

2010

Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation

Sang Hoon Joo, *University of California - Berkeley*

Jeong Y. Park, *University of California - Berkeley*

J. Russell Renzas, *University of California - Berkeley*

Derek R. Butcher, *University of California - Berkeley*

Wenyu Huang, *University of California - Berkeley*, et al.



Size Effect of Ruthenium Nanoparticles in Catalytic 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

ABSTRACT Carbon monoxide oxidation over ruthenium catalysts has shown an unusual catalytic behavior. Here we report a particle size effect on CO oxidation over Ru nanoparticle (NP) catalysts. Uniform Ru NPs with a tunable particle size from 2 to 6 nm were synthesized by a polyol reduction of Ru(acac)₃ precursor in the presence of poly(vinylpyrrolidone) stabilizer. The measurement of catalytic activity of CO oxidation over two-dimensional Ru NPs arrays under oxidizing reaction conditions (40 Torr CO and 100 Torr O₂) showed an activity dependence on the Ru NP size. The CO oxidation activity increases with NP size, and the 6 nm Ru NP catalyst shows 8-fold higher activity than the 2 nm catalysts. The results gained from this study will provide the scientific basis for future design of Ru-based oxidation catalysts.

KEYWORDS Ruthenium, nanoparticles, model nanocatalyst, CO oxidation, size effect

The catalytic oxidation of carbon monoxide (CO) to CO₂ has long been a benchmark reaction in heterogeneous catalysis.^{1–4} CO oxidation is of practical importance in many industrial processes, including the reduction of CO in 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 unusual 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 has thus been intensively pursued during the past decade, with the focus mainly on Ru single crystal surfaces.^{5–11} By contrast, studies of supported Ru NP catalysts for this reaction have only been sporadically reported.^{12–15} Particle size dependence of CO oxidation, the main focus of this study, has not been investigated previously.

The influence of metal particle size on catalytic reactivity has been a subject of continuous interest due to its significance from both fundamental and practical viewpoints.^{16–19} The trend of catalytic activity with varying

particle size is related to the various molecular scale factors including change of surface structure, electronic state, metal–support interaction, and oxidation states. 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 in particular are highly relevant to the size effect. The studies of particle size effects in most cases have been carried out using catalysts prepared by traditional methods such as impregnation and ion exchange. In these methods, however, the postsynthetic 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 two-dimensional (2D) and 3D NP-based model catalysts have been constructed for rational investigations of catalytic activity and selectivity.^{20–24}

In this paper, we present a particle size effect on 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 exhibits size dependence on catalytic activity.

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 as both the solvent and the reducing agent. The details of the synthesis conditions for

*To whom correspondence should be addressed. E-mail: (G.A.S.) somorjai@berkeley.edu; (J.Y.P.) jeongypark@kaist.ac.kr.

[†] 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.

Received for review: 05/13/2010

Published on Web: 06/22/2010



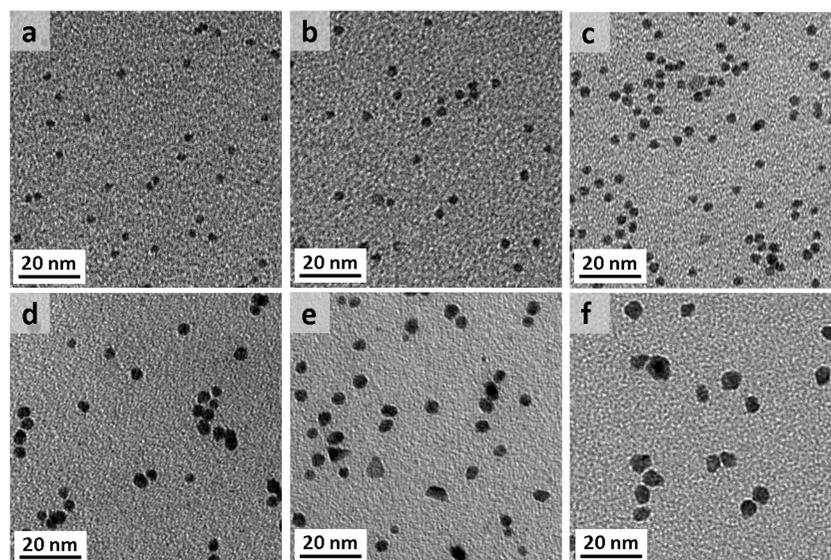


FIGURE 1. TEM images of Ru NPs: (a) 2.1, (b) 2.8, (c) 3.1, (d) 3.8, (e) 5.0, and (f) 6.0 nm. TEM images were taken using a Philips FEI Tecnai 12 machine, operated at 100 kV.

Ru NPs have been summarized in Table S1 in the Supporting Information. The smallest 2.1 nm Ru NPs were synthesized using EG, while the 2.8 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–f 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 the 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 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. The reaction studies were performed in an ultrahigh vacuum chamber with a base pressure of 5×10^{-8} Torr. After loading into the batch reactor, the Ru NP 2D catalysts were subjected

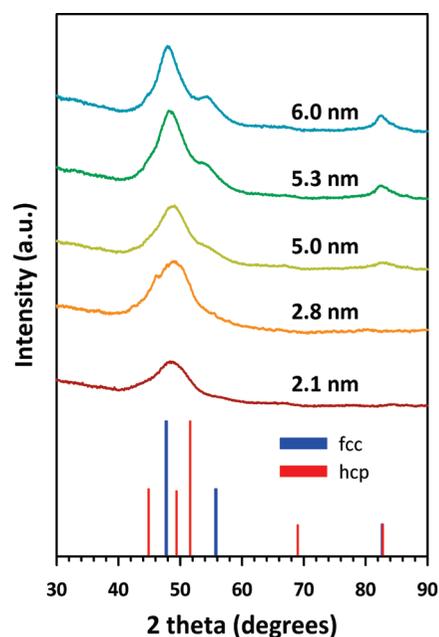


FIGURE 2. XRD patterns for Ru NPs of different sizes with assignment of hexagonal close-packed and face-centered cubic faces of Ru. XRD patterns were taken on a Bruker D8 GADDS diffractometer using Co K radiation (1.79 Å).

to CO oxidation at 200 °C for several hours until the production of CO₂ is stabilized. CO oxidation studies were carried out in a batch reaction system under 40 Torr CO, 100 Torr O₂, and 620 Torr He at a temperature range between 180 and 240 °C. The gases were circulated through the reaction line by a Metal Bellows recirculation pump at a rate of 2 L min⁻¹. An HP Series II gas chromatograph equipped with a thermal conductivity detector and a 150, 1/800 SS 60/80 Carboxen-1000 (Supelco) was used to separate the products for analysis. The measured reaction rates

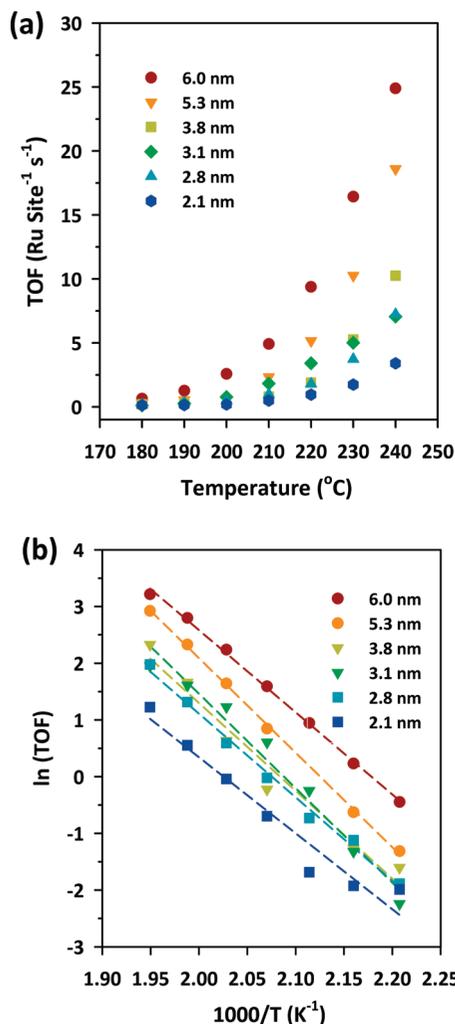


FIGURE 3. CO oxidation activity of 2D model catalysts based on Ru NPs: (a) change of CO oxidation activity with temperature and (b) Arrhenius plots for CO oxidation.

are reported as turnover frequencies (TOF) and are measured in units of product molecules of CO₂ produced per metal surface site per second of reaction time. 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 TOF with reaction temperature and Arrhenius plots for CO oxidation on different size Ru NP catalysts. 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-

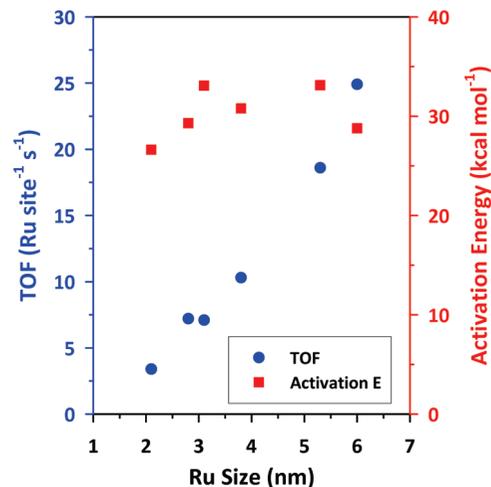


FIGURE 4. TOFs and activation energies measured on 2D model catalysts based on Ru NPs as a function of Ru size.

based catalysts with those from Ru single crystals⁶ and supported catalysts^{12–14} under stoichiometric reaction conditions (see Supporting Information 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 Supporting Information 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, diverse 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 trend on NP size dependence was observed over colloiddally synthesized Rh NPs in the range of 2 to 11 nm.²⁹ By contrast, supported Pt³⁰ and Ir¹² catalysts showed the opposite trend of size dependence compared to the Au and Rh catalysts with the larger particles exhibiting higher CO oxidation activity. Contrary to NP-based catalysts, it has been known that CO oxidation is structure insensitive on single crystal Pt, Rh, and Pd surfaces.^{31,32} For example, Peden et al. reported that the CO oxidation reaction was found to be insensitive to the structure of the surface revealing the same reaction rates, activation energies, and partial pressure dependencies measured on the Rh(111) and

Rh (100) surfaces.³² Ru single crystal surfaces were also reported to be structure insensitive in CO oxidation.¹⁰ This implies that the size dependence of CO oxidation observed on NP-based catalysts would have a different origin than that on single crystal surfaces.

The origin of size dependence of NPs on 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 surface oxide layer surrounding the metal core has been suggested as the catalytically active species, which was identified by advanced *in situ* analytical techniques, including ambient pressure X-ray photoelectron spectroscopy (APXPS),²⁹ scanning tunneling microscopy,³³ XRD,³⁴ and X-ray absorption spectroscopy.³⁵

For CO oxidation by Ru catalysts, Assmann et al. investigated active species and structural deactivation behaviors of various types of Ru catalysts from bulk single crystals to polycrystalline micrometer-scale powders and to supported NPs.^{10,14,15} They found that under oxidizing reaction conditions, the metallic Ru surface converts to a catalytically active thin ruthenium oxide layer which transforms into an inactive oxide phase. They claimed that the stability of the core–shell structure where the active RuO₂ shell layer is formed on the Ru metallic core is controlled by kinetics. An active oxide layer on the Ru single crystals or reduced RuO₂ powder is maintained under oxidizing conditions whereas such an active oxide on the supported Ru NPs is unstable, which indicates that the stability of catalytically active oxide layer appears to increase with the size of Ru catalysts. Therefore, it is reasonable that the stability of Ru NPs changes in a similar manner suggested by Assmann et al.; 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. Consequently, the stability of Ru NPs can be correlated with the size dependence found in the current study.

In summary, uniform, size-controlled Ru NPs from 2 to 6 nm were synthesized by a polyol method. Catalytic CO oxidation was carried out over model catalysts based on the Ru NP catalysts under oxidizing conditions. The results reveal higher activity on the 6 nm Ru NP catalysts than the 2 nm catalysts by a factor of 8. The observed trend of CO oxidation activity can be correlated with the stability of catalytically active core–shell particles composed of RuO₂ species thin layer formed on the Ru metallic core, which will be scrutinized in the near future. This study demonstrates the versatility of solution-based colloidal synthetic approaches that can yield catalytic NPs with a controlled particle size while maintaining size uniformity, which enables the systematic, reliable investigation of a particle size effect on the catalytic activity. The CO oxidation activity trend observed with size-controlled Ru NPs can provide the scientific basis for the design of Ru-based oxidation catalysts.

Acknowledgment. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. J.Y.P. acknowledges the support by WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science, and Technology (31-2008-000-10055-0). Authors thank the Berkeley Electron Microscopy Lab for the use of TEM machine, and also thank Professor A. Paul Alivisatos for use of XRD diffractometer.

Supporting Information Available. Experimental details for synthesis of Ru NPs, preparation of 2D and 3D model catalysts based on Ru NPs, characterization methods, Tables S1–S3, and Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Engel, T.; Ertl, G. *Adv. Catal.* **1979**, *28*, 1–78.
- Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley: New York, 1994.
- Chen, M. S.; Cai, Y.; Yan, Z.; Gath, K. K.; Axnanda, S.; Goodman, D. W. *Surf. Sci.* **2007**, *601*, 5326–5331.
- McClure, S. M.; Goodman, D. W. *Chem. Phys. Lett.* **2009**, *469*, 1–13.
- Lee, H.-I.; White, J. M. *J. Catal.* **1980**, *63*, 261–264.
- Peden, C. H. F.; Goodman, D. W. *J. Phys. Chem.* **1986**, *90*, 1360–1365.
- Over, H.; Kim, Y. D.; Seitsonen, A. P.; Wendt, S.; Lundgren, E.; Schmid, M.; Varga, P.; Morgante, A.; Ertl, G. *Science* **2000**, *287*, 1474–1476.
- Kim, Y. D.; Over, H.; Krabbes, G.; Ertl, G. *Top. Catal.* **2001**, *14*, 95–100.
- Over, H.; Muhler, M. *Prog. Surf. Sci.* **2003**, *72*, 3–17.
- Assmann, J.; Narkhede, V.; Breuer, N. A.; Muhler, M.; Seitsonen, A. P.; Knapp, M.; Crihan, D.; Farkas, A.; Mellau, G.; Over, H. *J. Phys.: Condens. Matter* **2008**, *20*, 184017.
- Gao, F.; Wang, Y.; Cai, Y.; Goodman, D. W. *Surf. Sci.* **2009**, *603*, 1126–1134.
- Cant, N. W.; Hicks, P. C.; Lennon, B. S. *J. Catal.* **1978**, *54*, 372–383.
- Kiss, J. T.; Gonzalez, R. D. *J. Phys. Chem.* **1984**, *88*, 892–897.
- Assmann, J.; Narkhede, V.; Khodeir, L.; Löffler, E.; Hinrichsen, O.; Birkner, A.; Over, H.; Muhler, M. *J. Phys. Chem. B* **2004**, *108*, 14634–14642.
- Aßmann, J.; Crihan, D.; Knapp, M.; Lundgren, E.; Löffler, E.; Muhler, M.; Narkhede, V.; Over, H.; Schmid, M.; Seitsonen, A. P.; Varga, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 917–920.
- Boudart, M. *Adv. Catal.* **1969**, *20*, 153–166.
- Che, M.; Bennette, C. O. *Adv. Catal.* **1989**, *36*, 55–172.
- Bond, G. C. *Chem. Soc. Rev.* **1991**, *20*, 441–475.
- van Santen, R. A. *Acc. Chem. Res.* **2009**, *42*, 57–66.
- Somorjai, G. A.; Frei, H.; Park, J. Y. *J. Am. Chem. Soc.* **2009**, *131*, 16589–16605.
- Narayanan, R.; El-Sayed, M. A. *Top. Catal.* **2008**, *47*, 15–21.
- Tao, A. R.; Habas, S.; Yang, P. *Small* **2008**, *4*, 310–325.
- Somorjai, G. A.; Park, J. Y. *Top. Catal.* **2008**, *49*, 126–135.
- Chen, J.; Lim, B.; Lee, E. P.; Xia, Y. *Nano Today* **2009**, *4*, 81–95.
- Yan, X.; Liu, H.; Liew, K. Y. *J. Mater. Chem.* **2001**, *11*, 3387–3391.
- Viau, G.; Brayner, R.; Poul, L.; Chakroune, N.; Lacaze, E.; Fievet-Vincent, F.; Fievet, F. *Chem. Mater.* **2003**, *15*, 486–494.
- Zhang, Y.; Grass, M. E.; Habas, S. E.; Tao, F.; Zhang, T.; Yang, P.; Somorjai, G. A. *J. Phys. Chem. C* **2007**, *111*, 12243–12253.
- Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175–192.

- (29) Grass, M. E.; Zhang, Y.; Butcher, D. R.; Park, J. Y.; Li, Y.; Bluhm, H.; Bratlie, K. M.; Zhang, T.; Somorjai, G. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8893–8896.
- (30) McCarthy, E.; Jahradnik, J.; Kuczynski, G. C.; Carberry, J. J. *Catal.* **1975**, *39*, 29–35.
- (31) Boudart, M.; Rumpf, F. *React. Kinet. Catal. Lett.* **1987**, *35*, 95–105.
- (32) Peden, C. H. F.; Goodman, D. W.; Blair, D. S.; Berlowitz, P. J.; Fisher, G. B.; Oh, S. H. *J. Phys. Chem.* **1988**, *92*, 1563–1567.
- (33) Hendriksen, B. L. M.; Frenken, J. W. M. *Phys. Rev. Lett.* **2002**, *89*, No. 046101.
- (34) Ackermann, M. D.; Pedersen, T. M.; Hendriksen, B. L. M.; Robach, O.; Bobaru, S. C.; Popa, I.; Quiros, C.; Kim, H.; Hammer, B.; Ferrer, S.; Frenken, J. W. M. *Phys. Rev. Lett.* **2005**, *95*, 255505–90.
- (35) Singh, J.; Alayon, E. M. C.; Tromp, M.; Safonova, O. V.; Glatzel, P.; Nachttegaal, M.; Frahm, R.; van Bokhoven, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9260–9264.