

Electronic Supplementary Information

Formaldehyde-assisted Synthesis of Ultrathin Rh Nanosheets for applications in CO oxidation

Changping Hou,^a Jing Zhu,^b Chang Liu,^a Xue Wang,^a Qin Kuang,^{a,*} and Lansun Zheng^a

^a State Key Laboratory for Physical Chemistry of Solid Surfaces & Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

^b Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

E-mail: qkuang@xmu.edu.cn.

1. Experimental section

1.1 Chemicals and Materials.

Rhodium(II) acetylacetonate (Rh(acac)) was purchased from Kunming institute of precious metals. Formaldehyde, acetaldehyde and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received without further purification. CO (99.99%) and H₂ (99.99%) were purchased from the Linde Group.

1.2 Syntheses of ultrathin Rh nanosheets

Ultrathin Rh nanosheets were synthesized via a simple solvothermal route. Typically, 20 mg Rh(acac)₃ and 0.8 mL formaldehyde were dissolved in DMF (9.2 mL) in a Teflon-lined autoclave with a capacity of 25 mL under stirring. After sealed, the autoclave was rapidly heated to 160°C in 30 min, and kept at 160°C for 24 hours. After reaction, the reaction solution changed from yellow to dark yellow in color. The final products, ultrathin Rh nanosheets, were separated by centrifugation, washed with ethanol for twice, and dried in vacuum oven. For TEM observations, the samples were commonly prepared by depositing a drop of diluted suspension in ethanol on a copper grid coated with carbon film. To observe their flat-lying morphology, ultrathin Rh nanosheets were firstly dispersed in oleic acid through being magnetically stirred for 4 hours, and then separated by centrifugation and washed with n-hexane twice. Finally, the Rh nanosheets were re-dispersed in n-hexane to form a diluted suspension.

For synthetic experiments under different atmospheres, 20 mg Rh(acac)₃ were firstly dissolved in 10 mL of DMF in a glass pressure vessel, and then a flow of CO,

H₂ or their mixed gas (CO:H₂ = 1:2) was introduced into the vessel. After the pressure being filled with to 0.2 MPa, the vessel was heated from room temperature to 160 °C in 30 min and kept at this temperature for 24 hours under stirring. The products were separated by centrifugation and washed with ethanol twice.

1.3 Characterization of ultrathin Rh nanosheets

The morphologies of the products were observed by transmission electron microscopy (TEM, JEM 2100) with an acceleration voltage of 200 kV. X-ray diffraction (XRD) measurements were recorded on a PANalytical X'pert PRO diffractometer using Cu K α radiation, operating at 40 kV and 30 mA. The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 330 spectrometer. The samples for FT-IR measurements were obtained by depositing the cyclohexane dispersion of ultrathin Rh nanosheets on a prepared KBr substrate, followed by the solvent evaporation. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI QUANTUM2000 photoelectron spectrometer using a monochromatic magnesium X-ray source. The binding energies were calibrated with respect to the signal for adventitious carbon (the binding energy of 284.6 eV).

1.4 Synthesis and measurement of Rh/CeO₂ catalysts for catalytic oxidation of CO.

In our experiments, Rh nanoparticles were loaded at 1 wt% on a homemade CeO₂ support, which was prepared by direct thermal decomposition of Ce(NO₃)₃·6H₂O at the temperature of 600 °C for 3 hours.¹ In a typical synthetic procedure, Rh/CeO₂ catalysts were prepared by stirring the ultrathin nanosheets and homemade CeO₂ particles for 1 hour in water with theoretically calculating value of 1 wt%, followed by centrifugation separation and drying in vacuum oven.

The activity test of the catalyst was carried out in a continuous-flow reactor. The reaction gas, 5% CO in nitrogen (99.999% purity) (10 mLmin⁻¹) and air (99.999% purity) (40 mLmin⁻¹) was fed to catalyst nanoparticles (0.10 g) which was set in a fixed-bed flow reactor made of glass with an inner diameter of 2.4 mm. Steady-state catalytic activity was measured at each temperature, with the reaction temperature being raised from 30 °C to 330 °C in steps of 10 °C. The effluent gas was analyzed online by using an on-stream gas chromatograph (FuLi 9790II) equipped with a TDX-01 column.

2. Supplementary experimental results

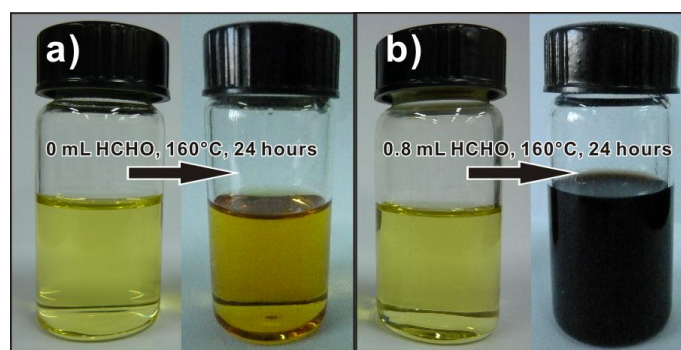


Fig. S1 The photographs of reaction solutions before and after reaction: a) without HCHO; and b) with HCHO (0.8 mL).

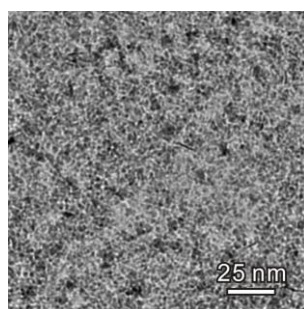


Fig. S2 TEM image of Rh nanoparticles synthesized in the presence of 1.6 mL formaldehyde.

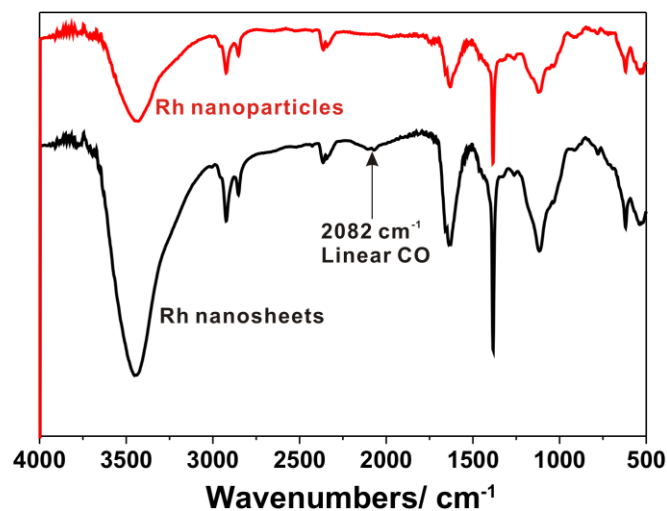


Fig. S3 FTIR spectra of the representative ultrathin Rh nanosheets and Rh nanoparticles.

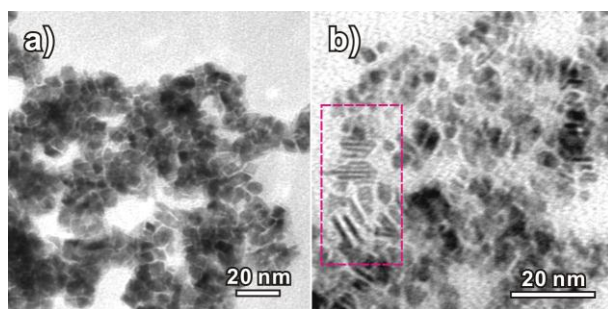


Fig. S4 TEM images of Rh nanoparticles synthesized under different conditions: a) reduced by acetaldehyde; b) reduced by acetaldehyde in the CO atmosphere.

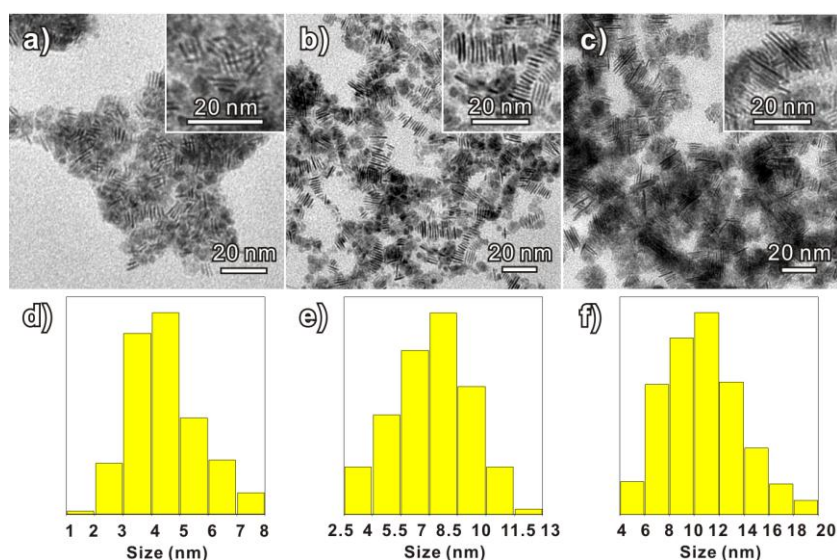


Fig. S5 TEM images and size distribution histograms of ultrathin Rh nanosheets synthesized with different amounts of precursor $\text{Rh}(\text{acac})_3$: a,d) 5 mg; b,e) 10 mg; c,f) 20 mg. Insets: high-magnification TEM images to show the thickness and size of ultrathin Rh nanosheets.

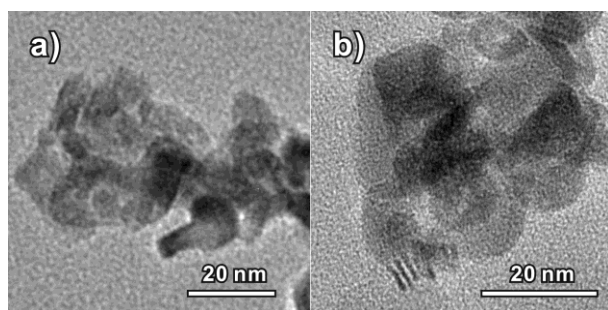


Fig. S6 TEM images of the blank CeO_2 and Rh-loaded CeO_2 catalysts.

Reference

1. Q. Li, Y. Zhang, G. Chen, J. Fan, H. Lan and Y. Yang, *J. Catal.* 2010, **273**, 167-176.