

# Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation

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## Experimental Section

### *1. Synthesis of Ru Nanoparticles*

The Ru nanoparticles (NPs) were prepared by a polyol reduction method based on the previous report on Rh NP synthesis<sup>1</sup> using ruthenium(III) acetylacetonate ( $\text{Ru}(\text{acac})_3$ , 97 %, Sigma-Aldrich) and poly(vinylpyrrolidone) (PVP,  $M_w$ : 55,000, Sigma-Aldrich) as the Ru precursor and the stabilizer, respectively. The syntheses of size-controlled Ru NPs were performed by varying the experimental factors including concentration of  $\text{Ru}(\text{acac})_3$ , type of polyol solvent, and use of the seeded-growth method. In a typical synthesis of 2.1 nm Ru NPs, a stoichiometric amount of  $\text{Ru}(\text{acac})_3$  and PVP (in terms of repeating unit) at a fixed Ru/PVP ratio of 1:10 were added to 20 mL of ethylene glycol (EG) in a 50 mL three-necked flask at room temperature. The stock solution was heated to 80 °C in a Glas-Col electromantle (60 W; 50 mL) with a Cole-Parmer temperature controller (Digi-sense) and was evacuated at this temperature for 20 min to remove water and oxygen under magnetic stirring. The solution was then heated to 180 °C at a rate of 10 °C min<sup>-1</sup> and maintained at this temperature for 2 h under Ar. When the reaction was complete, an excess of acetone was poured into the solution at room temperature to form a cloudy black suspension. This suspension was separated by centrifugation at 4200 rpm for 6 min, and the black product was collected by discarding the colorless supernatant. The precipitated Ru NPs were washed with acetone once, and were redispersed in ethanol. The syntheses of 2.8 and 3.1 nm Ru NPs were performed following the same method for the 2.1 nm Ru NP, except the type of solvent (1,4-butanediol), the evacuation temperature (140 °C), and final heating temperature (215 °C). The syntheses of Ru NPs larger than 3.1 nm Ru were achieved by applying a seeded-growth method using 3.1 nm Ru NP (1 mg in 1 mL 1,4-butanediol) as the seed particles. The details on the experimental conditions for Ru NPs with a controlled particle size are summarized in Table S1.

### *2. Preparation of Langmuir-Blodgett (LB) Films of Ru NPs*

For the preparation of two-dimensional (2D) model catalysts, the Ru NPs were extensively washed with several precipitation-redispersion cycles. The Ru NPs dispersed in ethanol were washed twice by

precipitation and redispersion with hexane and ethanol, respectively, followed by washing twice with chloroform and ethanol to remove the impurities and excess PVP. A monolayer of Ru NPs was formed by placing drops of a chloroform solution of Ru NPs onto the water subphase of an LB trough (Nima Technology, M611) at room temperature. The surface pressure was monitored with a Wilhelmy plate and was adjusted to zero before spreading the NPs. The resulting surface layer was compressed by a mobile barrier at a rate of  $20 \text{ cm}^2 \text{ min}^{-1}$ . The Ru nanoparticles were deposited onto Si wafers ( $1 \text{ cm} \times 1 \text{ cm}$ ) by lifting up the substrates at a rate of  $1 \text{ mm min}^{-1}$  at a surface pressure of  $\sim 12 \text{ mN m}^{-1}$ .

### *3. Preparation of Ru/SBA-15 catalysts*

To prepare 3D model catalysts, SBA-15 mesoporous silica<sup>2</sup> was added to the ethanol solution containing Ru NPs and the slurry was sonicated (VWR ultrasonic cleaner, 75T, 120 W, 45 kHz) for 3 h at room temperature. The Ru NP supported SBA-15 was separated from solution by centrifuging at 4200 rpm for 6 min. Following centrifugation, the solution was clear. The supernatant was separated by decanting and the precipitates were dried at  $100^\circ\text{C}$  overnight.

### *4. Characterization of Ru NPs and 2D and 3D Model Ru Catalysts*

The size and shape of the Ru NPs were analyzed using a Philips FEI Tecnai 12 transmission electron microscope, operated at 100 kV. X-ray diffraction patterns of Ru NPs were taken on a Bruker D8 GADDS diffractometer using  $\text{Co K}_\alpha$  radiation ( $1.79 \text{ \AA}$ ). The morphology of the 2D LB films was examined with a scanning electron microscope using a Zeiss Gemini Ultra-55 with a beam energy of 5 kV.

## **References**

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**Table S1.** Experimental conditions for synthesis of size-controlled Ru NPs.

Sample	Solvent	Ru (acac) <sub>3</sub> Concentration (mM)	Final Reaction Temp. (°C)	Overgrowth	NP size (nm)
1	EG	5	180		2.1
2	Butanediol	5	215		2.8
3	Butanediol	10	215		3.1
4	Butanediol	5	215	Yes	3.8
5	Butanediol	10	215	Yes	5.0
6	Butanediol	10	195	Yes	5.3
7	Butanediol	10	175	Yes	6.0

**Table S2.** Summary of kinetic data for CO oxidation over Ru catalysts.

Catalyst	CO / O <sub>2</sub> Pressure (Torr)	TOF (s <sup>-1</sup> )	E <sub>a</sub> (kcal mol <sup>-1</sup> )	Reference
Ru (0001)	16 / 8		19.5	1
5 wt% Ru/SiO <sub>2</sub>	9.8 / 4.9	1.63 <sup>1</sup>	22.5	2
3 wt% Ru/SiO <sub>2</sub>	32 / 8	0.006 <sup>2</sup>	22.2	3
	26.7 / 13.3	0.01 <sup>2</sup>	25.3	
	13.3 / 26.7	0.004 <sup>2</sup>	20.8	
3 wt % Ru/MgO	13.7 / 6.8		19.6	4

<sup>1</sup>Measured at 177 °C<sup>2</sup>Measured at 120 °C

#### References for Table S2

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**Table S3.** Size dependence of the activity of CO oxidation over noble metal catalysts.

Metal	Catalyst	Particle size ( <i>d</i> ) of catalysts (nm)	CO oxidation activity with increasing <i>d</i>	Reference
Pt	Pt/SiO <sub>2</sub>	1.4 - 18.2	Increase	1
Ir	Ir/SiO <sub>2</sub>	1.0 - 25	Increase	2
Au	Au/Co <sub>3</sub> O <sub>4</sub>	2 - 6	Decrease	3
	Au on TiO <sub>2</sub>	2 - 6	Decrease with maximum	4
Rh	Rh on Si	2 - 11	Decrease	5

**References for Table S3**

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**Figure S1.** Representative TEM image of Ru(3.1 nm)/SBA-15 catalyst.

