Supporting Information for

Significantly Enhanced CO Oxidation Activity Induced by CO Adsorption Site Change on

Pd Nanoparticles Covered with Metal–Organic Framework

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1. Experimental Procedures

Synthesis of Ru NPs

Ru NPs were prepared by a chemical reduction method. $RuCl_3 \cdot nH_2O$ (549 mg, 2.1 mmol) and poly(*N*-vinyl-2-pyrrolidone) (PVP) (111 mg, 1.0 mmol) was dissolved in 25 mL of ethylene glycol. The solution was heated at 200 °C under magnetic stirring for 2 h. After cooling to room temperature, the product was collected by centrifugation and washed with the mixture solution of water, acetone, and diethyl ether.

Preparation of Pd/ZrO₂ and Ru/ZrO₂

In Pd/ZrO₂ and Ru/ZrO₂ preparation, Pd or Ru NPs were dispersed in water (80 mL) with ultrasonication for 15 min, and ZrO₂ was dispersed in water (20 mL). The two solutions were mixed at room temperature and magnetically stirred for 24 h. After that, the water was removed using a rotary evaporator under vacuum at 50 °C.

Preparation of Pd/UiO-66

In Pd/UiO-66 preparation, 20 mg of Pd NPs were dispersed in water (80 mL) with ultrasonication for 15 min, while 200 mg of pre-synthesized UiO-66 was dispersed in water (20 mL). The two solutions were mixed at room temperature and magnetically stirred for 24 h. After that, the water was removed using a rotary evaporator under vacuum at 50 °C.

Preparation of Pd@terephthalic acid on ZrO₂

In Pd@terephthalic acid preparation, 20 mg of Pd NPs and 84 mg of 1,4-benzenecarboxylic acid were dispersed in dimethylformamide (DMF, 80 mL) with ultrasonication for 15 min, while 800 mg of ZrO_2 was dispersed in DMF (20 mL). The two solutions were mixed at room temperature and magnetically stirred for 24 h. After that, the product was collected by centrifugation and washed with DMF and ethanol.

X-ray fluorescence measurements

The Pd:Zr or Ru:Zr atomic ratios of Pd/ZrO₂ or Ru/ZrO₂ were investigated using a Rigaku ZSX Primus IV apparatus. The ratio of Pd or Ru to ZrO_2 in Pd/ZrO₂ and Ru/ZrO₂ was estimated to be 1.3 wt.% and 2.0 wt.%, respectively.

Inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopy was performed with a Shimadzu ICPE-9000 spectrometer. As sample preparation for the ICP–AES measurement, preweighed samples were dissolved in a 7:3 (v/v) solution of HNO_3 –HCl and were heated in a microwave reactor at 180 °C for 1 h.

N₂ sorption isotherm for UiO-66 and Pd@UiO-66

 N_2 sorption isotherms were collected at 77 K by BELSORP-mini (Microtrac BEL Corp., Japan) using volumetric techniques. The samples were activated over 15 h at 423 K under vacuum before the measurement.

Catalytic activity measurements

The CO oxidation catalytic reactivity measurements were measured with a BEL-CATB fix-bed flow reactor (Microtrac BEL Corp., Japan). The catalyst was loaded in a glass-tube reactor and

fixed with glass wool. The reaction was performed under a flow of 1% CO/1% O₂/He with a total flow rate of 50 cm³/min STP. The reaction temperature was increased from 35 °C to 300 with 5 °C/min steps. The effluent gas was analyzed by a BELMASS quadrupole mass spectrometer (Microtrac BEL Corp., Japan). As a pretreatment, Pd/ZrO₂ and Ru/ZrO₂ were treated under He flow at 250 °C for 30 min and under H₂ flow at 100 °C for 30 min. For Ru/ZrO₂, in addition, the sample was treated under 1% CO/1% O₂/He and heated to 300 °C once. The CO conversion rate was calculated according to the following equation:

CO conversion (%) = (([CO]_{inlet} – [CO]_{out}) / [CO]_{inlet}) × 100,

where [CO]_{inlet} and [CO]_{out} represent the inlet and outlet CO concentration, respectively.

TEM observation

The samples were dispersed in ethanol, and dropped onto a carbon-coated Cu grid, and dried by exposure to ambient conditions for 24 h. TEM images of the samples were recorded using a Hitachi HT7700 TEM instrument operated at 100 kV acceleration voltage.

High-resolution STEM and STEM-EDX analysis

The samples were dispersed in ethanol, dropped onto a carbon-coated Cu grid, and dried by exposure to ambient conditions for 24 h. High-resolution TEM and EDX mapping measurements were performed using a JEM-ARM200CF apparatus operated at 200 kV acceleration voltage.

FT-IR spectroscopy

The ex-situ infrared spectroscopy of all samples was performed using a ThermoNicolet NEXUS 670 FT-IR spectrometer.

Thermogravimetric analysis

Thermogravimetric analysis was performed using a Bruker AXS TGA-DTA 2000-SA in Pt pans under He flow at a rate of 5 °C/min.

XRD measurements

The XRD patterns were obtained using a Bruker D8 Advance diffractometer with a Cu K α radiation source. The XRD patterns were obtained with a 0.05° step.

In-situ FT-IR measurements

FT-IR spectra of adsorbed CO as a probe molecule were obtained to evaluate the CO adsorption state. A self-supporting sample disk of approximately 20 mg cm⁻² placed in an IR cell with CaF₂ windows was first pre-treated at 150, 200, 250 or 300 °C in a flow of 0.5% CO/0.5% O₂/He for 30 min and then purged with He at the same temperature for 5 min. Then, the temperature was decreased to 50 °C under He flow. The activated sample disk was exposed to 0.3% CO/He gas flow at 50 °C for 20 min. IR spectra were recorded using a Nicolet Nexus 670 FT-IR spectrometer, accumulating 64 scans at a resolution of 4 cm⁻¹.

Time-dependent in-situ FT-IR measurements

For time-dependent FT-IR spectroscopy, the sample was pre-treated at 300 °C in a flow of 0.5% CO/0.5% O₂/He for 30 min and then purged with He at the same temperature for 5 min. Then,

the temperature was decreased to 210 $^{\circ}$ C. After exposure to flow of 0.5% CO/He for 10 min, 0.5% CO/0.5% O₂/He was flowed. IR spectra were recorded at 30 s intervals using a Nicolet Nexus 670 FT-IR spectrometer, accumulating 64 scans at a resolution of 4 cm⁻¹.

2. The size distribution of Pd NPs inside



Fig. S1. The size distributions of (a) pristine Pd NPs, and Pd NPs in Pd@UiO-66 (b) before and (c) after CO oxidation reaction. The mean diameters and standard deviations were calculated by averaging 100 particles.

3. PXRD pattern and TEM image of Pd/ZrO₂



Fig. S2. (a) The XRD pattern of ZrO_2 (grey), Pd NPs (black) and Pd/ ZrO_2 (green). (b) TEM image of Pd/ ZrO_2 . The scale bar = 50 nm.

4. Le Bail fitting results of Pd@UiO-66



Fig. S3. The XRD pattern of Pd@UiO-66 (red circles), and the calculated pattern (black line). The bottom lines are difference profile (gray), the fitting curves of UiO-66 (blue) and Pd NPs components (green).

5. FT-IR spectroscopy



Fig. S4. IR spectra of Pd NPs (black), UiO-66 (cyan) and Pd@UiO-66 (red).

6. Thermogravimetric thermal curves



Fig. S5. Thermogravimetric thermal curves of UiO-66 (cyan) and Pd@UiO-66 (red).

7. N₂ sorption isotherms at 77 K



Fig. S6. N₂ sorption isotherms at 77 K for UiO-66 (cyan) and Pd@UiO-66 (red), and Pd@UiO-66 after CO oxidation (black). Closed circles: absorption; Open circles: desorption.



8. CO oxidation activity of Pd/ZrO₂ and Ru/ZrO₂

Fig. S7. CO conversion rate of (a) Pd/ZrO_2 and (b) Ru/ZrO_2 . The reactions were carried out under at a flow of 1% CO/1% O_2 /He with a total flow rate of 50 cm³/min STP.



9. Reproducibility of CO oxidation activity enhancement of Pd@UiO-66

Fig. S8. The CO conversion rate of Pd@UiO-66 with a different sample from Figure 3. The reactions were carried out under at a flow of $1\% \text{ CO}/1\% \text{ O}_2/\text{He}$ with a total flow rate of 50 cm³/min STP. The enhancement of CO oxidation activity was reproduced.





Fig. S9. (a) The XRD pattern of Pd@UiO-66 after CO oxidation reaction (red circles), and the calculated pattern (black line). The bottom lines are difference profile (gray), the fitting curves of UiO-66 (blue) and Pd NPs components (green) (b) TEM image of Pd@UiO-66 after the CO oxidation reaction, and (c) HAADF-STEM image of a Pd NP inside Pd@UiO-66 after CO oxidation. The distance of the lattice fringe was determined to be 2.3 Å, which is in agreement with the {111} lattice plane of Pd metal. The mean diameter of Pd NPs was 8.6 ± 1.3 nm.



11. Catalytic activity of Pd@UiO-66 after He flow pretreatment

Fig. S10. The CO conversion rate of Pd@UiO-66 after pretreatment at 300 $^{\circ}$ C under He flow for 1h. The reactions were carried out under at a flow of 1% CO/1% O₂/He with a total flow rate of 50 cm³/min STP.



12. PXRD pattern, TEM image, and catalytic activity of Pd/UiO-66

Fig. S11. (a) The XRD pattern of Pd NPs (black), UiO-66 (blue) and Pd/UiO-66 (red). (b) TEM image of Pd/UiO-66. The scale bar = 100 nm. (c) The CO conversion rate of Pd/UiO-66 at 300 $^{\circ}$ C. The reactions were carried out under at a flow of 1% CO/1% O₂/He with a total flow rate of 50 cm³/min STP. The ratios of Pd included in the Pd@UiO-66 was estimated to be 2.7 wt% by X-ray fluorescence measurements.





Fig. S12. (a) The XRD pattern of ZrO_2 (grey), Pd NPs (black), and Pd@terepthalic acid on ZrO_2 (red). (b) TEM image of Pd@terepthalic acid on ZrO_2 . The scale bar = 50 nm. (c) The IR spectra of Pd/ZrO₂ (black), terepthalic acid (orange), and Pd@terepthalic acid on ZrO_2 (red). (d) The CO conversion rate of Pd@terepthalic acid on ZrO_2 . The reactions were carried out under at a flow of 1% CO/1% O₂/He with a total flow rate of 50 cm³/min STP. The ratio of Pd included in the Pd@terepthalic acid on ZrO_2 was estimated to be 1.0 wt% by X-ray fluorescence measurement.



14. Time-dependent in-situ FT-IR spectroscopy under CO/O₂/He gas flow after CO/He gas exposure

Fig. S13. Time-dependent in-situ IR spectra of Pd@UiO-66 under CO/O₂/He gas flow at 210 $^{\circ}C$.

15. XPS measurements



Fig. S14. XPS spectra of (a) Pd 3*d* and (b) Zr 3*d* for Pd NPs (grey), UiO-66 (cyan), Pd@UiO-66 (red), and Pd@UiO-66 after reaction (green). The black dotted lines are fitting curve. The peak at ca. 333 eV in the Pd 3*d* spectra for Pd@UiO-66 is the Zr $3p_{3/2}$ peak.