Tuning of Catalytic CO Oxidation by Changing Composition of Rh–Pt Bimetallic Nanoparticles

Department of Chemistry, University of California, Berkeley, California 94720, Chemical and Materials Sciences Divisions, Lawrence Berkeley National Laboratory, I Cyclotron Road, Berkeley, California 94720, and College of Chemistry and Molecular Engineering, the State Key Lab of Rare Earth Materials Chemistry and Applications and PKU-HKU Joint Lab in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China

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ABSTRACT

Recent breakthroughs in synthesis in nanoscience have achieved control of size and composition of nanoparticles that are relevant for catalyst design. Here, we show that the catalytic activity of CO oxidation by Rh/Pt bimetallic nanoparticles can be changed by varying the composition at a constant size (9 \pm 1 nm). Two-dimensional Rh/Pt bimetallic nanoparticle arrays were formed on a silicon surface via the Langmuir–Blodgett technique. Composition analysis with X-ray photoelectron spectroscopy agrees with the reaction stoichiometry of Rh/(Pt + Rh). CO oxidation rates that exhibit a 20-fold increase from pure Pt to pure Rh show a nonlinear increase with surface composition of the bimetallic nanoparticles that is consistent with the surface segregation of Pt. The results demonstrate the possibility of controlling catalytic activity in metal nanoparticle-oxide systems via tuning the composition of nanoparticles with potential applications for nanoscale design of industrial catalysts.

Catalysts used in many commercial chemical processes consist of nanoparticles, usually in the 1-10 nm size regime, supported on metal oxides. Colloid nanoparticles of this size can be used as model catalysts to elucidate metal support interactions or the importance of metallic cluster size and composition. Dimensional and compositional tuning of monodispersed platinum and rhodium nanoparticles in the 1-10 nm range and the resulting changes in surface and electronic structure presents an opportunity to tailor particle surfaces to affect substrate interactions and eventually control catalytic activity and selectivity.¹⁻¹¹ We are now able to study the dependence of catalytic activity on the composition of bimetallic nanoparticles without variation in particle size. In this paper, we report on the composition dependence of CO oxidation for rhodium/platinum bimetallic nanoparticles of a constant size (9 \pm 1 nm). The Rh/Pt bimetallic nanoparticles were synthesized and prepared as films on silicon wafers, deposited by the Langmuir-Blodgett (LB) method, as model CO oxidation catalysts. The turnover rate

of Rh is 20 times that of Pt under the reaction condition used (100 Torr O_2 , 40 Torr (CO at 180 °C) while the activation energy increases from 25 to 27 kcal/mol with increasing rhodium content. X-ray photoelectron spectroscopy (XPS) was utilized to determine the Rh/Pt ratio. This investigation indicates that CO oxidation activity can be controlled by tuning the composition of bimetallic Rh/Pt nanoparticles.

Details on the synthesis of Rh nanoparticles have been described elsewhere.¹² In a typical synthesis of Rh_rPt_{1-r} binary nanoparticles (Table 1), a stoichiometric amount of rhodium(III) acetylacetonate (Rh(acac)₃, 97%, Sigma-Aldrich), platinum acetylacetonate (Pt(acac)₂, 97%, Sigma-Aldrich), and poly(vinylpyrrolidone) (PVP, $Mw = 55\ 000$, Sigma-Aldrich) (in terms of the repeating unit) at a fixed (Rh + Pt)/PVP ratio of 1:10 were added to 20 mL of 1,4butanediol (99%, Sigma-Aldrich) in a 50 mL three-necked flask at room temperature. The stock solution was heated to 140 °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, resulting in an optically transparent orange-yellow solution. The solution was then heated to the desired reaction temperature at a rate of 10 °C

^{*} To whom correspondence should be addressed. E-mail: somorjai@ berkeley.edu.

[†] University of California and Lawrence Berkeley National Laboratory. [‡] Peking University.

[§] These authors contributed equally to this work.

Table 1. Synthetic Conditions, Size, and XRD Results of Rh_xPt_{1-x} (x = 0-1) Nanocrystals

sample	Pt(acac) ₂ [mmol]	Rh(acac) ₃ [mmol]	H_2PtCl_6 [mmol]	T [°C]	<i>t</i> [h]	$size^{a}$ [nm]	$I_{(111)}/I_{(200)}$
Pt			0.1	185	1.5	9.5 ± 0.8	2.78
$\mathrm{Rh}_{0.2}\mathrm{Pt}_{0.8}$	0.02	0.005		225	1	9.2 ± 2.4	2.86
$Rh_{0.4}Pt_{0.6}$	0.015	0.01		225	1	9.3 ± 1.2	3.35
$Rh_{0.5}Pt_{0.5}$	0.0125	0.0125		225	1	8.1 ± 0.8	3.20
$Rh_{0.6}Pt_{0.4}$	0.02	0.03		220	1	8.5 ± 0.9	3.95
$Rh_{0.8}Pt_{0.2}$	0.005	0.02		225	1	9.2 ± 1.1	4.57
Rh	0	0.025		215	2	9.0 ± 0.8	6.68

^a Standard deviation determined by measuring 150 nanocrystals from a TEM image.

 min^{-1} and maintained at this temperature for 1 h under Ar. During the reaction, the color of the solution gradually turned from orange-yellow to black. 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 Rh_xPt_{1-x} nanocrystals were washed with acetone once then redispersed in ethanol. The synthetic procedure of Pt nanocrystals was the same as that used to synthesize Rh_xPt_{1-x} nanocrystals, except that 0.1 mmol of chloroplatinic acid hexahydrate (H₂PtCl₆, ACS reagent, Sigma-Aldrich), 4 mmol of tetramethylammonium bromide ((CH₃)₄NBr, >98%, Sigma-Aldrich), and 2 mmol of poly(vinylpyrrolidone) (PVP, Mw = 24000, Sigma-Aldrich) (in terms of the repeating unit) were added to 20 mL of ethylene glycol (>98%, EMD) in a 50 mL threenecked flask at room temperature.

The shape, size, and lattice structure of the Rh_xPt_{1-x} nanocrystals were analyzed using a Philips FEI Tecnai 12 (Conventional transmission electron microscope (TEM)) and Philips CM200/FEG (high-resolution TEM (HRTEM)), operated at 100 and 200 kV, respectively. The samples were prepared by placing a drop of a Rh_xPt_{1-x} nanocrystal sol in ethanol onto a continuous carbon-coated copper TEM grid.

For preparing two-dimensional nanoparticle arrays, the Rh_xPt_{1-x} nanocrystals were washed four times by precipitation and dispersion with hexanes and ethanol, respectively, followed by dispersion in chloroform (1 mL of Rh_xPt_{1-x} dispersion was precipitated by adding 4 mL of hexane and redispersed in 1 mL of ethanol or chloroform with sonication) to remove the impurities and excess PVP. Monolayers of Rh_xPt_{1-x} nanocrystals were formed by placing drops of Rh_xPt_{1-x} nanocrystal chloroform solution 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 nanocrystals. The resulting surface layer was compressed by moving the mobile barrier at a rate of 15 cm²/min. The Rh_xPt_{1-x} nanocrystals were deposited onto Si wafers (0.5 cm \times 1 cm) by liftup of the substrates at a rate of 1 mm/min. XPS spectra were taken on a 15 kV, 350 Watt PHI 5400 ESCA/XPS system equipped with an Al anode X-ray source.

The reaction studies were performed in an ultrahigh vacuum chamber with a base pressure of 5.0×10^{-8} Torr.¹³ CO oxidation studies were carried out under 40 Torr CO,

100 Torr O_2 , and 620 Torr He. The gases were circulated through the reaction line by a Metal Bellows recirculation pump at a rate of 2 L/min. The volume of the reaction loop is 1.0 L. An HP Series II gas chromatograph equipped with a thermal conductivity detector detector and a 15', 1/8" SS 60/80 Carboxen-1000 (Supelco) was used to separate the products for analysis. The measured reaction rates are reported as turnover frequencies (TOF) and are measured in units of product molecules of CO_2 produced per metal surface site per second of reaction time. The number of metal sites is calculated by geometrical considerations based on scanning electron microscopy (SEM) measurements of surface area of a nanoparticle array.

Rh/Pt bimetallic nanoparticles were synthesized with variable composition and were capped with PVP that was porous to both reactants and products. Figure 1 shows TEM images of the Rh_xPt_{1-x} nanocrystals; the inset in Figure 1d shows an HRTEM image of the Rh_{0.5}Pt_{0.5} nanocrystals exhibiting (111) and (100) facets. The Rh composition (*x*) is the molar ratio of Rh(acac)₃ to total amount of Rh(acac)₃ and Pt(acac)₂. The synthetic conditions, size of Rh_xPt_{1-x} (x = 0-1) nanocrystals, and the ratio of the intensity of the (111) to (200) diffraction peaks are shown in Table 1. The size distribution histograms and X-ray diffraction results of the Rh_xPt_{1-x} nanocrystals are presented in the Supporting Information.

The chemical composition and morphology of twodimensional LB films were characterized with XPS and SEM, respectively. Figure 2a shows XPS plots of LB films of Rh_xPt_{1-x} (x = 0-1) nanocrystals. For all nanoparticle films, N1s, C1s, Ols, Si2s, and Si2p peaks are observed. Of these, N1s is exclusively associated with the presence of the capping layer (PVP). As the composition of Rh increases, the intensity of the Rh3d peak increases while the Pt4f and Pt4d peaks decrease. Using the sensitivity factors of Rh and Pt and the integrated peak areas of Rh3d and Pt4f, the alloy compositions were estimated. Figure 2b shows alloy composition determined by XPS as a function of initial Rh composition (x). Within error, the XPS composition is consistent with the initial Rh composition (x).¹⁴

The catalytic oxidation of CO to CO_2 is environmentally and industrially important and thus is a well-studied reaction.^{3,15,16,17} On Pt(111), this reaction takes place in two main temperature regimes. Below the ignition temperature, CO and O combine on the platinum surface and desorb as CO₂. The reaction follows Langmuir–Hinshelwood (L-H) kinetics,



Figure 1. TEM images of the Rh_xPt_{1-x} nanocrystals: (a) x = 0; (b) x = 0.2; (c) x = 0.4; (d) x = 0.5; (e) x = 0.6; (f) x = 0.8. Inset shows the HRTEM image of the $Rh_{0.5}Pt_{0.5}$ nanocrystals.



Figure 2. (a) XPS spectra measured on Rh_xPt_{1-x} (x = 0-1) nanocrystals on silicon surface. (b) Plot of Rh composition determined by XPS measurement vs Rh composition (x).

and the dominant surface species on platinum during reaction is CO.¹⁷ Above the ignition temperature, the surface is mainly covered by oxygen adatoms.

We monitored reaction kinetics of Rh_xPt_{1-x} nanocrystals by gas chromatography. Figure 3a shows the turnover rate (at 180 and 200 °C) and activation energy measured on seven Rh_xPt_{1-x} (x = 0-1) nanoparticle arrays. As shown in the plot, the Rh nanoparticles have a higher TOF than Pt nanoparticles by a factor of 20 ± 4, while Rh_xPt_{1-x} (x =0.2–0.8) exhibit an intermediate activity. Also, the activation energy of Rh_xPt_{1-x} increases from 25.4 (±1.2) to 27.1 (±1.4) kcal/mol with increasing Rh content. The dependence of CO oxidation rate for $Rh_{0.5}Pt_{0.5}$ bimetallic nanoparticle on the partial pressure of CO and O₂ were studied at 473 K. The reaction rate is negative first order for CO and positive first order for O₂, consistent with CO oxidation of Rh(111) and Pt(111) below the ignition temperature.

The change of composition and morphology of bimetallic nanoparticles after CO oxidation up to 220 °C was checked with XPS and SEM. After the reaction, we did not observe any significant change in morphology of nanoparticles within the resolution of SEM (\sim 1 nm), indicating the absence of agglomeration of nanoparticles. The relative composition of



Figure 3. (a) Plot of turnover rate at 180 and 200 °C and activation energy of Rh_xPt_{1-x} (x = 0-1) nanoparticle arrays on silicon surface as a function of Rh composition determined with XPS. (b) Plot of turnover rate measured at 180 °C of Rh_xPt_{1-x} (x = 0-1) nanoparticle arrays and calculated TOF based on a surface segregation model with $A_0 = 0.27$ (best fit), $A_0 = 0.17$ (for (111) surface), A_0 = 0.51 (for (100) surface), and $A_0 = 1$ (no surface segregation).

Pt and Rh after reaction was within 3% of the initial composition. $^{18}\,$

Our observation that pure Rh nanoparticles are more reactive than Pt nanoparticles is consistent with the CO oxidation results of Kalinkin et al. on Rh, Pt, and Rh–Pt alloy thin films at low pressure ($\leq P \leq 2 \times 10^{-5}$ mbar).^{19,20} It was found that the activity of the alloy is intermediate between the activities of the individual metals, while a Rh thin film shows much higher activity than a Pt thin film.²⁰ We can also compare the activity of single-crystal Rh(111) with that of Pt(111). Peden et al. studied CO oxidation on Rh(111) and Rh(100).²¹ The activation energy for both Rh(111) and Rh(100) is 25.4 kcal/mol. By using the activation energy and reaction orders (first order for O₂ and negative first order for CO), the TOF at 100 Torr O₂, 40 Torr CO, and 500 K for Rh(111) is predicted to be ~20 (/metal site/second). Likewise, by using Su et al.'s CO oxidation result on Pt(111),¹⁶ the TOF for Pt(111) (at 100 Torr O₂ and 40 Torr CO, and 500 K) is \sim 1 (/metal site/second). Thus, our present results, indicating a 20-fold increase in Rh nanoparticle activity compared to Pt nanoparticle activity, is consistent with that of single-crystal Pt(111) and Rh(111).

The higher activity of Rh in this reaction should follow from (L-H) kinetics that was verified with our kinetics result. On both the metals, CO has similar heats of adsorption, which are equal to the activation energy for CO desorption. The surface reaction between adsorbed CO and O is also very efficient for all noble metals. Therefore, our result is likely to be associated with the adsorption of oxygen. Large differences in the rates of the O₂ dissociative adsorption on polycrystalline surfaces of these metals have been reported. The initial dissociative sticking probability is 0.2 on Pt and 1.0 on Rh.^{22,23} During the low-temperature competitive adsorption of CO and O₂, this difference in s₀ will result in a more efficient formation of Oads on the vacant sites of the Rh surface than on Pt, leading to faster subsequent formation of vacant sites via the reaction between neighboring Oads and CO_{ads}.

It is interesting that the reactivity of CO oxidation increases nonlinearly as a function of Rh composition as shown in Figure 3b. If the reactive sites of Rh and Pt have the same ratio as the bulk composition, the reactivity is likely to change linearly as a function of composition. This trend could be associated with preferential migration of Pt to the surface, giving rise to a higher surface concentration of Pt compared to the bulk concentration. The reactivity is dominated by Pt segregated to the surface at low Rh concentration, resulting in a lower than expected turnover rate. Surface segregation of Pt is consistent with the higher surface energy of Rh (2.799 J m⁻² for Rh(100)) relative to Pt (2.734 J m⁻² for Pt(100)).²⁴ Pt enrichment at the surface layer has been revealed in earlier experimental studies on Pt-Rh alloys utilizing ion scattering and Auger electron spectroscopy^{25,26} and theoretical studies using a combination of cluster expansion and Monte Carlo statistical simulations.27

We considered the influence of surface segregation on the chemical reactivity to first approximation. The surface concentrations of component 1 (x_1^{S}) and 2 (x_2^{S}) are given by the following equation for a binary alloy. $x_1^{S}/x_2^{S} = (x_1^{B}/x_2)^{S}$ x_2^{B})exp[$(\gamma_1 - \gamma_2)a/RT$] = $(x_1^{B}/x_2^{B})A_0$, where x_1^{B} and x_2^{B} are the bulk composition of components 1 and 2, respectively, γ_1 and γ_2 are the surface energy of components 1 and 2, and a is the area per atom. Turnover rate measured at 180 °C and calculated turnover rates for $A_0 = 1$ (no surface segregation) and $A_0 = 0.27$ (best fit) using TOF₁ = TOF_{Rh} = 4.78 (molecule/site/second), and $TOF_2 = TOF_{Pt} = 0.23$ (molecule/site/second). The calculated TOF for $A_0 = 0.51$ (for (100) surface), and $A_0 = 0.173$ (for (111) surface) are also included. measured turnover rate lies between those for $A_0 = 0.51$ and $A_0 = 0.17$. This is expected because our bimetallic nanoparticles have both (111) and (100) surfaces. Therefore, the agreement between our measured TOF and calculated TOF is good considering the structural complexity of nanoparticles. We note that we did not take into account complexities associated with the change of surface electronic structure of Pt-Rh nanoparticles.^{28,29}

In conclusion, we synthesized Rh/Pt binary alloy nanoparticles of 9 ± 1 nm. For catalysts designed using colloidal nanoparticles, particle size and capping layers can play a role in the catalytic properties. In this study, the capping layer and particle size are constant, while the composition is exclusively changed. We carried out CO oxidation on a two-dimensional model system of Rh/Pt bimetallic nanoparticle arrays and found that CO oxidation rates that exhibit 20 ± 4 fold increase from pure Pt to pure Rh show nonlinear increase with surface composition of the bimetallic nanoparticles. The nonlinear increase of reactivity with Rh composition can be associated with the preferential surface segregation of Pt. The kinetics indicates that the oxidation reaction occurs below ignition where the (L-H) mechanism dominates. This can permit us to control the catalytic activity via tuning composition of alloy constituent.

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Supporting Information Available: Size and surface structure of Rh/Pt bimetallic nanoparticles and influence of CO oxidation on chemical composition and morphology of nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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