# Size Effect of Ruthenium Nanoparticles in Carbon Monoxide Oxidation

*Sang Hoon Joo,[†,‡] Jeong Y. Park,[*,†,§] J. Russell Renzas,[†] Derek R. Butcher,[†] Wenyu Huang,[†] and Gabor A. Somorjai[*,†]*

Department of Chemistry, University of California, Berkeley, and Chemical Sciences and Materials Sciences Divisions, Lawrence Berkeley National Laboratory, Berkeley, California 94720.

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* To whom correspondence should be addressed. E-mail: somorjai@berkeley.edu, jypark@lbl.gov.

[†] University of California, and Lawrence Berkeley National Laboratory

[‡] Present address: School of Nano-Biotechnology and Chemical Engineering, UNIST, Banyeon-ri 100, Ulsan 689-798, Republic of Korea.

[§] Present address: Graduate School of EEWS (WCU), KAIST, Daejeon 305-701, Republic of Korea.

**ABSTRACT**

Carbon monoxide oxidation over ruthenium catalysts have shown an intriguing catalytic behavior, thus has been a subject of intense interests. Here we report a particle size effect in CO oxidation over Ru nanoparticle (NP) catalysts. Uniform Ru NPs with a tunable particle size from 2 to 6 nm were synthesized by polyol reduction of Ru(acac)$_3$ precursor in the presence of poly(vinylpyrrolidone) stabilizer. The catalytic activity of CO oxidation over model catalysts based on size-controlled Ru NPs under oxidizing reaction conditions (40 Torr CO and 100 Torr O$_2$) was found to show a dependence of activity on the Ru NP size; the CO oxidation activity increases with the Ru size, and 6 nm Ru NP catalyst shows 8-fold higher activity than 2 nm catalyst. The results gained from this study would provide the scientific basis for the future design of Ru-based oxidation catalysts.

**KEYWORDS**

The catalytic oxidation of carbon monoxide (CO) to $CO_2$ has long been a benchmark reaction in heterogeneous catalysis.[1-4] The CO oxidation is of practical importance in many industrial processes, including the purification of automobile exhaust gases and the selective oxidation of fuel streams for polymer electrolyte fuel cells. During the last several decades, considerable efforts have been devoted to CO oxidation by noble metals in the forms of single crystal surfaces and supported nanoparticles (NPs), and the results have been well-documented.[1-4] Of the noble metal catalysts, ruthenium has shown an intriguing catalytic behavior for CO oxidation[5-15]; while the Ru single crystal surface is the least active among noble metals under ultrahigh vacuum conditions,[5] it turns out to be highly active under oxidizing and high pressure conditions.[6] CO oxidation over Ru catalysts have thus been intensively pursued during the last decade, with focus mainly on Ru single crystal surfaces.[5-11] By contrast, studies of supported Ru NP catalysts for this reaction have been sporadically reported.[12-15] Particle-size dependence of CO oxidation, the main focus of this study, has not yet been investigated.

The influence of metal particle size on catalytic reactivity has been a subject of continuous interest, due to its significance from fundamental and practical viewpoints.[16-19] Studying the trend of catalytic activity with varying particle size can suggest a structure sensitivity of catalytic reactions, as the change of particle size goes hand-in-hand with variation in the surface atomic structure of NPs. As such, the nature of active sites for catalytic reactions can be assessed, which may in turn allow for the rational design of catalysts for practical use. Particle sizes from 1 to 10 nm are in particular highly relevant to the size effect. In this regime, the coordination number of surface metal atoms dramatically changes and the notion of structure sensitivity can arise. The studies of particle size effects in most cases have been carried out by using catalysts prepared by traditional methods, such as impregnation and ion exchange. In these methods, however, the post-synthetic activation and/or reduction inevitably yield a broad size distribution of the resulting catalysts. Recent progress in nanoscience, particularly in colloidal synthetic methods, has enabled the synthesis of metal NPs with precisely controlled size, shape, and composition from which new 2-dimensional (2D) and 3D NP-based model catalysts have been constructed for rational investigations of catalytic activity and selectivity.[20-24]

In this contribution, we present a particle size effect in CO oxidation over Ru NP catalysts. Uniform Ru NPs with a controlled size from 2 to 6 nm were synthesized by colloidal synthesis and were deposited on a silicon wafer to produce 2D arrays of Ru NPs. The catalytic activity of CO oxidation over Ru catalysts under oxidizing reaction conditions was measured as a function of particle size. It was found that the CO oxidation over Ru NPs is structure sensitive, as the activity increased with increasing Ru size.

Colloidal Ru NPs from 2 to 6 nm were synthesized by a polyol reduction method using $Ru(acac)_3$ as the precursor and poly(vinylpyrrolidone) (PVP) as the surface-capping stabilizer. The polyols, such as ethylene alcohol (EG) and butanediol, were used both as the solvent and as the reducing agent. The details for synthesis conditions for Ru NPs have been summarized in Table S1 in the Supplementary Information. The smallest 2.1 nm Ru NPs were synthesized using EG, while the 2.8 nm and 3.1 nm Ru NPs were prepared with the butanediol solvent in a one-step synthesis. A seeded-growth method was effective in synthesizing larger Ru NPs (3.8 to 6.0 nm) using 3.1 nm Ru NPs as the seeds. In general, the concentration of the Ru precursor and the final reduction temperatures were found to be critical factors in controlling Ru NP size. The higher precursor concentration and lower reduction temperature generally yielded larger Ru NPs, which are consistent with the results from previous syntheses of noble metal NPs using polyol methods.[25-27]

TEM images in Figure 1a to 1f show the formation of uniform Ru NPs ranging from 2 to 6 nm with narrow particle size distributions below 15 % of the mean size. The smaller Ru NPs are mostly composed of spherical particles, while the larger NPs contain a portion of well-faceted particles. Figure 2 displays X-ray diffraction (XRD) patterns for size-controlled Ru NPs. The trend of XRD patterns is consistent with TEM observations, as the line widths of the diffraction lines become sharper with increasing Ru NP size. The crystalline sizes of Ru NPs calculated from the XRD line width were smaller than those from TEM, which is presumably due to the polycrystalline nature of particles. Interestingly, it was observed that the small Ru NPs exhibit diffraction lines corresponding to the

hexagonal close-packed structure, whereas bigger NPs show the mixed phase of face-centered cubic (*fcc*) and hexagonal close-packed structures.

The 2D model catalysts were generated by forming a monolayer of the size-controlled Ru NPs on a Si wafer using the Langmuir-Blodgett technique. The CO oxidation reactions were carried out under oxygen-excess conditions (CO 40 Torr and $O_2$ 100 Torr). After loading into the batch reactor, the Ru NP 2D catalysts were subjected to CO oxidation at 200 °C for several hours until the production of $CO_2$ stabilized. Following this treatment, the CO oxidation activity was measured from 180 – 240 °C (see Supplementary Information for details). Scanning electron microscope images revealed that the Ru NPs on the Si wafer maintained the original morphology after CO oxidation. Figure 3 shows the changes of turnover frequency (TOF) with reaction temperature and Arrhenius plots for CO oxidation on different size Ru NP catalysts, and Figure 4 presents the change of TOF and activation energy ($E_a$) as a function of Ru NP size. These plots clearly indicate that Ru NP catalysts exhibit the trend of increasing catalytic activity with increasing Ru particle size for CO oxidation under high pressure and oxidizing reaction conditions. The 2D catalyst based on the 6 nm Ru NPs exhibits 8-fold higher TOF than 2.1 nm Ru catalyst at 240 °C. The values of $E_a$ derived from the Arrhenius plots range from 26 to 33 kcal mol$^{-1}$ with no distinct size-dependency over the Ru NP size of 2 – 6 nm. Comparison of kinetic data of Ru NP-based catalysts with those from Ru single crystals[6] and supported catalysts[12-14] under stoichiometric reaction conditions (see Table S2) indicates that the values of the TOFs and activation energies of the former catalysts are similar to the latter ones.

The trend of CO oxidation by size-controlled Ru NP catalysts was also investigated using 3D model catalysts. For this purpose, Ru NPs of 2.1, 3.1, and 5.0 nm were incorporated inside the pores of SBA-15 mesoporous silica via sonication-induced capillary inclusion (see TEM image of Ru(3.1 nm)/SBA-15 catalyst in Figure S1). The CO oxidation activity trend of the Ru/SBA-15 3D supported catalysts was similar to that of 2D arrays of Ru NPs, with the activity being higher for larger Ru NPs. This result confirms that the size dependence of catalytic activity for CO oxidation examined with 2D arrays of Ru

NPs, and indicates that the trend of increasing catalytic activity as Ru particle size increases is a general observation for both 2D and 3D supported catalysts.

In particle size effect studies of CO oxidation, multi-fold trends have emerged from different types of metals. Au NP catalysts exhibited a marked increase in CO oxidation activity with diminishing Au size below 5 nm when they were supported on semiconducting oxide supports.[28] A similar sensitivity was observed over colloidally synthesized Rh NPs in the range of 2 to 11 nm.[29] By contrast, supported Pt[30] or Ir[12] catalysts showed the opposite trend of size dependence compared to the Au and Rh catalysts, with the larger particles exhibiting higher CO oxidation activity. The origin of structure sensitivities in CO oxidation have been attributed to various factors, including structural effects, electronic effects, metal-support interactions, and an active surface oxide layer. Particularly, the role of the oxide layer surface surrounding the metal core has been suggested as the catalytically active species, which was identified by advanced *in situ* analytical techniques such as ambient pressure X-ray photoelectron spectroscopy,[29] scanning tunneling microscopy,[31] XRD,[32] and X-ray absorption spectroscopy.[33]

For Ru NP catalysts studied here, under oxidizing reaction conditions, smaller Ru NPs would be subject to a higher degree of oxidation than larger ones, thus exposing a larger portion of catalytically inactive species on their surfaces, which can be correlated with structure sensitivity found in the current study. In conjunction with this claim, Aßmann et al. investigated structural deactivation of polycrystalline $RuO_2$ powder, and suggested that a core-shell particle composed of a $RuO_2$ shell layer formed on the metallic Ru core-shell is catalytically most reactive.[15] Based on this argument, they predicted that in supported Ru NP catalysts, catalytically active oxide species are more stable if the Ru particles become larger, which is in agreement with our results.

In summary, uniform, size-controlled Ru NPs from 2 to 6 nm were synthesized by a polyol method. CO oxidation over model catalysts based on the Ru NP catalysts under oxidizing conditions revealed structure sensitivity as 6 nm Ru NP catalyst shows 8-fold higher activity than 2 nm catalyst. This study demonstrates the versatility of solution-based colloidal synthetic approach that can yield the catalytic NPs with a controlled particle size while maintaining size uniformity, which enables the systematic

study of structural parameters affecting catalytic reactivity. The CO oxidation activity trend observed with size-controlled Ru nanoparticles would provide the scientific basis for the future design of Ru-based oxidation catalysts.

**Supporting Information Available:** Experimental details for synthesis of Ru NP, preparations of 2D and 3D model catalysts based on Ru NPs, characterization methods, and CO oxidation reaction, Tables S1-S3, and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.
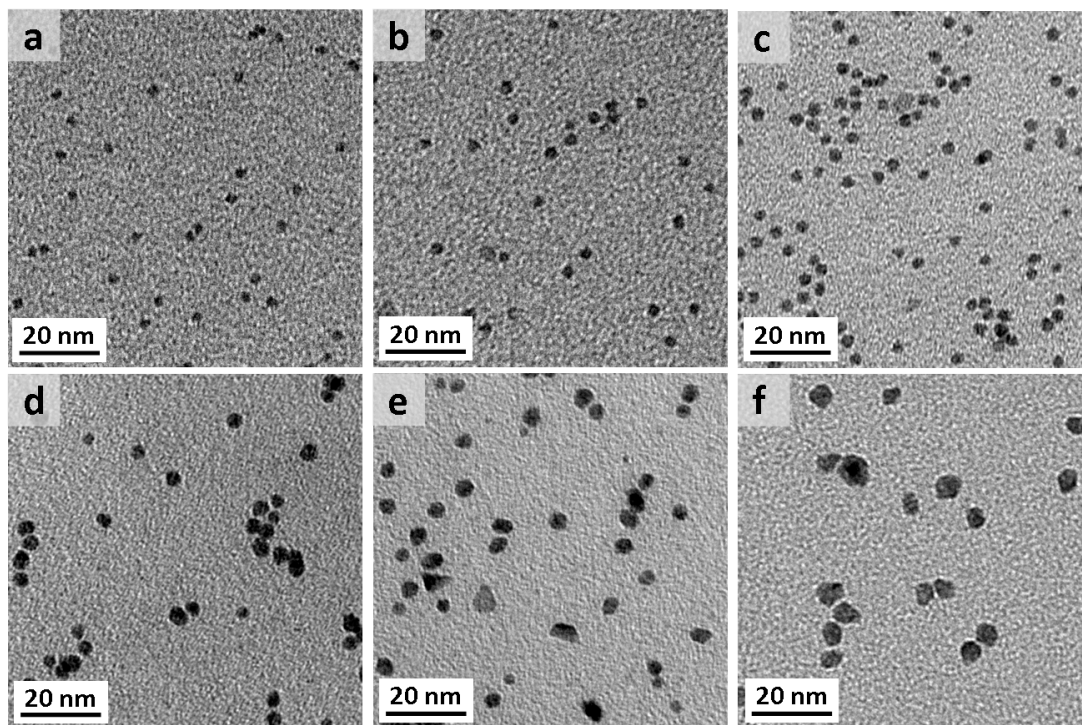
**Figure 1.** TEM images of Ru NPs: (a) 2.1 nm, (b) 2.8 nm, (c) 3.1 nm, (d) 3.8 nm, (e) 5.0 nm, and (f) 6.0 nm. TEM images were taken using a Philips FEI Tecnai 12, operated at 100 kV.
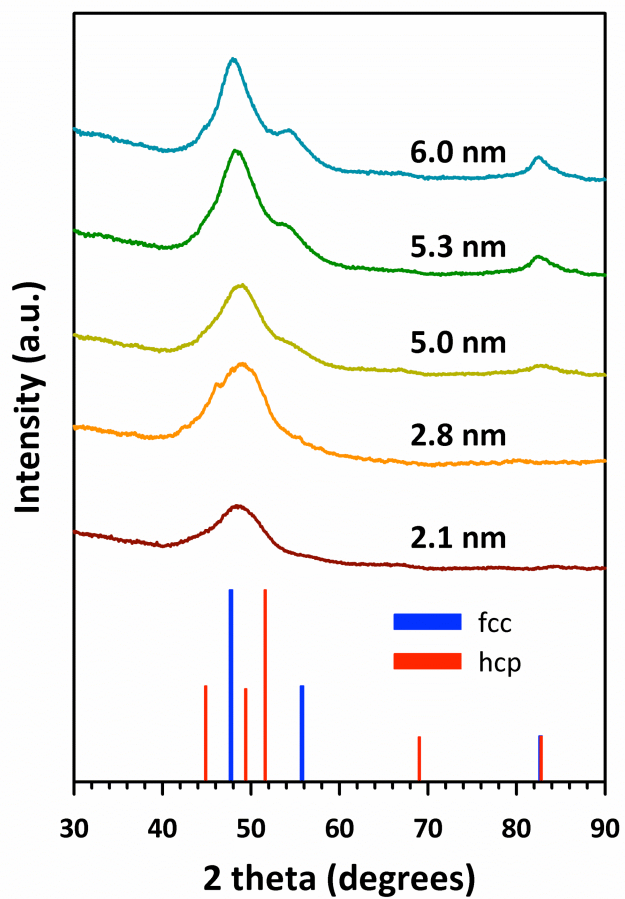
**Figure 2**. XRD patterns for Ru NPs of different sizes with assignment of hexagonal close-packed and face-centered cubic faces of Ru. XRD patterns were taken on a Bruker D8 GADDS diffractometer using Co K radiation (1.79 Å).
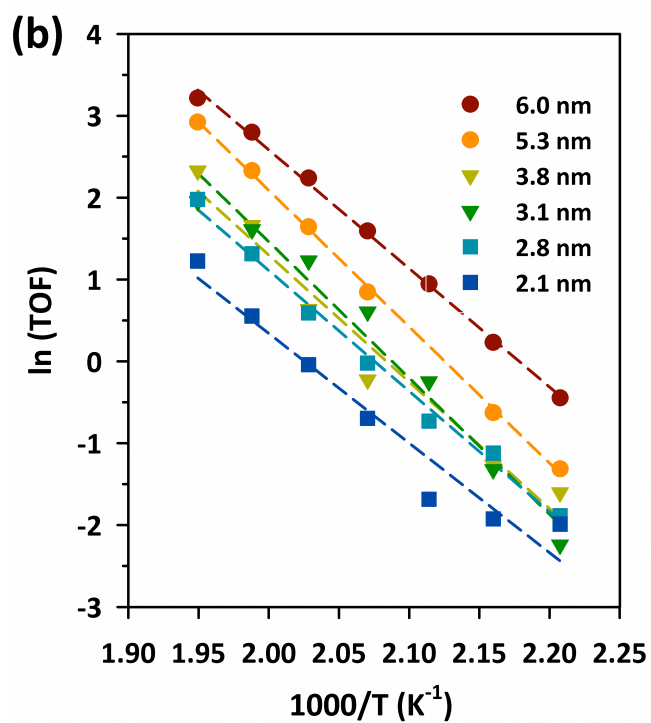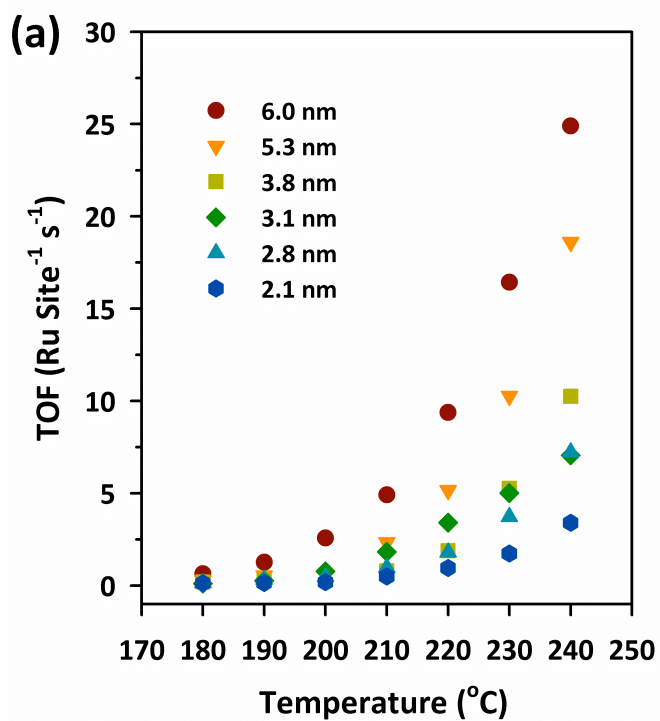
**Figure 3.** CO oxidation activity of 2D model catalysts based on Ru NPs: (a) change of CO oxidation activity with temperature, and (b) Arrhenius plots for CO oxidation.
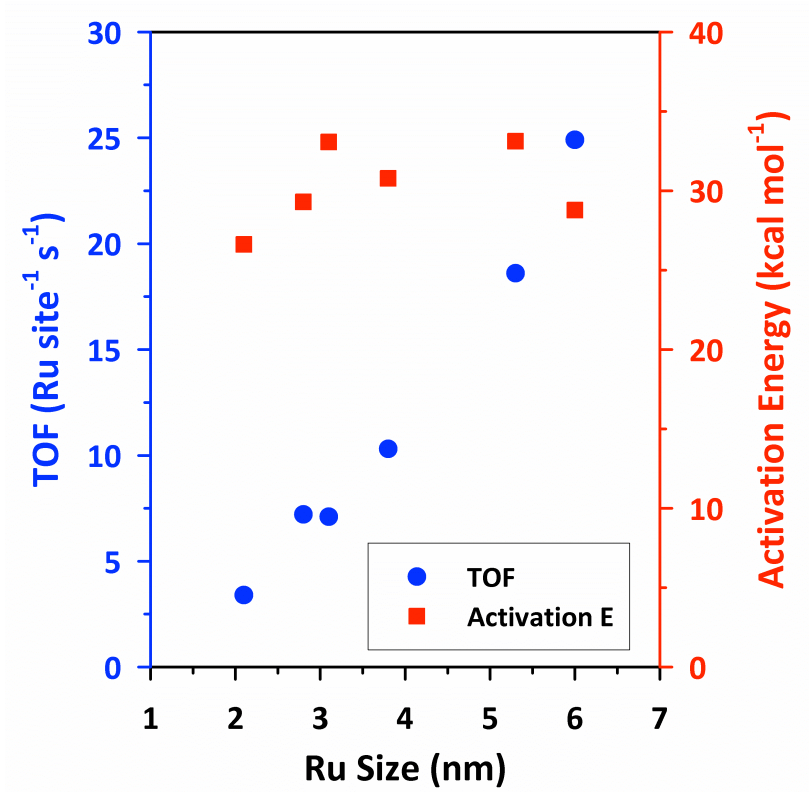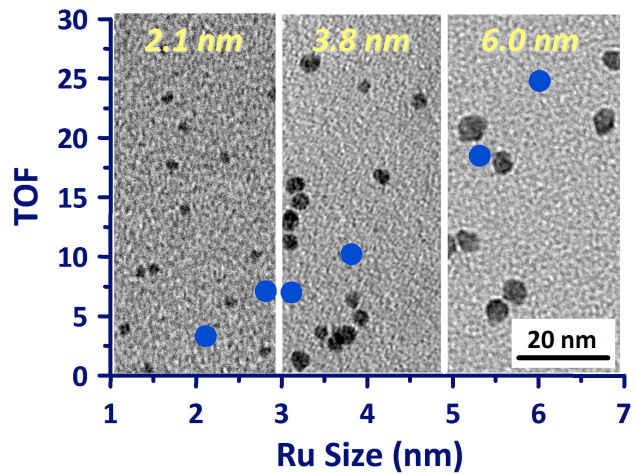
**Figure 4.** TOFs and activation energies measured over on 2D model catalysts based on Ru NPs as a function of Ru size.

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**SYNOPSIS TOC**

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