Evolution of surface of Pd-Rh bimetallic nanocubes and its correlation with CO oxidation

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ABSTRACT Typically, varying pretreatment conditions probably results in the different catalytic performances for the bimetallic catalysts, and this originates from the surface evolution of catalysts during catalytic process. Hence, it is crucial to correlate surface chemistry (e.g., composition, chemical valence, etc.) of bimetallic nanocatalysts with their corresponding performances upon different pretreatments for the fundamental understanding of catalysis. Herein, composition-varied (100) facet terminated Pd-Rh nanocubes (NCs) with the similar shape and sizes were prepared by a facile one-pot hydrothermal method to exclude the possible size and shape effect. Surface composition and valence state of these Pd_{0.8}Rh_{0.2}, Pd_{0.6}Rh_{0.4}, and Pd_{0.2}Rh_{0.8} NCs were tracked under different reaction conditions and during catalysis using a home-built ambient pressure X-ray photoelectron spectrometer (AP-XPS). The correlation of active surface of Pd-Rh NCs and their corresponding catalytic performance was established.

Keywords: controllable synthesis, bimetallic nanocubes, ambient-pressure XPS, CO oxidation, surface chemistry

INTRODUCTION

An industrial catalyst typically consists of nanoparticles (NPs) with diverse morphologies, sizes, compositions, and interfaces. Its catalytic performance is the integrated contribution of these interplayed structural and compositional factors [1,2]. Hence, fundamental understanding of how a structural or compositional factor tunes catalytic performance, cannot be simply accomplished by using structure-undefined industrial catalysts as model catalysts [3–6].

It has been demonstrated that size [7–9] and shape [5,10–15] have significant influences on the catalytic performance of metal catalysts, while the fine manipula-

tion of the two factors has been achieved by tuning kinetics of the crystal growth of colloidal NPs. Hence, controllable synthesis provides an ideal platform for the catalytic study of well-defined nanocatalysts, and bridges surface science investigations with industrially catalytic applications. Nevertheless, controllable synthesis of nanocrystals [6,7,16,17] can readily tune overall composition of a single particle, but the surface composition of as-synthesized bimetallic NPs usually appears to be very different from the overall composition. It is because that a variety of factors (e.g., surface capping agent, surrounding environment, surface energy, etc.) will probably change the surface composition during synthesis or storage [18,19]. And it has been demonstrated that surface reconstruction or segregation will take place by altering the reaction atmospheres [20]. So we still know little about the surface chemistry of these well-defined nanocrystals, particularly during the catalytic reaction.

What's more, pretreatments of catalysts, i.e., activation procedures which usually are conducted before the catalytic evaluations, can significantly influence their overall performances [21–24]. Hence, an “appropriate” activation method will lead to an optimal property of a catalyst. Variation of surface chemistry (e.g., composition, chemical valence, crystalline phase, etc.) is one of the key reasons for the elevated activity in light of the prior mechanism research [20,25–28]. In many cases, bimetallic site and metal/oxide interface generated from the commercial bimetallic or oxide-supported metallic catalysts will essentially determine the reaction energy barriers, and lead to diverse catalytic performances, such as Cu/ZnO/Al₂O₃ for CO₂ hydrogenation [29–31]. Therefore, to correlate the surface chemistry of model catalysts with their catalytic performance after various pretreatments

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with the aid of controllable syntheses and *operando* techniques will provide us a rational image to understand the evolution of surface chemistry of nanocatalysts during realistic catalytic reactions.

In this work, bimetallic $\text{Pd}_x\text{Rh}_{1-x}$ NPs are chosen as the probe catalysts due to the high sensitivity of Pd and Rh to the reductive and oxidative atmospheres. Since the surface composition may change during the reaction according to the previous reports [20], exposed facet and size are kept the same *via* a wet chemistry synthetic method to exclude the probable structural effects. Herein, three sub-10 nm (100)-terminated Pd-Rh nanocubes (NCs) (i.e., $\text{Pd}_{0.8}\text{Rh}_{0.2}$, $\text{Pd}_{0.6}\text{Rh}_{0.4}$, and $\text{Pd}_{0.2}\text{Rh}_{0.8}$) with different compositions but the same shape and size were synthesized *via* a facile hydrothermal method. CO oxidation was taken as the benchmark reaction. Activation barriers of CO oxidation on these as-synthesized and treated catalysts under different pretreatments were measured under kinetically controlled regime. These activation barriers were used as a descriptor of the catalytic performance of the real surface observed during catalysis. Surface composition and oxidation state of bimetallic NCs during pretreatments and catalysis were tracked with AP-XPS. Correlations between the surface chemistry of these catalysts and their catalytic performances upon different pretreatments were finally established.

EXPERIMENTAL SECTION

Chemicals

$\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ ($\geq 98\%$; Sigma-Aldrich), PdCl_2 ($\geq 99.9\%$; Sigma-Aldrich), NaCl ($\geq 99\%$; Sigma-Aldrich), Na_2PdCl_4 (It was prepared by mixing 2 eqv. NaCl and 1 eqv. PdCl_2 in water, and stirring overnight.), HCl (AR; Xilong Chemical Co., Ltd., China), KBr (99.999%; Strem Chemicals, Inc.), poly(vinylpyrrolidone) (PVP; M_w : ~29,000; Sigma-Aldrich), acetone ($\geq 99.5\%$; Alfa Aesar), ethanol (96%; Alfa Aesar) and deionized water (Millipore, 18.2 M Ω cm) were used during the experiments.

Synthesis of $\text{Pd}_x\text{Rh}_{1-x}$ NPs

In a typical synthesis of $\text{Pd}_{0.6}\text{Rh}_{0.4}$ NCs, 6.0 mmol of KBr and 100 mg of PVP were added to a 25-mL Teflon-lined stainless steel autoclave and dissolved in 5 mL of deionized water. Then, 0.030 mmol of 0.116 mol L^{-1} Na_2PdCl_4 and 0.030 mmol of $0.0956 \text{ mol L}^{-1}$ RhCl_3 aqueous solution were added with stirring. The solution was diluted to 15 mL by deionized water. After that, the autoclave was sealed and kept at 180°C for 2 h. After it cooled down to room temperature, the solution was centrifuged at the rate of 8,000 rpm for 5 min at room temperature after introducing 40 mL of acetone. The black precipitates were washed with the mixture of water/acetone (1:4, v/v). The as-obtained NPs were dispersed well in water and ethanol. As illustrated in Fig. S1b, energy dispersive X-ray spectroscopy (EDS) analysis showed PdRh NCs were composed of 58.5% Pd and 41.5% Rh in atomic percentage (abbreviated as $\text{Pd}_{0.6}\text{Rh}_{0.4}$ NCs).

The synthesis of Pd NCs, $\text{Pd}_{0.8}\text{Rh}_{0.2}$ NCs, $\text{Pd}_{0.2}\text{Rh}_{0.8}$ NCs and Rh NCs, and the post-treatment procedures were similar to the synthesis of $\text{Pd}_{0.6}\text{Rh}_{0.4}$ NCs, only with the changes on the addition amount of reactants (see Table 1 for detailed feed ratios of the reactants).

Preparation of SiO_2 supported Pd-Rh NCs catalysts

200 mg of SiO_2 powder (200–300 nm; Sigma Aldrich) was dispersed in 10 mL of Pd-Rh NCs aqueous solution. Then the suspension was processed under ultrasonic for 4 h. After centrifugation of the above suspension, the black precipitate was dried at 70°C overnight. As illustrated by the transmission electron microscopy (TEM) image (Fig. S2), Pd-Rh NCs were uniformly dispersed on the support without significant changes in morphology and size.

Structural characterization

TEM, high-resolution TEM (HRTEM), and EDS were conducted on an FEI TITAN 80-300 TEM operated at 300 kV with an Oxford EDS attachment. The samples for TEM characterizations were prepared by dropping the

Table 1 Feed ratios of the reactants for synthesis of $\text{Pd}_x\text{Rh}_{1-x}$ NPs ($x = 0, 0.2, 0.4, 0.8, 1.0$)

Sample	Na_2PdCl_4 (mmol)	RhCl_3 (mmol)	KBr (mmol)	PVP (mg)	Composition analysis by EDS
Pd NCs	0.12		6.0	200	
$\text{Pd}_{0.8}\text{Rh}_{0.2}$ NCs	0.096	0.024	6.0	200	Pd 83.9%, Rh 16.1%
$\text{Pd}_{0.6}\text{Rh}_{0.4}$ NCs	0.030	0.030	6.0	100	Pd 58.5%, Rh 41.5%
$\text{Pd}_{0.2}\text{Rh}_{0.8}$ NCs	0.024	0.096	12.0	200	Pd 17.3%, Rh 82.7%
Rh NCs		0.12	6.0	75	

colloid solution on copper grids coated with amorphous carbon and drying. Powder X-ray diffraction (PXRD) analyses were performed on a Rigaku D/MAX-2000 diffractometer (Japan) with Cu K α 1 line ($\lambda=1.54$ Å) as the X-ray source. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were conducted on a Profile Spec ICP-AES spectrometer (Leeman, USA).

Measurements of catalytic performance

The catalytic performance of Pd-Rh bimetallic NCs for CO oxidation was measured in a fixed-bed flow reactor at atmospheric pressure. The gas composition of the mixture of reactants was 8% CO, 20% O₂, and 72% Ar. The flow rate of the mixture was typically 100 mL min⁻¹. In the case for pretreatments with H₂ or O₂, the catalysts were treated *in-situ* under a flow of H₂ (5% in argon) or O₂ (5% in argon) with a flow rate at 50 mL min⁻¹ at a certain temperature for 60 min. There were two types of pretreatment methods applied in the study: one was successively treated with H₂ (5% in argon) and O₂ (5% in argon) before the reaction (abbreviated as H₂-O₂); the other was only treated with H₂ (5% in argon) before the reaction, and then was treated with only O₂ (5% in argon) before the 2nd cycle of reaction (abbreviated as H₂-reaction-O₂). In the following text, we used the symbol “-” between different atmosphere treatments to represent the successive operation. The activation energy was measured in kinetically controlled range at which the conversion of CO was below 15%. The catalytic evaluations were conducted in the temperature interval from 25–250°C to obtain the apparent activation energies.

As shown in Fig. S2, before being loaded into the catalytic reactor for catalytic measurements, the Pd-Rh bimetallic NCs were deposited on silica, in order to prevent the NCs from aggregating during the reactions. Typically, 5 mg of Pd-Rh/SiO₂ catalysts were used for kinetics study. The reliability of the fix-bed reactor was checked through a blank experiment with the same experimental parameters including reactant gases, flow rate, and reaction temperature. In the blank experiment, only silica supporting material was loaded. The blank experimental tests confirmed that there was no CO₂ formed from reactor, gas lines, or other part in the temperature range of 25–250°C.

In-situ/operando characterization

The *in-situ* characterization of surface chemistry of Pd-Rh bimetallic catalysts during catalysis was performed with AP-XPS [32–39]. Monochromated Al K α line is used as X-ray source. Unlike traditional under ultrahigh-vacuum

(UHV) studies, reactant gases are introduced to the reaction cell of AP-XPS and the gas flows through the catalyst surface at a desired temperature while data is collected with AP-XPS. The reaction cell is incorporated into the UHV chamber of AP-XPS system. Gas flows through the cell and exits through the exit port and an aperture that interfaces the gaseous environment in the reaction cell and vacuum environment of the pre-lens. Flow rate in the reaction cell is measured through a mass flow meter installed between each gas source and the entrance of the reaction cell. In this study, the typical flow rate of pure gas is in the range of 1–4 mL min⁻¹. It approximately equals to the flow rate of 10–40 mL min⁻¹ of gas with 10% reactants in catalytic measurement of a fixed-bed flow reactor. The total pressure of the mixture gas in the entrance is measured with a capacitance gauge, while the pressure at the exit is measured with another capacitance gauge. An average of the pressures at entrance and exit is defined to be the pressure above the catalyst in the reaction cell. More detailed description of the AP-XPS system can be found in the previous publications [32–39].

Thermal stability tests

Thermal stability tests under different atmospheres were performed on all the five SiO₂-supported NCs samples. All the experiments were conducted in the atmosphere-protected tube furnace. To simulate the pretreatment conditions, the samples were respectively treated by 5% O₂/Ar, 5%H₂/Ar, and 5%H₂/Ar–5%O₂/Ar atmospheres at 280°C for 1 h with the heating rate of 2°C min⁻¹. TEM was applied to confirm the shape evolution and agglomeration of the samples after the thermal treatments.

RESULTS

Shape-controlled syntheses of Pd-Rh NCs

As illustrated in the TEM images (Fig. 1a–e), monodisperse Pd-Rh NCs were synthesized in a high selectivity ($\geq 90\%$) *via* a facile hydrothermal method by the fine adjustment of synthetic parameters. The average sizes of Pd_{0.8}Rh_{0.2} NCs, Pd_{0.6}Rh_{0.4} NCs, and Pd_{0.2}Rh_{0.8} NCs were 9.4 $\pm$ 1.1 nm, 8.9 $\pm$ 1.1 nm, and 6.7 $\pm$ 0.8 nm, respectively (more than 100 particles were counted for each sample). In addition, pure Pd NCs and Rh NCs were synthesized as shown in Fig. 1. HRTEM image of Pd_{0.6}Rh_{0.4} NCs (Fig. 1f) confirmed that the morphology of Pd_{0.6}Rh_{0.4} NCs was a typical cube enclosed by six {100} facets. Both HRTEM image and PXRD pattern (Fig. S3) confirmed that the as-synthesized Pd-Rh NCs were in an fcc structure. As

Figure 1 TEM images of the synthesized Rh NCs (a), Pd_{0.2}Rh_{0.8} NCs (b), Pd_{0.6}Rh_{0.4} NCs (c), Pd_{0.8}Rh_{0.2} NCs (d), and Pd NCs (e). The insets were the corresponding size distribution histograms. HRTEM image of the Pd_{0.6}Rh_{0.4} NCs (f).

shown in Fig. S3, the peaks of Pd_xRh_{1-x} NCs XRD patterns shifted to low angles with the increase of Pd concentration, indicating a lattice expansion due to the incorporation of Pd into Rh. The detail shape-control synthesis mechanism of Pd-Rh NCs by halide ions has been discussed in our previous reports [40–42].

Thermal stability of Pd-Rh bimetallic NCs under different atmosphere treatments

To confirm the possible aggregation or shape evolution of the monodispersed NCs after the thermal treatments of various atmospheres, TEM was utilized to check the SiO₂-supported samples after the thermal treatments. As shown in Fig. S2, all the samples retained their cubic morphology after loading onto the SiO₂ supports, and no aggregation was observed in the scope. TEM images of all the five samples treated by H₂, O₂, and H₂-O₂ atmospheres are shown in Figs S4–S6, respectively. From these

TEM images, no aggregation of particles was observed, but the cubic particles gradually turned round while only a few of particles retained the cubic morphology. It was demonstrated that the particles anchored onto the support after the successive ultrasonic and thermal treatments. So the size factor was controlled the same by the atmosphere treatments. However, due to the instability of high-unsaturated corner sites, the cubic particles finally turned thermodynamic-favored sphere after the thermal annealing. Nevertheless, all the shapes were still uniform after the atmosphere treatments anyhow. Furthermore, it has been demonstrated that both of Rh and Pd are structure-insensitive catalysts to CO oxidation [43,44], so the shape evolution upon thermal treatments did not affect much on the activity. Hence, the thermal stability tests confirmed that the size and shape factors during the atmosphere treatments could be excluded in the following discussion.

In-situ studies of composition-varied Pd-Rh bimetallic NCs under reaction conditions with AP-XPS

To identify the active phase of catalysts in CO oxidation reaction condition, the evolution of the surface chemistry of Pd-Rh bimetallic catalysts under reaction conditions was tracked with AP-XPS. The XPS spectra obtained at room temperature under H₂ atmosphere represented the surface chemistry status of the NCs before the pretreatments and reactions. For the data collected with the H₂ or O₂ pretreatment conditions, the catalyst remained in the flowing gas of H₂ or O₂ with a pressure of 0.5 Torr at 280°C for 1 h prior to the acquisition of the XPS spectra. For *operando* studies during the CO oxidation, the catalyst remained in a flowing mixture of CO and O₂ with a pressure of 0.4 Torr CO and 1.0 Torr O₂ in the cell. All original XPS data giving surface composition and oxidation state in this work were collected while the catalysts were in the gas phase and temperature as marked.

The as-synthesized Pd_{0.8}Rh_{0.2} NC catalyst was partially oxidized at room temperature. Fig. 2 shows the photoemission feature of Pd 3d_{5/2} and Rh 3d_{5/2} of Pd_{0.8}Rh_{0.2} NC catalyst at different reaction conditions and during catalysis. After annealing with H₂ at 280°C, the catalyst is termed Pd_{0.8}Rh_{0.2}-H₂ here. Its binding energy of Pd 3d_{5/2} shifted from 335.3 to 335.6 eV (Fig. 2a1 and 2a2). This shift was likely due to the formation of Pd hydride when the catalyst was exposed to H₂ at an elevated temperature. The 0.3 eV upshift of binding energy of Pd 3d_{5/2} for Pd hydride agreed well with literatures [45,46]. After H₂ treatment, the catalyst was cooled down to room temperature in H₂. Then, a mixture of CO and O₂ was in-

Figure 2 The photoemission feature of Pd 3d_{5/2} (a) and Rh 3d_{5/2} (b) of Pd_{0.8}Rh_{0.2} NCs catalyst during CO oxidation after H₂ pretreatment and H₂–reaction–O₂ treatment. Evolution of atomic fraction of Pd and Rh during catalysis (c).

troduced into the reaction cell and kept flowing through Pd_{0.8}Rh_{0.2}–H₂; the catalyst during CO oxidation is termed as Pd_{0.8}Rh_{0.2}–H₂–CO oxidation. Along with the increase of catalysis temperature of CO oxidation (Fig. 2b3–2b5), the XPS spectra collected at different temperatures showed that Rh remained as metallic while Pd changed from Pd hydride to metallic Pd (Fig. 2a3–2a5).

After the CO oxidation at 280°C, CO was purged and the catalyst was further treated with O₂ at 280°C, termed as Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂. Rh 3d spectra of Pd_{0.8}Rh_{0.2}–H₂–CO oxidation after O₂ treatment clearly showed that Rh was partially oxidized, as evidenced by the appearance of a peak at 308.2 eV (Fig. 2b6) which was assigned to RhO_x [47,48]. XPS spectra of Pd 3d of Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂ showed that Pd remained as a metallic state after treated with O₂ at 280°C (Fig. 2a6). The lack of Pd oxide and the appearance of RhO_x on Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂ (Fig. 2b6 and 2a6) suggested that RhO_x covered the surface after H₂–CO oxidation–O₂ treatment. After this treatment, a flowing mixture of CO and O₂ was introduced and CO oxidation was performed on Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂ again. In the mixture of CO and O₂ at 200°C, RhO_x was reduced back to metallic Rh (Fig. 2b8). As shown in Fig. 2c, there was no significant change in the surface atomic fraction of Rh and Pd, indicating that surface segregation did not happen in the well-shaped Pd_{0.8}Rh_{0.2} NPs.

Notably, when the treatment protocol was changed from H₂–CO oxidation–O₂ to H₂–O₂, the active phase of the Pd_{0.8}Rh_{0.2} during CO oxidation (Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂) was completely different. As shown in Fig. 3a2, Pd hydrides formed on Pd_{0.8}Rh_{0.2}–H₂ (i.e., Pd_{0.8}Rh_{0.2}–

treated with H₂). After the following treatment with O₂ (Fig. 3a3), Pd 3d spectrum of Pd_{0.8}Rh_{0.2}–H₂–O₂ does not have the photoemission feature of Pd hydride at 335.6 eV. Alternatively, a new intense peak at 336.7 eV appeared in Pd 3d of Pd_{0.8}Rh_{0.2}–H₂–O₂ (Fig. 3a3), which was probably assigned to PdO_x based on prior reports [49–51]. The Pd 3d_{5/2} peak of the formed PdO_x remained in the temperature range of 90–280°C (Fig. 3a4–3a10). During CO oxidation in the temperature range of 90–280°C (Fig. 3b4–3b10), oxidized Rh of Pd_{0.8}Rh_{0.2}–H₂–O₂ was progressively reduced to metallic Rh. It suggested that the active surface of Pd_{0.8}Rh_{0.2}–H₂–O₂–CO oxidation consists of both Rh and PdO_x during CO oxidation. Hence, the active surface of Pd_{0.8}Rh_{0.2}–H₂–O₂–CO oxidation was different from that of Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂ (Fig. 2a8, 2a9, 2b8 and 2b9) during CO oxidation at 200–280°C, as the protocols of pretreatments before CO oxidation (H₂–CO oxidation–O₂ versus H₂–O₂) were different. These parallel studies using slight different protocols of treatment on the same Pd_{0.8}Rh_{0.2} NCs (Figs 2 and 3) suggested that different pretreatment conditions could tailor surface active phases of the same catalyst significantly.

Similar to Pd_{0.8}Rh_{0.2} (Figs 2 and 3), our *in-situ* studies of Pd_{0.6}Rh_{0.4} NCs under pretreatment and during catalysis by AP-XPS showed that surface composition and valence state of Pd_{0.6}Rh_{0.4} NCs during CO oxidation also depended on their pretreatment conditions. Fig. 4 shows the photoemission features of Pd 3d_{5/2} and Rh 3d_{5/2} of Pd_{0.6}Rh_{0.4} NCs which experienced a sequential pretreatment at 280°C in H₂, a mixture of CO and O₂, O₂ at 280°C, and then the mixture of CO and O₂ again. After H₂ pre-

Figure 3 The photoemission feature of Pd 3d_{5/2} (a) and Rh 3d_{5/2} (b) of Pd_{0.8}Rh_{0.2} NCs catalyst during CO oxidation after H₂ at 280°C and then O₂ at 280°C pretreatment. Evolution of atomic fraction of Pd and Rh during catalysis (c).

Figure 4 The photoemission feature of Pd 3d_{5/2} (a) and Rh 3d_{5/2} (b) of Pd_{0.6}Rh_{0.4} NCs catalyst during CO oxidation after H₂ pretreatment and H₂-reaction-O₂ treatment. Evolution of atomic fraction of Pd and Rh during catalysis (c).

treatment at 280°C (Fig. 4a2), the photoemission feature of Pd of Pd_{0.6}Rh_{0.4}-H₂ showed that Pd was hydrogenated to Pd hydrides due to a significant upshift by 0.5 eV compared to the metallic state. However, the Rh 3d_{5/2} of Pd_{0.6}Rh_{0.4}-H₂ downshifts by 0.4 eV (Fig. 4b2). The two simultaneous opposite shifts of Rh 3d_{5/2} (Fig. 4b2) and Pd 3d_{5/2} (Fig. 4a2) of Pd_{0.6}Rh_{0.4}-H₂ clearly showed that the electrons were transferred from Pd hydride to Rh due to the H₂ treatment. The unexpected low Rh 3d of binding energy at 306.8 eV of Pd_{0.6}Rh_{0.4}-H₂ was a solid evidence that the electrons of Pd hydrides were transferred to Rh atoms. This pretreatment formed a mixture of Rh and Pd hydride.

After the introduction of a mixture of CO and O₂, the surface of Pd_{0.6}Rh_{0.4}-H₂ experienced a significant change

even at 90–120°C. Pd 3d_{5/2} of palladium hydride in the mixture of CO and O₂ progressively downshift to metallic Pd (Fig. 4a3–4a6); this downshift probably resulted from the oxidation of palladium hydride to metallic Pd. Meanwhile, negatively charged Rh was progressively oxidized as shown in Fig. 4b3–4b6. In terms of the status of CO oxidation at 280°C (Fig. 4a6 and 4b6), the active surface consisted of RhO_x and metallic Pd. Under the sequential O₂ atmosphere at 280°C (Fig. 4a7 and 4b7), there was no obvious change in the valence states of Pd and Rh. It suggested that metallic Pd of Pd_{0.6}Rh_{0.4}-H₂-CO oxidation-O₂ was in the subsurface covered by RhO_x. Since metallic Pd in subsurface was observed by the surface sensitive AP-XPS technique, the thickness of RhO_x should be less than 2 nm. Then, Pd_{0.6}Rh_{0.4}-H₂-CO

Figure 5 The photoemission feature of Pd 3d_{5/2} (a) and Rh 3d_{5/2} (b) of Pd_{0.6}Rh_{0.4} NCs catalyst during CO oxidation after H₂–O₂ treatment. Evolution of atomic fraction of Pd and Rh during catalysis (c).

oxidation–O₂ exposed to the mixture of CO and O₂ again; at this state, the catalyst was termed as Pd_{0.6}Rh_{0.4}–H₂–CO oxidation–O₂–CO oxidation (Fig. 4a8–4a11 and 4b8–4b11). Its photoemission feature and surface composition at this temperature range (90–280°C) were the same as that of Pd_{0.6}Rh_{0.4}–H₂–CO oxidation–O₂ before CO oxidation. Thus, the active phase of Pd_{0.6}Rh_{0.4}–H₂–CO oxidation–O₂–CO oxidation during CO oxidation in the temperature range of 90–280°C (Fig. 4a8–4a11 and 4b8–4b11) was RhO_x. And the composition and valence state of the active surface of Pd_{0.6}Rh_{0.4}–H₂–CO oxidation–O₂–CO oxidation in this temperature range remained constant (Fig. 4c).

As the quantitative analyses of Pd_{0.6}Rh_{0.4} under different conditions, surface compositions of Rh and Pd during these treatments and catalysis conditions were analyzed. As shown in Fig. 4c, atomic fraction of Rh and Pd exhibited significant change along with the change of reaction conditions. The decrease of atomic fraction of Rh in the step of H₂ pretreatment at 90–280°C (Fig. 4c) was attributed to the formation of palladium hydride in surface region and the immigration of Rh to deep layers (Fig. 4a1, 4a2, 4b1 and 4b2). The significant restructuring of this alloy by H₂ was driven by two factors: (1) Rh has a higher surface energy than Pd, and (2) Pd can form palladium hydride but rhodium cannot. Then, when the atmosphere was switched from H₂ to CO+O₂, the atomic fraction of Rh in the mixture of CO and O₂ continuously increased with the increase of reaction temperature (Fig. 4c). Although palladium hydride could be readily oxidized to a metallic state, it was not further oxidized to PdO_x during CO oxidation (Fig. 4a3–4a6 and 4b3–4b6);

this was because the formation of rhodium oxide in the mixture of CO and O₂ was more thermodynamically favorable than the formation of palladium oxide. As shown in Fig. 4b3–4b6, Rh atoms were preferentially oxidized to rhodium oxide; thus, the atomic fraction of Rh was continuously increased. The preferential formation of rhodium oxide on surface prevented palladium from being further oxidized to palladium oxide. Thus, the active phase of Pd_{0.6}Rh_{0.4}–H₂–CO oxidation was RhO_x instead of metallic Pd or Rh.

Fig. 5 shows the XPS spectra of Pd 3d_{5/2} and Rh 3d_{5/2} of Pd_{0.6}Rh_{0.4} NCs under another set of pretreatment conditions (H₂–O₂). Compared with the previous pretreatment of H₂–CO oxidation–O₂, the treatment of Pd_{0.6}Rh_{0.4} NCs in Fig. 5 did not build the step of CO oxidation between the treatment in H₂ and that in O₂. As shown in Fig. 5a1, 5a2, 5b1 and 5b2, after H₂ pretreatment, Pd was hydrogenated to Pd hydrides; the downshift of Rh 3d by 0.4 eV suggested the charge transfer from Pd hydrides to metallic Rh and thus formed negatively charged Rh atoms. O₂ was introduced to the reaction cell of Pd_{0.6}Rh_{0.4}–H₂, forming Pd_{0.6}Rh_{0.4}–H₂–O₂. Upon the O₂ treatment, Pd hydrides were changed into metallic Pd *via* an oxidation process of palladium hydride to metallic Pd. However, compared to the formation of RhO_x of Pd_{0.6}Rh_{0.4} at the step of O₂ at 280°C (Fig. 4b7) after the treatment of H₂–CO oxidation (Pd_{0.6}Rh_{0.4}–H₂–CO oxidation–O₂), the Rh 3d of Pd_{0.6}Rh_{0.4} at the step of O₂ at 280°C (Pd_{0.6}Rh_{0.4}–H₂–O₂) was in a metallic state. This distinctive difference between the oxidizing state of Rh in RhO_x of Pd_{0.6}Rh_{0.4}–H₂–CO oxidation–O₂ (Fig. 4b2–4b6) and the metallic state of Rh of Pd_{0.6}Rh_{0.4}–H₂–O₂ after only H₂ (Fig. 5b2)

Figure 6 The photoemission feature of Pd 3d_{5/2} (a) and Rh 3d_{5/2} (b) of Pd_{0.2}Rh_{0.8} NCs catalyst during CO oxidation after H₂ pretreatment and H₂-reaction-O₂ treatment. Evolution of atomic fraction of Pd and Rh during catalysis (c).

was probably related to their different surface structures. As shown in Fig. 4c, the atomic fraction of Rh of surface Pd_{0.6}Rh_{0.4}-H₂-CO oxidation-O₂ was about 56% and all measured Rh atoms were at oxidizing state; obviously, the surface region consisted of RhO_x shell and metallic Pd subsurface. In the case of Pd_{0.6}Rh_{0.4}-H₂-O₂, both Pd and Rh were observed and at metallic state, suggesting that Rh and Pd atoms existed in alloy. As illustrated in Fig. 5c, significant surface segregation was also observed for the Pd_{0.6}Rh_{0.4} NCs under this H₂-O₂ pretreatment condition. The overall composition probably affected the energy barrier of surface segregation.

Overall, for the sample of Pd_{0.6}Rh_{0.4} NCs, the active phase during CO oxidation after the H₂-O₂ treatment was Pd_{0.45}Rh_{0.55} alloy (Fig. 5a2–5a10, 5b7–5b10, and 5c). However, it was RhO_x after the treatment of H₂-reaction-O₂ (Fig. 4b8–4b11). This difference suggested that different active phases could be generated from the same as-synthesized catalyst if a different treatment was used. It further suggested that a specific pretreatment condition could be chosen to generate an active phase which could exhibit a different catalytic performance.

Photoemission features of Pd 3d_{5/2} and Rh 3d_{5/2} of Pd_{0.2}Rh_{0.8} NCs catalyst during pretreatments and CO oxidation were tracked as shown in Fig. 6. Apparently, both Pd and Rh of the catalyst at 280°C in the mixture of CO and O₂ after treatment in H₂ maintained in metallic states. After subsequently annealing at 280°C in O₂ (Fig. 6a6 and 6b6), about half of Rh was oxidized to RhO_x but all Pd atoms remained at metallic state. However, in the temperature range of 90–200°C, RhO_x was gradually reduced back to metallic Rh during the CO oxidation. Thus, the active phase of the catalysts during CO oxidation at

180–280°C after treatment of H₂-reaction-O₂ was the Pd_{0.25}Rh_{0.75}. As shown in Fig. 6c, no significant surface segregation took place during the pretreatment and the CO oxidation.

Fig. 7 shows photoemission features of Pd 3d_{5/2} and Rh 3d_{5/2} of Pd_{0.2}Rh_{0.8} NCs catalyst during CO oxidation reaction after a treatment of H₂-O₂. Pd remained in metallic state after the treatment of H₂-O₂ (Fig. 7a3), while Rh was partially oxidized to Rh oxides (Fig. 7b3). In the following CO oxidation reaction, Pd remained at metallic state and Rh oxide was gradually reduced to metallic with the increase of temperature. Similarly, there was no significant change in the atomic fraction of Pd and Rh on the surface. Hence, the active phase during CO oxidation at 200–280°C after H₂-O₂ treatment was Pd_{0.35}Rh_{0.65} alloy.

Unlike the previous two cases, Pd_{0.2}Rh_{0.8} NCs exhibited the same metallic alloy reaction sites (slightly different in composition) to CO oxidation upon the two pretreatment conditions (H₂-reaction-O₂-reaction, and H₂-O₂-reaction) without significant surface segregation.

Apparent activation energies of Pd-Rh NCs in CO oxidation

To measure activation barriers of CO oxidation on these catalysts, CO oxidation was performed in the kinetically controlled region (the conversion of CO ≤ 15%). Fig. 8 presents the Arrhenius plots of Pd_xRh_{1-x} bimetallic NCs, Pd_{0.8}Rh_{0.2}, Pd_{0.6}Rh_{0.4}, and Pd_{0.2}Rh_{0.8} upon the two different pretreatment methods (H₂-reaction-O₂ versus H₂-O₂). Because Pd_{0.2}Rh_{0.8}-H₂-reaction-CO and Pd_{0.2}Rh_{0.8}-H₂-O₂ exhibited the same surface composition and the same valence state (Figs 6 and 7), only Pd_{0.2}Rh_{0.8}-H₂-O₂ was evaluated by the kinetic study. Table 1 lists the activation

Figure 7 The photoemission feature of Pd 3d_{5/2} (a) and Rh 3d_{5/2} (b) of Pd_{0.2}Rh_{0.8} NCs during CO oxidation after H₂–O₂ treatment. Evolution of atomic fraction of Pd and Rh during catalysis (c).

energies calculated from the Arrhenius plots for the catalysts pretreated by different methods.

As was shown in Table 2, the activation energies of CO oxidation reactions catalyzed by H₂ pretreated pure Pd NCs and pure Rh NCs were 60 and 98 kJ mol^{−1}, respectively. The *in-situ* XPS study showed that the active surface phases of the as-synthesized pure Pd NCs and Rh NCs to CO oxidation were metallic Pd and metallic Rh, respectively. The activation energies of metallic Pd and Rh for CO oxidation reaction were in qualitative agreement with the values reported in literatures [52–54].

For Pd_{0.8}Rh_{0.2} after H₂–CO oxidation–O₂ pretreatment (Fig. 4), the activation energy of CO oxidation was 61 kJ mol^{−1}. XPS spectra (Fig 4a8 and 4b8) showed that in this condition the active surface was Pd_{0.75}Rh_{0.25} bimetallic alloy. The similar activation barrier for CO oxidation on the sample of Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂ (61 kJ mol^{−1}) and pure metallic Pd (60 kJ mol^{−1}) was consistent with the high atomic fraction of Pd in Pd_{0.8}Rh_{0.2}. The activation energy of Pd_{0.8}Rh_{0.2}–H₂–O₂ (66 kJ mol^{−1}) was slightly higher

Figure 8 Arrhenius plots of Pd-Rh bimetallic catalysts for CO oxidation with varying compositions of Pd/Rh and different pretreatments in the gaseous environment before CO oxidation.

than that of Pd_{0.8}Rh_{0.2}–H₂–CO oxidation–O₂ due to the diverse active phases. The activation energy for the sample

Table 2 Activation energies of Pd-Rh bimetallic catalysts for CO oxidation with a varied composition of Pd/Rh and experienced with different pretreatments in the gaseous environment before CO oxidation

Sample	Pretreatments	Activation energy (kJ mol ^{−1})	Temperature (°C)	Active phase
Pd NCs	H ₂ pretreatment	60	150–200	Metallic Pd
Pd _{0.8} Rh _{0.2} NCs	H ₂ –reaction–O ₂	61	200–240	Pd _{0.75} Rh _{0.25} alloy
Pd _{0.8} Rh _{0.2} NCs	H ₂ –O ₂ pretreatment	66	150–200	Pd _{0.67} Rh _{0.33} /PdO
Pd _{0.6} Rh _{0.4} NCs	H ₂ –reaction–O ₂	63	170–220	RhO _x /PdRh
Pd _{0.6} Rh _{0.4} NCs	H ₂ –O ₂ pretreatment	69	170–220	Pd _{0.45} Rh _{0.55} alloy
Pd _{0.2} Rh _{0.8} NCs	H ₂ –O ₂ pretreatment	76	150–220	Pd _{0.35} Rh _{0.65} alloy
Rh NCs	H ₂ pretreatment	98	150–220	Metallic Rh

of $\text{Pd}_{0.6}\text{Rh}_{0.4}\text{-H}_2\text{-O}_2$ treatment was 69 kJ mol^{-1} ; the active phase of $\text{Pd}_{0.6}\text{Rh}_{0.4}\text{-H}_2\text{-O}_2$ tracked with AP-XPS was $\text{Pd}_{0.45}\text{Rh}_{0.55}$ bimetallic alloy (Fig 5a7–5a9 and 5b7–5b9). For $\text{Pd}_{0.2}\text{Rh}_{0.8}\text{-H}_2\text{-O}_2$, the activation barrier was 76 kJ mol^{-1} ; its surface phase was $\text{Pd}_{0.35}\text{Rh}_{0.65}$ bimetallic alloy (Fig. 7). Apparently, the activation energies of $\text{Pd}_x\text{Rh}_{1-x}$ bimetallic NCs increased in the order of the tracked active surfaces: $\text{Pd}_{0.75}\text{Rh}_{0.25}$ (61 kJ mol^{-1}) < $\text{Pd}_{0.45}\text{Rh}_{0.55}$ (69 kJ mol^{-1}) < $\text{Pd}_{0.35}\text{Rh}_{0.65}$ (76 kJ mol^{-1}) (Table 2). Such observation was consistent with the conclusion reported in the literature where the activation barriers of $\text{Pd}_x\text{Rh}_{1-x}$ NPs decreased with the increased atomic fraction of Pd [53]. On the other hand, the activation energy of the $\text{Pd}_{0.6}\text{Rh}_{0.4}\text{-H}_2\text{-CO oxidation-O}_2$ for CO oxidation was 63 kJ mol^{-1} . AP-XPS studies of $\text{Pd}_{0.6}\text{Rh}_{0.4}\text{-H}_2\text{-CO oxidation-O}_2$ during CO oxidation uncovered that its active phase was RhO_x loaded on PdRh bimetallic alloy [53]. This was consistent with the reports where the active RhO_x was the active phase of Rh NPs with a size $\leq 2.5\text{ nm}$ [48,55], in which the activation barrier of RhO_x was reported at ca. 68 kJ mol^{-1} .

CONCLUSIONS

$\text{Pd}_x\text{Rh}_{1-x}$ NCs enclosed with (100) facets have been synthesized with high selectivity for the formation of bimetallic NC *via* a facile one-pot hydrothermal method with the aid of halide ions. By using $\text{Pd}_x\text{Rh}_{1-x}$ NCs with the same shape and similar size, we investigated the correlation between surface composition of these bimetallic NCs and their corresponding catalytic performances after varied pretreatments with the assistance of AP-XPS and kinetic analysis. In general, these *in-situ* studies of the three Pd-Rh bimetallic NCs revealed a strong dependence of surface chemistry on exposed atmospheres (e.g., $\text{CO} + \text{O}_2$, H_2 , O_2 , etc.) and their overall compositions. Upon the pretreatments of H_2 and $\text{H}_2\text{-O}_2$, bimetallic sites and metal/oxide interface could be created in CO oxidation at surface of $\text{Pd}_{0.8}\text{Rh}_{0.2}$ NCs and $\text{Pd}_{0.6}\text{Rh}_{0.4}$ NCs, respectively, while only alloy sites were observed for $\text{Pd}_{0.2}\text{Rh}_{0.8}$ NCs during the reaction. And surface segregation only took place during the $\text{Pd}_{0.6}\text{Rh}_{0.4}$ NCs-catalyzed CO oxidation, while surface compositions remained unchanged in the cases of $\text{Pd}_{0.8}\text{Rh}_{0.2}$ NCs and $\text{Pd}_{0.2}\text{Rh}_{0.8}$ NCs. This study not only demonstrates the surface chemistry evolution of bimetallic catalysts during different pretreatments and catalysis, but also puts forward a post-synthesis method by atmosphere treatments to create bimetallic or metal/oxide site for the reaction.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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PdRh双金属纳米立方体表面化学原位研究与CO氧化反应催化性能的关联

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摘要 随着原位表征技术的进步, 最新的研究结果表明, 纳米催化剂在活化或催化反应条件下会发生表面结构或组分的变化, 进而影响其催化性能。而开展以具有明确结构和组分纳米晶为模型催化剂的原位催化反应研究, 对深入理解催化剂在反应中的活性中心状态和构效关系能起到重要推进作用。本研究利用水热法制备了具有一系列组成、相似尺寸及相同形貌的PdRh双金属纳米立方体, 针对CO催化氧化反应, 结合原位X射线光电子能谱技术, 研究了不同预处理条件下和不同组成的纳米晶表面化学演化历程。研究发现Pd_{0.6}Rh_{0.4}和Pd_{0.8}Rh_{0.2}两种组分的纳米晶催化反应活性中心取决于其预活化条件, 而PdRh体系的元素偏析现象仅在Pd_{0.6}Rh_{0.4}一种条件下发生。因此, 本研究进一步明晰了双金属催化剂表面结构在反应条件下的演变与催化性能的关联。