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**Rh$_{1-x}$Pd$_x$ nanoparticle composition dependence in CO oxidation by oxygen: catalytic activity enhancement in bimetallic systems**

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Bimetallic 15 nm Rh$_{1-x}$Pd$_x$ nanoparticle catalysts of five different compositions and supported on Si wafers have been synthesized, characterized using TEM, SEM, and XPS, and studied in CO oxidation by O$_2$ in two pressure regimes: atmospheric pressure and 100–200 mTorr. The RhPd bimetallic nanocrystals exhibited similar synergetic effect of increased reaction activity at both atmospheric (760 Torr) and moderate (100–200 mTorr) pressures compared with pure Pd or Rh. The magnitude of the effect depends on the relative pressures of the CO and O$_2$ reactant gases and the reaction temperature. The catalytic activity of the nanocrystals measured at moderate pressure is directly correlated to the APXPS studies, which were carried out in the same pressure. The APXPS studies suggest that the Pd–Rh interfaces are important for the enhanced activity of the bimetallic nanoparticles.

**Introduction**

Bimetallic catalysts are frequently utilized for industrial applications and they are important model systems for furthering the understanding of catalytic mechanisms and processes. These catalysts often exhibit increased activity, favorable selectivity, and reduced rates of deactivation.$^{1-9}$ For example, one recent study by Stamenkovic et al. on a Pt$_3$Ni(111) single crystal in the oxygen reduction reaction demonstrated a 10-fold enhancement in catalytic activity over the corresponding Pt(111) surface.$^1$ This effect was determined to be a result of compositional oscillation in the top three layers of the catalysts. Another study by Gao et al. found that CO oxidation kinetics on AuPd(100) depend on whether Pd sites are isolated or contiguous, because of significant differences in CO binding on the two types of sites.$^2$

The studies by Stamenkovic and Gao both used bimetallic single crystals. Single crystals, however, are known to behave quite differently from nanoparticles.$^{10}$ Nanoparticle reactivity is often dependent on size and oxidation state,$^{11}$ in part because small particles can oxidize much more easily than large particles and, especially, single crystals. In order to expand control and understanding of bimetallic nanoparticle catalysts there is a need for detailed studies on the roles of nanoparticle size, surface composition, and in situ oxidation state on catalytic behavior.

Among the large number of possible nanoparticle compositions, Rh, Pt, and Pd-based mono-, bi-, and trimetallic nanocrystals with controlled composition, size, and shape are of special interest because of their role in three-way automotive exhaust catalysis.$^{12}$ Although CO oxidation has been studied extensively, many open questions remain regarding catalyst behavior in these systems, especially with regard to composition and oxidation state$^{13,14}$ and how these factors affect catalyst deactivation,$^{15}$ synergism,$^{16}$ and surface segregation.$^{17}$

Previous work in our lab on 15 nm Rh$_{0.5}$Pd$_{0.5}$ bimetallic Pd-core Rh-shell nanoparticles supported on Si wafers used ambient pressure X-ray photoelectron spectroscopy (APXPS) to examine the dependence of surface composition and oxidation state on the local chemical environment.$^{17}$ This study found significant reversible changes in the catalyst composition when the nanoparticles were exposed to NO, CO, O$_2$, H$_2$, and mixtures of NO + CO at 300 °C. However, the catalytic reaction kinetics and surface composition of these nanoparticles has not previously been studied under the CO oxidation reaction conditions.
In this work, the synthesis of near-monodisperse Rh$_{1-x}$Pd$_x$ ($x = 0–1$) nanocrystals at a constant size of 15 nm by a one-step polyol method is reported. The as-synthesized bimetallic nanocrystals have Rh-rich surfaces. The RhPd bimetallic nanoparticle catalysts showed activity enhancement (synergy) in CO oxidation by O$_2$ compared with pure Pd or Rh. APXPS studies showed that CO interacts more strongly with Pd than with Rh, while O$_2$ has the opposite behavior. Based on the observation from APXPS studies, the reaction synergy could be explained by spillover of O atoms from Rh onto CO- and/or C-covered Pd reaction sites under reaction conditions.

### Experimental details

1. **Nanoparticle synthesis**

Rhodium(III) acetylacetonate (Rh(acac)$_3$, 97%), palladium(II) acetylacetonate (Pd(acac)$_2$, 99%), 1,4-butanediol (99%), and poly(vinylpyrrolidone) (PVP, $M_w = 55 000$) were purchased from Sigma-Aldrich. All the solvents, including acetone, ethanol, hexane, and chloroform, were of analytical grade and were used without further purification.

Given amounts of Rh(acac)$_3$ and Pd(acac)$_2$ (0.1 mmol total) and 1 mmol PVP (monomer concentration) were added to 20 ml of 1,4-butanediol in a 50 ml three-necked flask at room temperature. The stock solution was heated to 50 °C using a Glas-Col electromantle (60 W, 50 ml) with a Cole-Parmer temperature controller (Diqisense). All the solvents, including acetone, ethanol, hexane, and chloroform, were of analytical grade and were used without further purification.

Given amounts of Rh(acac)$_3$ and Pd(acac)$_2$ (0.1 mmol total) and 1 mmol PVP (monomer concentration) were added to 20 ml of 1,4-butanediol in a 50 ml three-necked flask at room temperature (Table 1). The stock solution was heated to 50 °C using a Glas-Col electromantle (60 W, 50 ml) with a Cole-Parmer temperature controller (Diqi-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 flask was then heated to 220 °C at a rate of 10 °C min$^{-1}$ and was maintained at this temperature (±2 °C) for 1.5 h under Ar. The solution was then poured into the solution at room temperature to form a cloudy black suspension. This suspension was separated by centrifugation at 4200 rpm for 10 min and the black product was collected by discarding the colorless supernatant. The precipitated Rh$_{1-x}$Pd$_x$ nanocrystals were washed with acetone once then re-dispersed in ethanol.

The synthetic procedure used to produce Pd nanocrystals was the same as that used to synthesize Rh$_{1-x}$Pd$_x$ ($x = 0–0.8$) nanocrystals, except that 0.1 mmol Pd(acac)$_2$ was added to 20 ml of 1,4-butanediol in a 50 ml three-necked flask at room temperature for reaction at 220 °C for 0.5 h (Table 1).

The synthetic procedure used for Rh nanocrystals was the same as that used to synthesize Pd nanocrystals, except that 0.2 mmol Rh(acac)$_3$ was added to 20 ml of 1,4-butanediol in a 50 ml three-necked flask at room temperature and evacuated at 140 °C for 20 min, followed by reaction at 205 °C for 2 h (Table 1).

2. **Preparation of the Langmuir–Blodgett film**

The Rh$_{1-x}$Pd$_x$ nanocrystals were washed several times by repeated cycles of precipitation and dispersion. Precipitation was performed by adding 1 ml of the nanocrystal solution to 4 ml of hexane. The supernatant was decanted and the remaining precipitated nanoparticles were dispersed by sonication in 1 ml of ethanol (in early wash cycles) or chloroform (in later wash cycles) to remove the impurities and excess PVP. Monolayer of Rh$_{1-x}$Pd$_x$ nanocrystals was formed by placing drops of Rh$_{1-x}$Pd$_x$ nanocrystal chloroform solution onto the water surface of a LB trough (Nima Technology, M611) at room temperature.$^{15}$ The surface pressure was monitored with a Wilhelmy plate, which was adjusted to zero prior to spreading the nanocrystals. The resulting surface layer was compressed by moving the mobile barrier at a rate of 15 cm$^2$ min$^{-1}$. A typical surface pressure was 11 mN m$^{-1}$, which resulted in nanocrystal surface coverage of 15–30%. The Rh$_{1-x}$Pd$_x$ nanocrystals were deposited onto Si wafers (1 cm $\times$ 1 cm) by lift-up of the substrates at a rate of 1 mm min$^{-1}$ using the Langmuir–Schäffer horizontal lift-off method. This 2D sample geometry was used for reaction studies and the APXPS studies.

3. **CO oxidation reactions at atmospheric (760 Torr) and moderate (100–200 mTorr) pressure**

CO oxidation reactions were performed using two setups: one atmospheric-pressure setup, and one moderate-pressure setup. The first setup was used to obtain turnover frequency (TOF) and activation energy using gas chromatography (GC) at a total pressure of one atmosphere. The second setup was used to obtain light-on temperatures and qualitative comparison of reaction rates at total pressures of 100–200 mTorr. This setup was built specifically to mimic the conditions used in APXPS studies of surface segregation and oxidation behavior in bimetallic nanoparticle catalyst systems, such as Rh$_{1-x}$Pd$_x$ catalysts,$^{17}$ in order to bridge the pressure gap between conventional kinetic studies and photoelectron-based studies.

The atmospheric-pressure setup consisted of a laboratory scale batch reactor with continuous gas recirculation between 160 and 200 °C. Samples were loaded into quartz reactors with a type-K thermocouple touching the reactor near the sample. Prior to the reaction, the manifold was filled with 40 Torr CO (Praxair, UHP), 100 Torr O$_2$ (Praxair, UHP), and a balance of He (Praxair, UHP) initially at atmospheric pressure, all regulated by mass flow controllers. Gas composition was analyzed with a HP 5890 Series II gas chromatograph equipped with a thermal conductivity (TCD) detector. Turnover frequency (reported as product molecules site$^{-1}$ s$^{-1}$) was calculated by extrapolating the conversion data to the initial

### Table 1 Synthetic conditions, lattice constants, and crystallite sizes of PVP-capped Rh$_{1-x}$Pd$_x$ ($x = 0–1$) nanocrystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rh(acac)$_3$/mmol</th>
<th>Pd(acac)$_2$/mmol</th>
<th>T/°C</th>
<th>t/h</th>
<th>a/Ånm</th>
<th>Size/Ånm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>0.2</td>
<td>0</td>
<td>205</td>
<td>2</td>
<td>0.385</td>
<td>14.4 ± 1.4*</td>
</tr>
<tr>
<td>Rh$<em>{0.8}$Pd$</em>{0.2}$</td>
<td>0.08</td>
<td>0.02</td>
<td>220</td>
<td>1.5</td>
<td>0.385</td>
<td>15.1 ± 2.9</td>
</tr>
<tr>
<td>Rh$<em>{0.6}$Pd$</em>{0.4}$</td>
<td>0.06</td>
<td>0.04</td>
<td>220</td>
<td>1.5</td>
<td>0.387</td>
<td>15.4 ± 2.4</td>
</tr>
<tr>
<td>Rh$<em>{0.5}$Pd$</em>{0.5}$</td>
<td>0.05</td>
<td>0.05</td>
<td>220</td>
<td>1.5</td>
<td>0.387</td>
<td>16.0 ± 1.9</td>
</tr>
<tr>
<td>Rh$<em>{0.4}$Pd$</em>{0.6}$</td>
<td>0.04</td>
<td>0.06</td>
<td>220</td>
<td>1.5</td>
<td>0.390</td>
<td>15.1 ± 2.0</td>
</tr>
<tr>
<td>Rh$<em>{0.2}$Pd$</em>{0.8}$</td>
<td>0.02</td>
<td>0.08</td>
<td>220</td>
<td>1.5</td>
<td>0.397</td>
<td>14.9 ± 2.0</td>
</tr>
<tr>
<td>Pd</td>
<td>0</td>
<td>0.1</td>
<td>220</td>
<td>0.5</td>
<td>0.395</td>
<td>15.6 ± 2.4</td>
</tr>
</tbody>
</table>

*The standard deviation statistic from 100 nanocrystals.
time and by correcting the Rh<sub>1-x</sub>Pd<sub>x</sub> surface area using the method described above.

The moderate-pressure setup, in contrast, uses a two-chamber system in order to feed very small pressures of the reaction gas mixture to a low-pressure chamber for detection. Reactants are fed to a high-pressure reaction chamber (0.3 L) using two leak valves—one for O<sub>2</sub> and one for CO. The contents of the high-pressure chamber are sampled into a low-pressure chamber through a leak valve. The low-pressure chamber is kept at a pressure of 5 × 10<sup>-8</sup> Torr using a turbomolecular pump. Reactant and product concentration is measured using a mass spectrometer (Stanford Research Systems) in the low-pressure chamber. Sample temperature is controlled using a ceramic button heater (Momentiv), and a type-K thermocouple. Gas mixing was found to be very efficient and changes in the reaction chamber are registered by the mass spectrometer almost immediately. The system functions similarly to a batch reactor due to the low flow rate of gas in and out of the reaction chamber.

(4) APXPS studies

APXPS was carried out on the Scienta 4000-HiPP endstation at beamline 9.3.2 of the Advanced Light Source.<sup>19</sup> A Rh<sub>0.5</sub>Pd<sub>0.5</sub>, pure Rh, and pure Pd sample were mounted together on a 1 cm button heater. Pd 3d, Rh 3d, C 1s, and Si 2p spectra were measured using two leak valves—one for O<sub>2</sub> and one for CO. The reaction gas mixture to a low-pressure chamber for detection. The moderate-pressure setup, in contrast, uses a two-chamber system in order to feed very small pressures of the reaction gas mixture to a low-pressure chamber for detection. Reactants are fed to a high-pressure reaction chamber (0.3 L) using two leak valves—one for O<sub>2</sub> and one for CO. The contents of the high-pressure chamber are sampled into a low-pressure chamber through a leak valve. The low-pressure chamber is kept at a pressure of 5 × 10<sup>-8</sup> Torr using a turbomolecular pump. Reactant and product concentration is measured using a mass spectrometer (Stanford Research Systems) in the low-pressure chamber. Sample temperature is controlled using a ceramic button heater (Momentiv), and a type-K thermocouple. Gas mixing was found to be very efficient and changes in the reaction chamber are registered by the mass spectrometer almost immediately. The system functions similarly to a batch reactor due to the low flow rate of gas in and out of the reaction chamber.

Characterization of the RhPd bimetallic nanoparticles

The size, shape, and lattice structure of the Rh<sub>1-x</sub>Pd<sub>x</sub> nanocrystals were analyzed using a Philips FEI Tecnai 12 transmission electron microscope (TEM) and Philips CM200/FEG high-resolution TEM (HRTEM), operated at 100 kV and 200 kV, respectively. The samples were prepared by placing a drop of the nanocrystal solution in ethanol onto a continuous carbon-coated copper TEM grid. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 GADDS diffractometer using Co-K<sub>α</sub> radiation (λ = 1.79 Å). Lattice parameters of the nanocrystals were calculated with the least-squares method. X-Ray Photoelectron Spectroscopy (XPS) experiments were performed on a Perkin-Elmer PHI 5300 XPS spectrometer with a position-sensitive detector and a hemispherical energy analyzer in an ion-pumped chamber (evacuated to 2 × 10<sup>-9</sup> Torr). The Al-K<sub>α</sub> (1486.6 eV) X-ray source of the XPS spectrometer was operated at 350 W with a 15 kV acceleration voltage. XPS was also carried out in UHV at the Advanced Light Source Beamline 9.3.2 for energy-dependent (and therefore depth-dependent) composition analysis. This system has been described previously.<sup>17</sup> The binding energy (BE) for the samples was calibrated by setting the measured BE of the broad C 1s, which is dominated by carbon from the PVP capping agent, to 285 eV. The elemental ratio was calculated from the integrated peak areas of the Rh 3d, Pd 3d, and O 1s core levels. The morphological changes of the Rh<sub>1-x</sub>Pd<sub>x</sub> nanocrystals, Rh thin films, and Pd thin films before and after reaction were observed with a Zeiss Gemini Ultra-55 analytical scanning electron microscope (SEM). The total number of surface sites was calculated from coverage determined by a minimum of ten SEM images taken from randomly selected locations on each sample and taking into account the lattice parameters determined from XRD. This calculation is purely geometric and does not account for site blocking by strongly-bound capping agent molecules or other species.

Panels a–f of Fig. 1 display TEM images of the Rh<sub>1-x</sub>Pd<sub>x</sub> (x = 0–0.8) nanocrystals. The bimetallic nanocrystals are faceted, but show a mix of various shapes in 2D projection, such as hexagons, pentagons, triangles, and cubes. All the bimetallic nanocrystals have an average crystallite size near 15 nm, with standard size distributions of around 15% (Table 1). XRD measurements determined that all the bimetallic nanocrystals have a face-centered cubic (fcc) structure with lattice parameters lying between 0.385 and 0.397 nm (Table 1).

The surface compositions and structure of the bimetallic nanocrystals were measured experimentally by XPS in ultra-high vacuum. Two systems were used—one system with an Al K-α source with X-ray Photon Energy of 1486.6 eV (photoelectron mean free path ~1.6 nm) and another system with a tunable synchrotron source set to 645 eV (photoelectron mean free path ~0.7 nm). As shown in Fig. 2, the atomic fraction of Pd is significantly lower at the surface of the bimetallic nanoparticles than in the bulk. This demonstrates that the as-synthesized nanoparticles have clear core–shell geometry, with a Pd-rich core and Rh-rich shell. The transition between these regions is gradual and comprised of mixed Rh–Pd phases. Changes in the local chemical environment dramatically affect the surface composition and oxidation state of the nanocrystals by inducing selective phase-segregation of the nanoparticle components.<sup>17</sup>

Reaction and APXPS results and discussion

CO oxidation tests in 40 Torr CO, 100 Torr O<sub>2</sub> and 620 Torr He using the atmospheric-pressure reactor revealed that all the bimetallic nanocrystals are active for CO oxidation between 170–210 °C. SEM measurements before and after reaction showed that no severe aggregation occurred, as shown in Fig. 3. The turnover frequency was strongly dependent on nanoparticle composition, as shown at 180 °C and 190 °C in Fig. 4a. The maximum turnover frequency was 1.34 molecules site<sup>-1</sup> s<sup>-1</sup> at 190 °C on the Rh<sub>0.6</sub>Pd<sub>0.4</sub> nanocrystals. Turnover frequencies were also compared to the theoretical activity of a linear combination of pure Rh and pure Pd nanocrystals, calculated as TOF<sub>linear-combination</sub> = (TOF<sub>Rh</sub> × (1 – x)) + (TOF<sub>Pd</sub> × x). The maximum measured enhancement was 5.0× at 180 °C for the Rh<sub>0.6</sub>Pd<sub>0.4</sub> nanocrystals versus the theoretical activity of a linear combination of pure Rh and pure Pd nanoparticles. The enhancement factor decreased with increasing temperature for all samples.

The CO oxidation reaction was also carried out at in both a mixture of 100 mTorr O<sub>2</sub> and 40 mTorr CO, and a mixture of 100 mTorr O<sub>2</sub> and 100 mTorr CO. Rh and Rh<sub>0.5</sub>Pd<sub>0.5</sub> nanoparticles were both very active in these conditions, while the
Pd nanoparticles had a very low turnover frequency. The turnover frequency measured from each nanoparticle catalyst at 175 °C and 100 mTorr O₂ in 40 mTorr CO and 100 mTorr CO is compared in Fig. 4b. At 175 °C in 100 mTorr O₂ and 40 mTorr CO, the Rh nanoparticles had a turnover frequency of 0.078 molecules site⁻¹ s⁻¹, as compared to a turnover frequency of 0.211 molecules site⁻¹ s⁻¹ for the Rh₀.₅Pd₀.₅ nanoparticles and a turnover frequency of 0.0018 molecules site⁻¹ s⁻¹ for the Pd nanoparticles. These turnover frequencies are lower than those measured at high pressure, as expected from entropic considerations. Notably, the turnover frequency measured on the bimetallic nanoparticles was significantly larger than on either the Rh or Pd monometallic nanoparticles. This trend is consistent with studies on pure Rh and Pd nanoparticles. At low pressure (100 mTorr O₂ and 100 mTorr CO), the apparent activation energy measured for the bimetallic nanoparticles followed the same trend as those obtained at atmosphere pressure.

The turnover frequencies measured using bimetallic nanoparticles were greater than those measured on the monometallic nanoparticles. This indicates that the enhancement effect is too large to be explained simply by complete coverage of the nanoparticle surface with Rh. Consequently, the synergetic effect must be due to interaction between Rh and Pd or their adsorbates. These results are consistent with previous studies, which found synergistic behavior in Rh–Pd catalysts prepared by sequential impregnation and co-impregnation and lower ignition temperature for Rh nanoparticle catalysts as on nanoparticle composition. At atmosphere pressure, it decreased with increased Pd molar fraction, from a maximum of 108 kcal mol⁻¹ for pure Rh to a minimum of 51 kJ mol⁻¹ for pure Pd nanoparticles. This trend is consistent with studies on pure Rh and Pd nanoparticles. At low pressure (100 mTorr O₂ and 100 mTorr CO), the apparent activation energy measured for the bimetallic nanoparticles followed the same trend as those obtained at atmosphere pressure.
compared to Pd nanoparticle catalysts studied in similar conditions.\textsuperscript{23–25} Previous studies also determined that synergism does not occur in physical mixtures in this system.\textsuperscript{23,26}

To better understand the mechanism of the observed synergetic effect, we used APXPS to study the surface composition and the oxidation state of Pd and Rh under reaction conditions. The as-synthesized Rh\textsubscript{0.5}Pd\textsubscript{0.5} nanoparticles have a Rh rich surface (Fig. 2). When we first introduce 100 mTorr O\textsubscript{2} and 40 mTorr CO at 175 °C, the surface composition of Pd increased slightly from 10% to 11%. When the CO pressure was increased to 100 mTorr, the surface Pd increased to 23%, which indicates that CO has a stronger interaction with Pd than with Rh. Further evidence for the stronger interaction of O\textsubscript{2} with Rh and CO with Pd was observed by exposing the NPs to 100 mTorr O\textsubscript{2} or 100 mTorr CO separately or to a mixture of 100 mTorr of both gases. The Pd 3d and Rh 3d spectra are shown in Fig. 5. Rh 3d is 70% oxidized in pure O\textsubscript{2} while Pd 3d is only 29% oxidized. In pure CO, however, the Pd 3d peak shows increased intensity at higher BE, indicating a strong interaction with CO or dissociated C atoms. In pure O\textsubscript{2}, however, the Rh 3d indicates a large degree of oxidation (approximately 70%) while the Pd 3d indicates only a relatively modest degree of oxidation (29%).

In the reaction rate observed because isolated Pd on the Rh-dominated surface ensures an adequate supply of adsorbed CO for the reaction while oxygen dissociatively adsorbs on Rh. In this model, the reaction rate is increased by reaction at Pd sites between oxygen spillover from Rh and the CO-covered Pd sites. In this case, the synergetic effect is
heavily dependent on the distribution of Rh and Pd in the top layers. This observation also supports the mechanism originally proposed for Rh–Pt by Oh and Carpenter and later extended to Rh–Pd by Araya and Diaz, that surface oxygen from RhO₅ species may react with CO adsorbed on reduced Pt atoms.

In order to gain a better understanding of the equilibrium Rh/Pd ratio under these reaction conditions, the NPs were heated to 220 °C in 100 mTorr O₂ + 100 mTorr CO for 3 hours, followed by checking again the original conditions of 100 mTorr O₂ + 40 mTorr CO at 175 °C and then increasing the CO pressure to 100 mTorr. After 3 hours at 220 °C in 100 mTorr O₂ + 100 mTorr CO, the surface Pd increased to 30%. After decreasing the CO pressure to 40 mTorr and the temperature to 175 °C, the surface was only 26% Pd. Upon increasing the CO pressure back to 100 mTorr, the surface Pd again increased to 31% (Fig. 6). This indicates that at higher relative oxygen pressures, Pd sites are increasingly isolated on an ever more Rh-dominated surface for the Rh₀·₅Pd₀·₅ nanoparticles. It is also evident from Fig. 6 that at lower CO pressure, the Rh 3d peak shifts to higher BE (approximately 8% oxidized), while the Pd 3d peak does not shift (no oxidation). This observation further supports our claim that more RhO₅ species form at higher P⁰₂/PCO ratio, leading to an enhanced synergistic effect. Both the formation of RhO₅ species and the decreased surface Pd content may contribute to the enhanced synergistic effect with increasing P⁰₂/PCO ratios.

The measured enhancements in both this study and similar studies by Yoon et al., and Araya and Weissman are consistent with the APXPS observations. In each study, the P⁰₂/PCO is different and the measured enhancement changes as we would predict. Our reaction, as previously stated, was carried out in P⁰₂/PCO = 2.5 at 180 °C and 190 °C at high pressure, and P⁰₂/PCO = 2.5 at 1 at 175 °C, while Weissman et al.’s study was carried out at P⁰₂/PCO = 5 at 135 °C and Yoon et al.’s study was in P⁰₂/PCO = 1 at 180 °C. Weissman et al.’s study, which had the highest P⁰₂/PCO ratio, also found the highest synergistic enhancement, while Yoon et al.’s study, with the lowest P⁰₂/PCO ratio, found the lowest synergistic enhancement. The present study confirms this correlation, as our high pressure work, which was carried out at an intermediate P⁰₂/PCO ratio, found an intermediate synergetic enhancement, and our low pressure work found a significantly higher enhancement when P⁰₂/PCO = 2.5 than when P⁰₂/PCO = 1 under otherwise-identical conditions. It is important to note that this correlation is independent of reaction order because these enhancements are relative to linear combinations of pure Pd and pure Rh catalyst activity.

Conclusions

Rh₁₋ₓPdₓ nanocrystals or 15 nm in diameter were synthesized, characterized, and studied in catalytic CO oxidation in two pressure regimes. A model based on APXPS studies was proposed to help explain the observed catalytic behavior. The nanocrystals were found to exhibit significant composition-dependent synergetic effects in CO oxidation. This observed synergy could be related to preferential adsorption of CO on isolated Pd atoms or islands on the bimetallic catalyst surface and spillover of oxygen adsorbates from Rh to CO-covered Pd reaction sites. Our APXPS and reaction results resolve questions arising from discrepancies in the degree of synergetic enhancement measured on bimetallic nanoparticles in the CO oxidation reaction by demonstrating a clear correlation between the O₂ : CO ratio, surface composition and bimetallic nanoparticle synergy. This unique and desirable synergetic behavior in bimetallic catalysts will hopefully lead to greater understanding of the many complex factors governing reactivity in these systems.

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