

Preferential CO Oxidation in H₂ over Au/La₂O₃/Al₂O₃ Catalysts: Effect of Catalyst Reduction Method

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Materials and Methods

Loading of gold on La₂O₃/Al₂O₃ support by deposition precipitation with urea method (DPU):

First, 2 g of calcined and finely powdered La₂O₃/Al₂O₃ support was dispersed in deionized water. The slurry temperature was fixed at 80 °C and a solution of H₂AuCl₄·xH₂O (Acros) was then added, followed by mixing of urea (Wako Pure Chemical Industries, Ltd., >99.0%). The resulting mixture was stirred for 12 h in a reactor at 80 °C, covered by opaque aluminum foil. The solid was collected by centrifugation, washed three times with deionized water, and then dried under vacuum at room temperature. In the following, the sample obtained after drying under vacuum is referred to as “as-prepared” sample.

Reduction of gold by chemical reduction with glycerol (CRG) method:

In a typical CRG process, 0.150 g of finely powdered as-prepared sample was mixed with 30 mL of glycerol and stirred vigorously at ambient temperature for 30 min. The resulting mixture was subsequently heated in an oil bath at 75 °C under vigorous stirring for 1 h, after which the sample was cooled and washed with deionized water for three times. Centrifugation was then performed to recover the catalyst. The obtained sample was dried under vacuum at ambient temperature. Finally, the resulting catalyst was reduced under flowing H₂ at 200 °C for 2 h, prior to the CO-PROX reaction. This sample is denoted Au/La₂O₃/Al₂O₃ (G) in the following. The contents of Au and La were determined to be 0.3 and 3.8 wt%, respectively, by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Characterization of catalysts:

The specific surface area of the sample was measured using a Micromeritics ASAP 2020 system and calculated by the Brunauer-Emmett-Teller (BET) method. Prior to the measurement, the sample was degassed under vacuum for 6 h at 200 °C. Powder X-ray diffraction (XRD) experiments were carried out on a Rigaku D/Max instrument with a Cu K α source ($\lambda = 1.5406 \text{ \AA}$). The gold contents of all catalysts were determined by ICP-AES using a Thermo Scientific iCAP 6500 spectrometer. TEM images were obtained using a Tecnai G2 TEM (FEI) instrument operated at 200 kV, and then used to determine the size of the gold particles. The samples were finely ground in a mortar and then ultrasonically dispersed in ethanol. Afterward, they were deposited on a Cu grid covered by a holey carbon film. *In situ* DRIFTS experiments were performed on pellets of the different gold catalysts using a Nicolet 6700 FT-IR (Thermo Scientific) spectrometer equipped with a mercury-cadmium-telluride detector with a resolution of 1.92 cm⁻¹. Prior to CO adsorption, the sample was reduced *in situ* in the DRIFTS cell at 200 °C for 1 h, using H₂ at a flow rate of 30 mL/min, followed by cooling to 80 °C under He flow. Before the introduction of CO, the cell was purged with He with a flow rate of 30 mL/min, and a background spectrum was recorded under He. Subsequently, CO adsorption was performed for 30 min and the first spectrum was recorded before purging with He. Spectra were then

recorded at different time intervals during He purging at 80 °C for 30 min. For studying the methanol adsorption, after reduction at 200 °C under H₂, the sample was cooled under He flow to 160 °C. The cell was purged with He before introduction of methanol, and a background spectrum was recorded under He. Subsequently, methanol adsorption was performed for 30 min. Spectra were recorded at various time points during He purging at 160 °C. XPS measurements were performed using a K-Alpha spectrometer (Thermo Scientific, USA) with an Al K α X-ray source (1486.6 eV). The C 1s peak at 284.8 eV was used as the reference for all binding energies.

Catalytic activity tests:

The catalytic activities of the catalysts were evaluated at atmospheric pressure using a continuous fixed-bed reactor. Generally, 0.10 g of the catalyst was loaded in the quartz reactor and brought into contact with a feed composed of 1 mol% CO, 1 mol% O₂, 50 mol% H₂, and 48 mol% He at a flow rate of 100 mL/min. In order to find out the effect of water and CO₂ on the CO-PROX performance, the same amount of catalyst was contacted with a feed consisting of 1 mol% CO, 2 mol% O₂, 50 mol% H₂, 10 mol% H₂O, 10 mol% CO₂ and 27 mol% He. The reaction temperature was measured by a thermocouple placed in the catalyst bed. The reactant and products were separated with a packed column filled with Carbosphere and analyzed using an online gas chromatograph (HP 6890) with a thermal conductivity detector. The CO and O₂ conversions and the selectivity toward CO₂ were calculated using the following equations:

$$\text{CO conversion (\%)} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/[\text{CO}]_{\text{in}} \times 100, \quad (1)$$

$$\text{O}_2 \text{ conversion (\%)} = ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}})/[\text{O}_2]_{\text{in}} \times 100 \quad (2)$$

$$\text{CO}_2 \text{ selectivity (\%)} = 0.5 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) \times 100, \quad (3)$$

where [CO]_{in} and [O₂]_{in} represent the concentrations of CO and O₂ in the feed stream, respectively, and [CO]_{out} and [O₂]_{out} denote the concentrations of CO and O₂ in the effluent stream, respectively. A moisture trap was installed before the gas chromatograph to remove the moisture formed during the reaction.

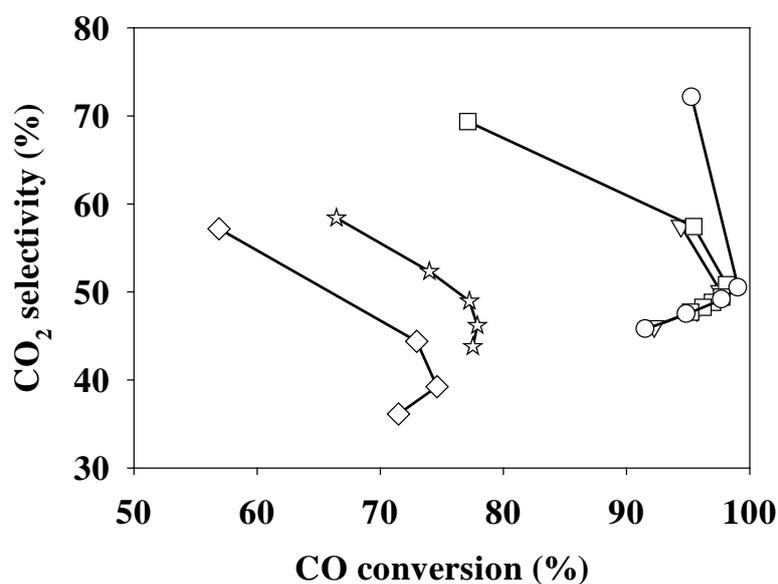


Figure S1. CO-PROX performance of Au/La₂O₃/Al₂O₃ catalysts such as Au/La₂O₃/Al₂O₃ (H) (▽), Au/La₂O₃/Al₂O₃ (S5) (○), Au/La₂O₃/Al₂O₃ (S35) (□), Au/La₂O₃/Al₂O₃ (S115) (☆) and Au/La₂O₃/Al₂O₃ (G) (◇). Reaction conditions: 1 mol% CO, 1 mol% O₂, 50 mol% H₂ and 48 mol% He, F/W = 60,000 mL g_{cat}⁻¹ h⁻¹.

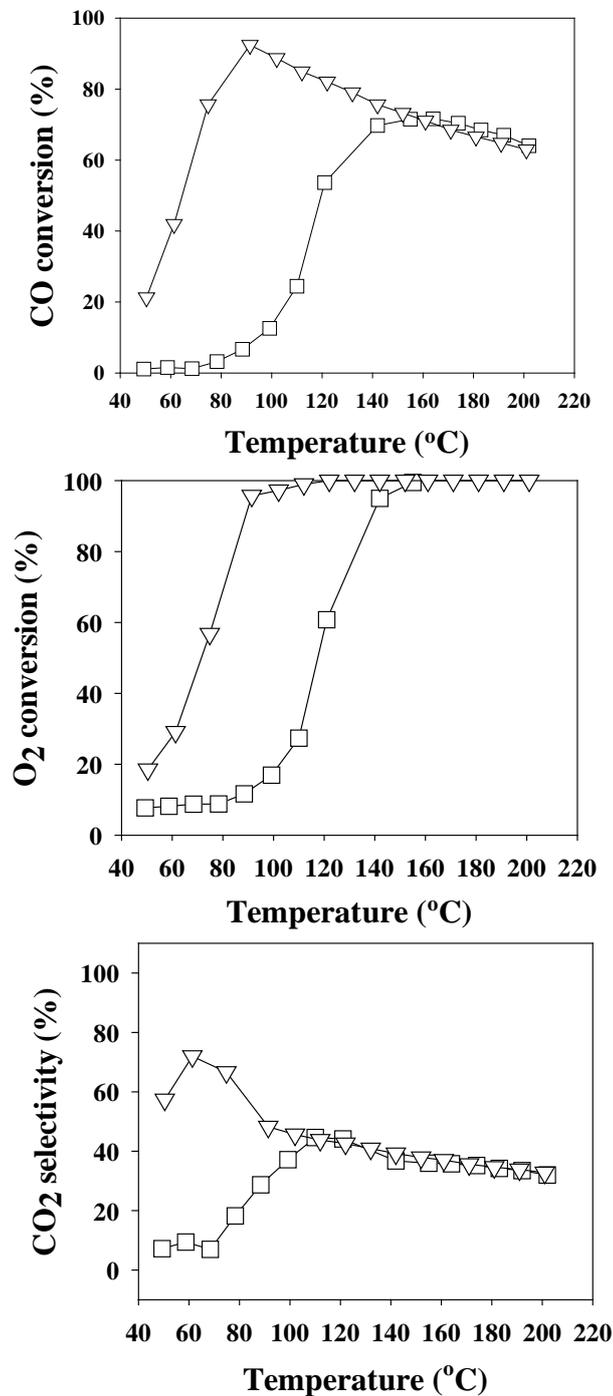


Figure S2. CO-PROX performance of Au/La₂O₃/Al₂O₃ catalysts such as Au/La₂O₃/Al₂O₃ (S35) without reduction under H₂ (▽) and Au/La₂O₃/Al₂O₃ (G) without reduction under H₂ (□). Reaction conditions: 1 mol% CO, 1 mol% O₂, 50 mol% H₂ and 48 mol% He, F/W = 60,000 mL g_{cat}⁻¹ h⁻¹.

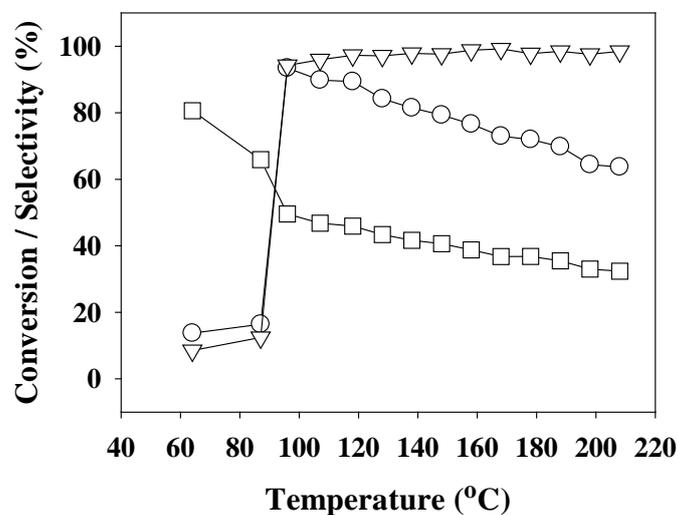


Figure S3. Effect of water and CO₂ on the CO-PROX performance of Au/La₂O₃/Al₂O₃ (S35): CO conversion (O); O₂ conversion (V); selectivity to CO₂ (□). Reaction conditions: 1 mol% CO, 2 mol% O₂, 50 mol% H₂, 10 mol% H₂O, 10 mol% CO₂ and 27 mol% He, F/W = 60,000 mL g_{cat}⁻¹ h⁻¹.

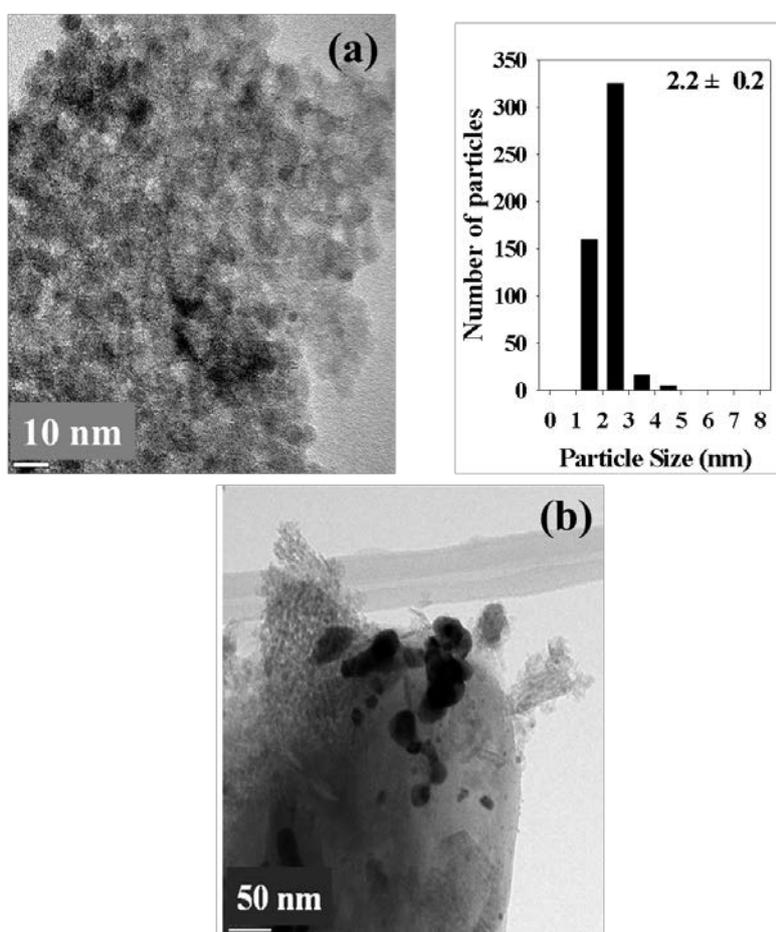


Figure S4. TEM images of Au/La₂O₃/Al₂O₃ (S5) (a) and Au/La₂O₃/Al₂O₃ (S115).

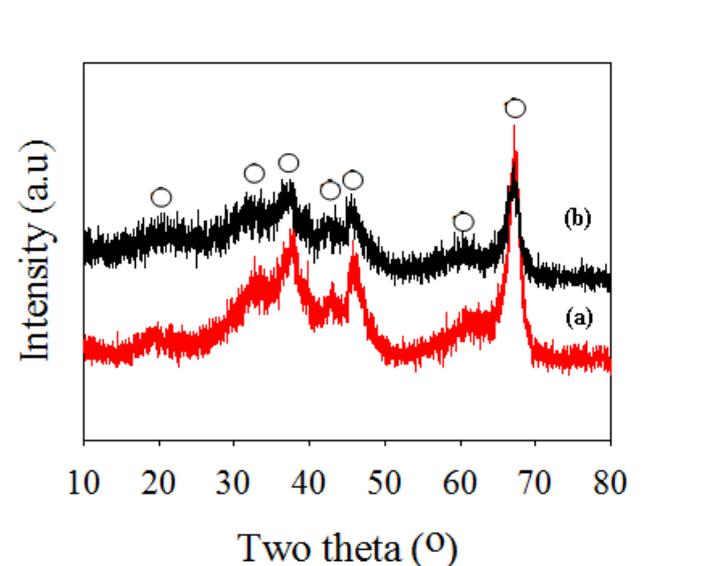


Figure S5. XRD patterns of Al_2O_3 (a) and $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ (b). γ -alumina (o)

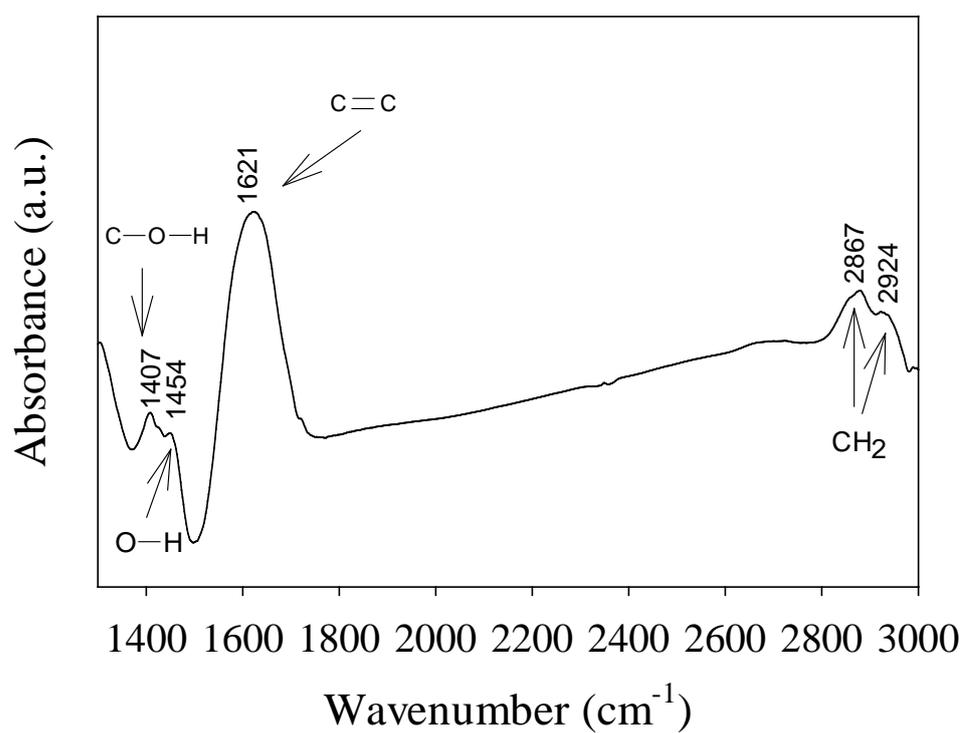


Figure S6. FT-IR spectra of *as prepared* $\text{Au}/\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ (G) sample.