that, the catalyst was heated from 40 ^{o}C to 800 ^{o}C (10 ^{o}C/min) in 8 vol.% H_2/Ar mixed gas flows. *In situ* diffuse reflectance FTIR spectra (DRIFTS) were collected using a Nicolet 6700 FT-IR spectrometer equipped with a MCT detector. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG ESCALAB 250 spectrometer with contaminated C 1s peak as internal standard (284.6 eV).

4. Supporting results

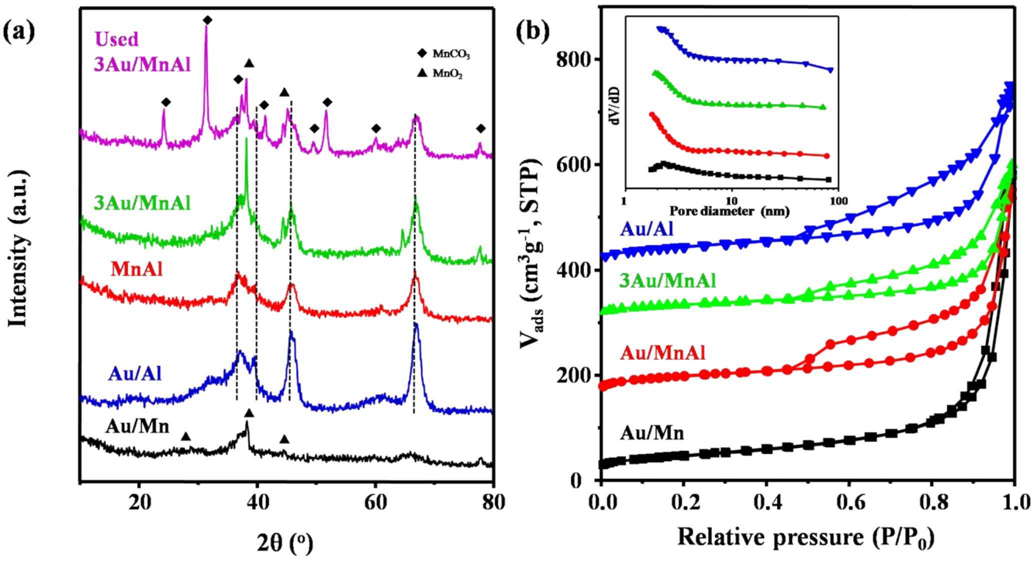


Fig. S1 (a) XRD patterns of different catalysts, (b) Nitrogen sorption isotherms of the catalysts (inset are the corresponding pore size distribution curves). The isotherms of Au/MnAl, 3Au/MnAl and Au/Al were offset vertically by 150, 300 and 400 cm^3g^{-1}, STP, respectively.

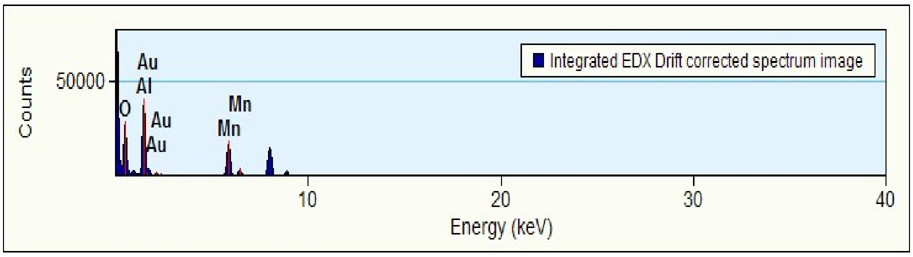


Fig. S2 The EDX patterns of the 3Au/MnAl catalyst based on the selected area shown in Fig. 1e.

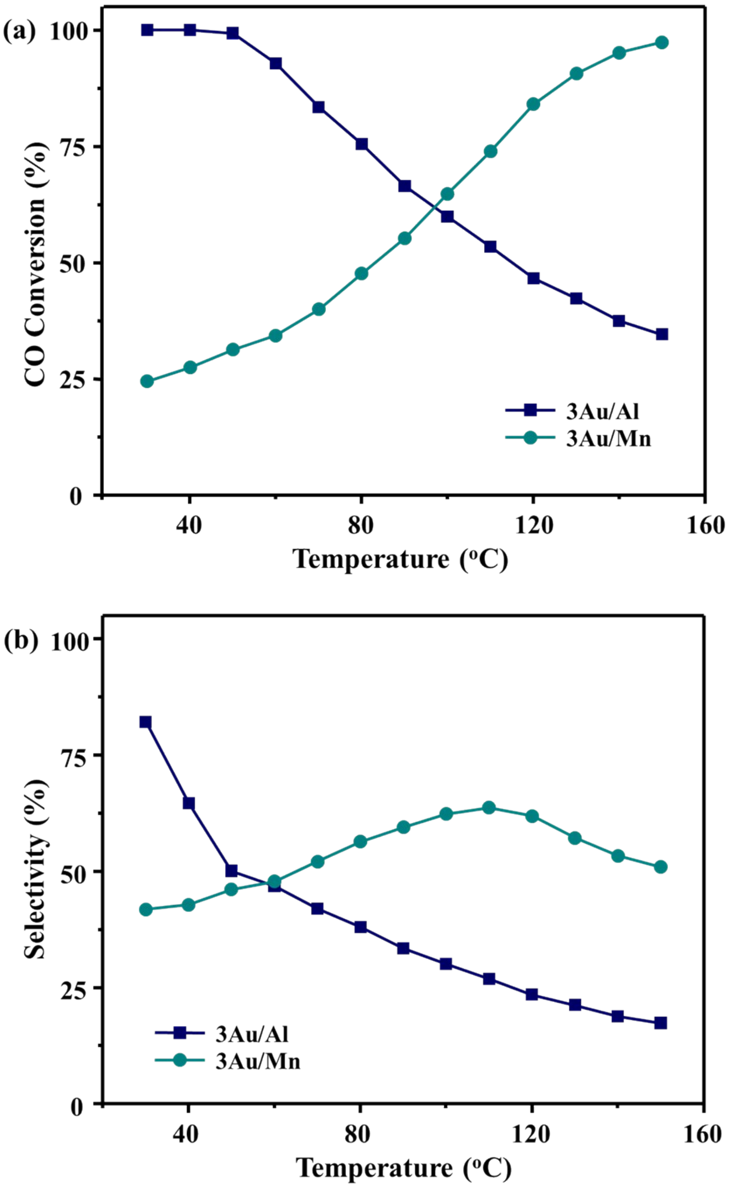


Fig. S3 (a) Conversion and (b) selectivity as a function of reaction temperatures for CO-PROX of 3Au/Al and 3Au/Mn catalysts. Reaction conditions: 1 vol.% CO + 1 vol.% O_2 + 40 vol.% H_2 and balance N_2. Weight hourly space velocity (WHSV) = 40,000 mL/h·g_{cat}.

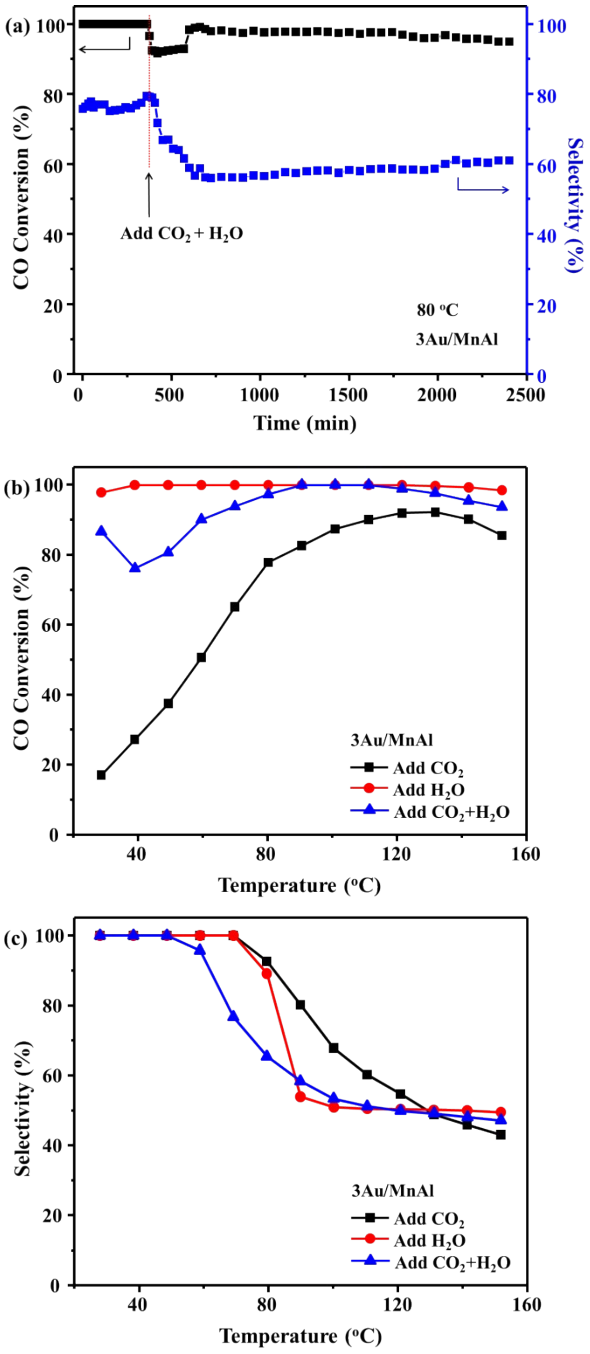


Fig. S4 (a) Stability test of 3Au/MnAl catalyst with a time-on-stream at 80 ^{o}C. (b) Conversion and (c) selectivity as a function of reaction temperatures for CO-PROX of 3Au/MnAl catalyst. Reaction conditions: 1 vol.% CO + 1 vol.% O_2 + 40 vol.% H_2 + (10 vol.% H_2O, 20 vol.% CO_2, and 10 vol.% H_2O + 20 vol.% CO_2), and balance N_2. WHSV = 40,000 mL/h·g_{cat}.

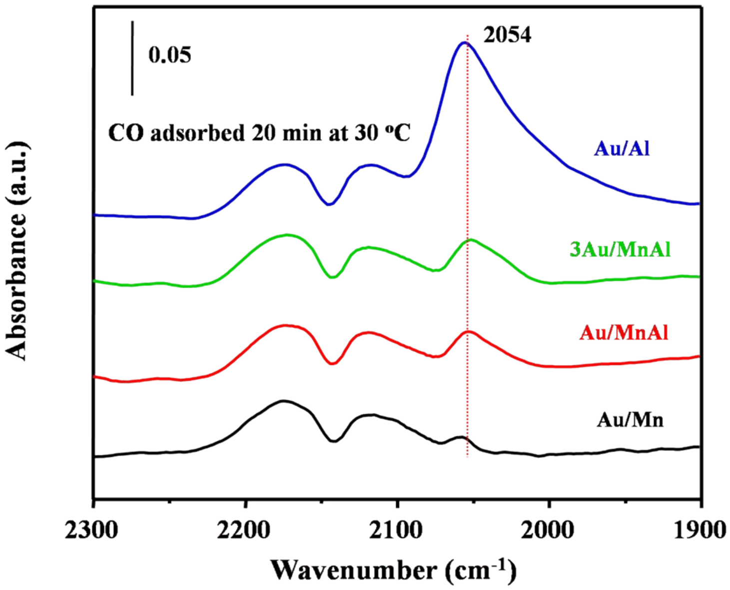


Fig. S5 DRIFTS spectra of CO adsorption on different catalysts at 30 ^{o}C.

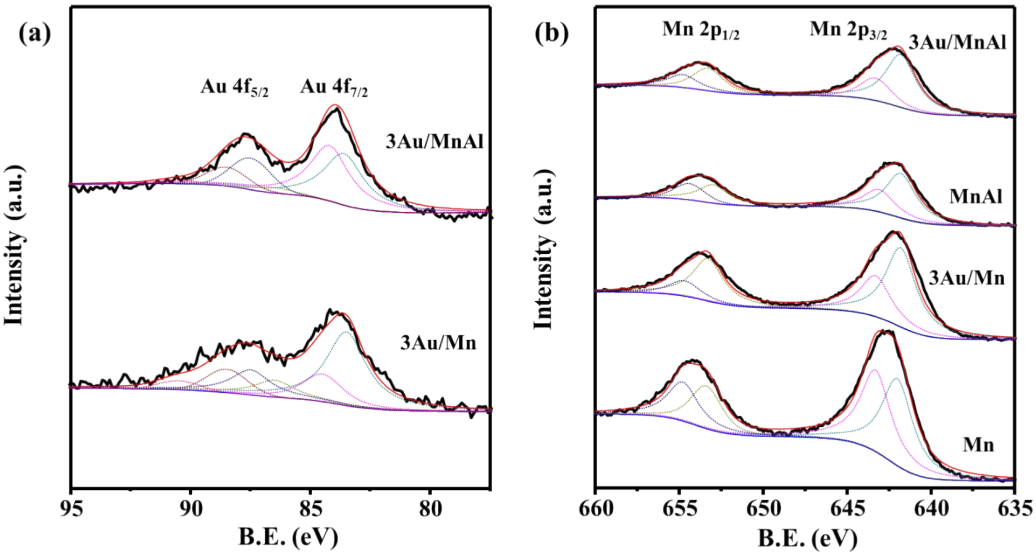


Fig. S6 XPS spectra of different catalysts (a) Au 4f, (b) Mn 2p.

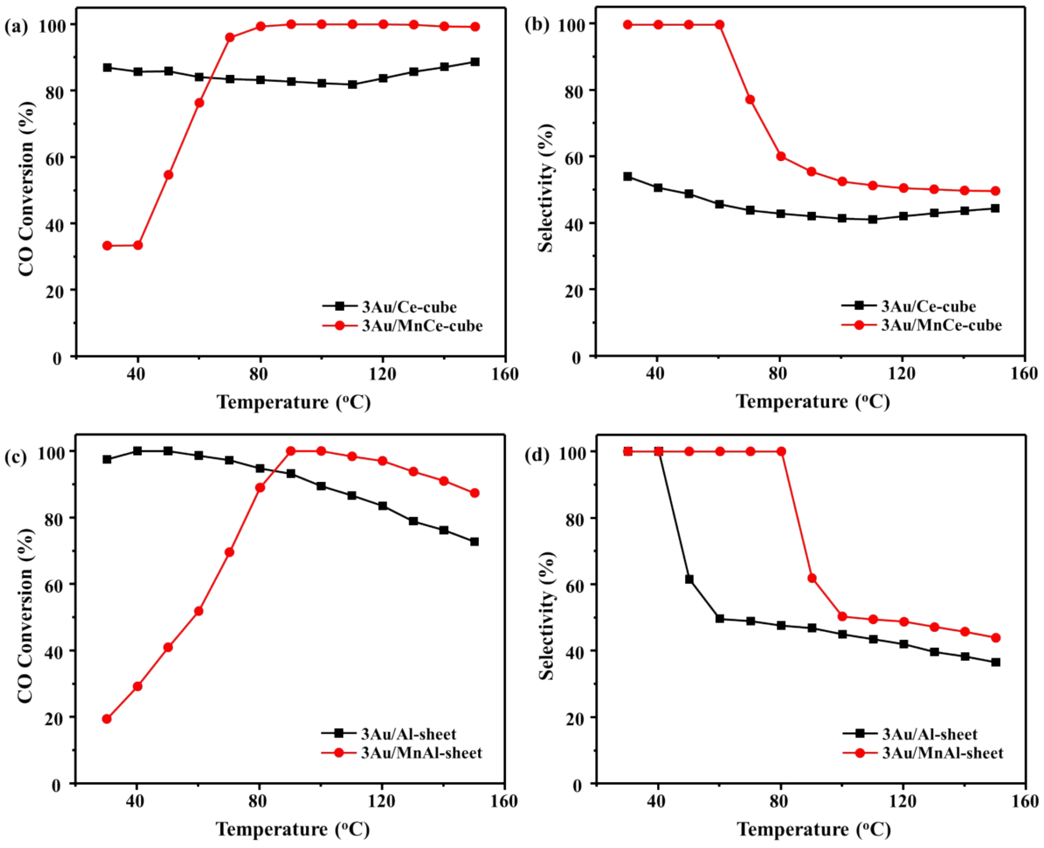
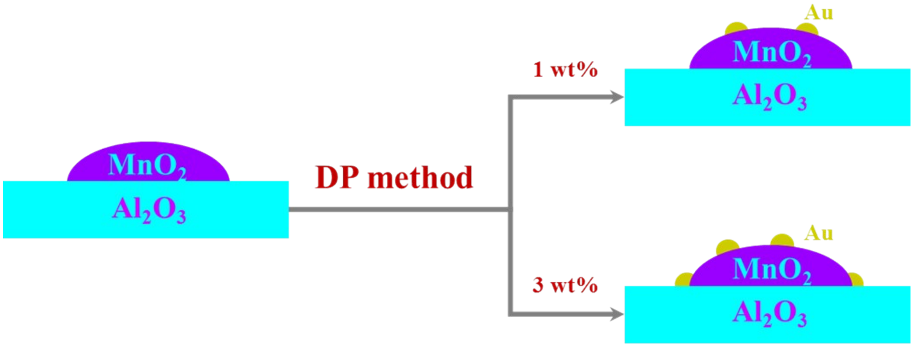


Fig. S7 (a, c) Conversion and (b, d) selectivity as a function of reaction temperatures for CO-PROX of different Au catalysts. Reaction conditions: 1 vol.% CO + 1 vol.% O_2 + 40 vol.% H_2 and balance N_2. Weight hourly space velocity (WHSV) = 40,000 mL/h·g_{cat}.



Scheme S1. Evolution of the structure of the prepared catalyst after precipitation gold. (Left) Starting MnAl support after calcined; (Right Top) after deposition-precipitation (DP) 1wt% Au; (Right Bottom) after DP 3wt% Au.

Table S1. Physicochemical properties of the synthesized Au catalysts

catalyst	Au loading (wt.%)[a]	Mn loading (wt.%)[a]	S_{BET} (m^2/g)[b]	V_{total} (cm^3/g)[b]
Au/Al	0.92	0	160	0.54
Au/Mn	1.2	-	168	0.90
Au/MnAl	1.3	23.9	167	0.62
3Au/Al	3.0	0	151	0.64
3Au/Mn	3.1	-	169	1.13
3Au/MnAl	3.1	18.1	120	0.46

[a] The actual loadings of Au and Mn were determined by an ICP technique.

[b] S_{BET} = specific surface area calculated by the Brunauer-Emmett-Teller (BET) method, V_{total} = total pore volumes at $P/P_0 = 0.99$.

Table S2. A catalytic performance comparison list of the Au catalysts

catalysts	Au loading (wt.%)	feed gas (vol.%) WHSV ($mL/h \cdot g_{cat}$)	Temperature of X_{max} (°C)	80 °C X_{CO} (%)	80 °C S (%)	Ref
Au/Al	0.92	1% CO, 1% O_2 40% H_2, 58% N_2 40,000	30-50	80	40	This work
Au/Mn	1.2		150	45	100	This work
Au/MnAl	1.3		130	36	100	This work
3Au/MnAl	3.1		80-120	100	80	This work
Au/MnO_2-TiO_2	0.58	1.33% CO, 1.33% O_2 65.33% H_2, He 30,000	80	98	51	5
Au/MnO_2-CeO_2	1.0	1.33% CO, 1.33% O_2 65.33% H_2, He 30,000	80	98	49	6
Au/MnO_x-CeO_2 (Mn/Ce=1:1)	1.0	1.5% CO, 1.5% O_2 50% H_2, He 12,000	120	55	45	7
Au/MnO_x-CeO_2 (M=Mn, Fe, Co, Ni)	2.5	1.5% CO, 1.5% O_2 50% H_2, He 12,000	120	73	41	8
Au/CeO_2-Co_3O_4	1.0	1% CO, 1% O_2 50% H_2, Ar 30,000	80	94	52	9
Au/CeO_2-Fe_2O_3	3.5	1% CO, 1.25% O_2 50% H_2, He [a]	80	100	40	10

Au/HMS-M (M = Fe/Ce/Ti)	2.84	0.5% CO, 1% O_2 50% H_2, 48.5% N_2 [b]	130-170	50	60	11
Au/ZnO-TiO_2	ca. 0.7	1.33% CO, 1.33% O_2 65.33% H_2, He 30,000	50-80	100	50	12
Au/CeO_2-M (M = Zr/Zn/Fe)	1.0	2% CO, 1% O_2 50% H_2, Ar 30,000	70	75	68	13
Au/CeO_2-MO_x/Al_2O_3 (M = La, Ni, Cu, Fe, Cr, Y)	2.0	1% CO, 1.5% O_2 50% H_2, He 12,000-60,000	80	93	65	14
Au/MnO_x/MgO/Al_2O_3	5.0	2% CO, 1% O_2 4% H_2, He 12,000	50	90	47	15

[a] W/F = 0.03 g·s/cm^3.

[b] The molar flow rate of the CO in this gas mixture was 3.72×10^{-7} mol s^{-1}.

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