A Pathway for the Growth of Core–Shell Pt–Pd Nanoparticles

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Supporting Information

ABSTRACT: The aging of both Pt–Pd nanoparticles and core–shell Pt–Pd nanoparticles has been reported to result in alloying of Pt with Pd. In comparison to monometallic Pt catalysts, the growth of Pt–Pd bimetallics is slower; however, the mechanism of growth of particles and the mechanism by which Pd improves the hydrothermal durability of bimetallic Pd–Pt particles remains uncertain. In our work on hydrothermal aging of core–shell Pt–Pd nanoparticles, synthesized by solution methods, with varying Pd:Pt ratio of 1:4, 1:1, and 4:1, we compare the growth of core–shell Pt–Pd nanoparticles and find that particles grow by migrating and joining together. The unique feature of the observed growth is that Pd shells from both particles open up and join, thereby allowing the cores to merge. At high temperatures, alloying occurs in good agreement with reports by other workers.

1. INTRODUCTION

The role of platinum as a catalyst spans chemical and petrochemicals manufacturing, automotive emission treatment, and fuel cells.1,2 While freshly prepared platinum catalyst, supported on metal oxide supports, is highly dispersed, the extended exposure to operating conditions, especially those of emission treatment catalysts, results in sintering.3 Because sintering results in a reduction of the number of catalytic sites, a high loading of platinum is necessary to maintain catalyst performance over the operational lifetime, resulting in increased production costs.4 There are two potential approaches that have been explored to reduce platinum sintering, with limited success. The first involves nanoparticles of platinum with open surface structures which were expected to sinter slowly.5–6 The second approach involves bimetallic systems7–16 such as Pt–Pd which have been shown to be quite promising for formic acid oxidation and fuel cell catalysts.11–16

The structure of bimetallic Pt–Pd systems depends on the synthetic route.17 Physical vapor deposition methods generally lead to bimetallic surfaces under ultrahigh-vacuum conditions.18–22 Impregnation with Pt and Pd salts and subsequent pyrolysis and sintering results in Pt–Pd bimetallic systems supported on the metal oxide surface. The fresh samples generally contain single atoms and rafts of Pt and Pd and alloying occurs during sintering.23 The Pt–Pd core–shell nanoclusters are synthesized by stepwise reduction of dilute solutions of Pt and Pd salts in the presence of surfactants.8,10 For Pd–Pt core–shell nanoclusters, the sequence is reversed.14 The core–shell nanoclusters can then be deposited on a substrate (e.g., alumina) for catalyst preparation. Henkelman and Crooks et al.24 report the impact of synthetic route on the attempted synthesis of core–shell Pd147@Pt162 DENs (dendrimer encapsulated particles), resulting in Pt147@Pd147Pt15 with inverted structure after a galvanic exchange step from Pd147@Cu162.

Density functional theoretical modeling has been extensively employed to calculate surface segregation energies of bimetallic systems with different adsorbates.17 The segregation of Pd–Pt systems has been studied in vacuum, and in the presence of adsorbed H2, O2, OOH, and O.25–27 For a core–shell Pt–Pd system, a 38-atom truncated octahedron was chosen as a model for bimetallic nanoparticles. Those results show that there is minimal change in surface composition under different gaseous conditions, which was also experimentally observed.28,29 Growth of the core–shell particle has been monitored after exposure to operating conditions, and some of the systems have been found to be hydrothermally stable. For example, Schmidt et al. demonstrated that the growth of nanoalloy Pd/Pt was largely confined when compared to pure Pt nanoparticles under thermal treatment.30 Somorjai and Salmeron et al. described their results on Rh0.5Pd0.5 and Pt0.5Pd0.5 during oxidizing, reducing, and catalytic reaction conditions. While Rh0.5Pd0.5 underwent reversible changes in composition, Pt0.5Pd0.5 was quite stable.10,28 The melting behavior of (Pd,Pt)n nanoparticles confined in single-walled carbon nanotubes have been investigated by molecular dynamics simulations.31 Core–shell Pd–Au with Pd on the surface could be alloyed at 300 °C which is proposed to prevent migration and sintering.32 Molecular dynamics studies of core–shell Pt–Pd nanoparticles suggest that sintering occurs in two stages, from surface to core.33

McCabe et al.34 showed that very large particles (300–400 nm) of platinum commonly observed after aging of Pt/alumina

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under automotive exhaust treatment conditions do not form when Pd−Pt/alumina is aged. Graham et al. report growth and alloying of Pt−Pd particles after oxygen-rich hydrothermal aging at 500 °C and 900 °C and found that there was 20% improvement in dispersion as compared with a hydrothermally aged Pt-only catalyst. 34 Ward et al. reported that vehicle-aged Pt−Pd catalysts remain spherical, did not show segregation, and were randomly alloyed. 35 The mechanism of Pd-induced improvement in Pt performance was proposed by both groups to be due to a surface Pd oxide layer that decreases emission of volatile Pt oxide. 34,35 However, the aberration-corrected transmission electron microscopic (AC-TEM) images from both groups did not show evidence of surface oxide. 34,35 A detailed study by Datye et al. shows that after 10 h of aging in air at 750 °C, the Pt−Pd system contains fully reduced Pt and almost 30% oxidized Pd. 36 Interestingly, the PdO was not present on Pt−Pd particles but as a separate phase dispersed over the alumina. The metallic particles showed a uniform distribution of Pt and Pd with no core−shell structures. For these hydrothermal aging studies, both Datye et al. and Graham et al. prepared the bimetallic Pt−Pd samples by impregnation from Pt and Pd salts. Ward et al. do not report the synthetic method but mention that diesel oxidation catalysts were supplied by an anonymous source.

Thus, the aging of both Pt−Pd nanoparticles and core−shell Pt−Pd nanoparticles results in alloying of Pt with Pd. In comparison to monometallic Pt catalysts, the growth of Pd−Pt bimetallics is slower; however, the mechanism of growth of particles and the mechanism by which Pd improves the hydrothermal durability of bimetallic particles remain uncertain. In this paper, we present our results on hydrothermal aging of Pt nanoparticles and core−shell Pt nanoparticles, synthesized by solution methods, with varying Pd:Pt ratio of 1:4, 1:1, and 4:1 and compare the growth of core−shell Pt−Pd nanoparticles. We find that PdPt core−shell particles grow by migrating and joining together and forming larger core−shell particles. At high temperatures, alloying occurs as observed by other workers.

2. EXPERIMENTAL DETAILS

Poly(N-vinyl-2-pyrrolidone) (PVP40, average MW 40 000), PdCl2 (99.999%), hexachloroplatinic(IV) acid (99.995%), and anhydrous ethanol (HPLC grade) were purchased from Sigma-Aldrich and used without further purification. The bimetallic Pt−Pd nanoparticles were synthesized by a slight modification of the literature procedure. 37 In a typical synthesis, PVP40 was added to PdCl2 solution in ethanol prepared by stirring PdCl2 in ethanol for 12 h and filtering the solution. An aqueous solution of hexachloroplatinic acid in PVP40 was added to the PdCl2 solution, and the resulting reaction mixture was heated under reflux for 1 h. A sample of alumina powder was added to the reaction mixture, and the slurry was allowed to stir for 48 h, centrifuged, and washed with water to obtain a gray powder which was dried at room temperature overnight and calcined at 350 °C for 1 h (heating rate 1 °C/min). The samples obtained by this synthetic method are labeled as PdPt14, PdPt11, and PdPt41 with 14, 11, and 41 referring to Pd:Pt ratios of 1:4, 1:1, and 4:1, respectively.

The elemental analysis of samples was performed by Galbraith Laboratory using ICP techniques. For the electron microscopy research, ground catalyst fine powders were dispersed on holey carbon film-coated copper grids. Low-magnification scanning transmission electron microscopy (STEM) measurements were carried out on a Hitachi HD2000 instrument at the Center for Nanophase Materials Sciences of Oak Ridge National Laborato-

ratory, operating at 200 kV under high angle annular dark field (HAADF) Z-contrast mode with a resolution of 0.24 nm. Histograms of particle size were obtained after measurements of hundreds of randomly selected particles for each sample. Statistical analysis of particle size distributions was performed using the Digital Micrograph software package. Atomic-resolution STEM imaging and electron energy loss spectroscopy (EELS) elemental mapping were obtained from a Nion UltraSTEM 200, operating at 200 kV with sub-Å resolution. The probe-forming angle was ~30 mrad, and the inner angle of the HAADF detector was about 63 mrad. The Pt M45 edge at 335 eV and Pt M45 edge at 2122 eV were used for the EELS elemental maps with a collection angle of ~36 mrad.

The samples were hydrothermally aged 25 by heating a 0.7 g sample of Al2O3-supported Pd/Pt bimetallic nanoparticles for 2.5 h under a total flow of 5 L/min of a gas mixture consisting of O2 (5%), H2O (10%), and N2 (balance), for 3 h at 500 °C, 600 °C, 750 °C, or 900 °C. The samples were cooled under pure N2. The average size of fresh and aged particles as determined by STEM is summarized in Table S1, Supporting Information.

3. RESULTS AND DISCUSSION

In our synthetic procedure, γ-alumina powder was added to freshly prepared samples of Pt, PdPt14, PdPt11, and PdPt41 nanoparticles before removing volatiles. This led to loading of Pt, PdPt14, PdPt11, and PdPt41 nanoparticles on γ-alumina. The elemental analysis shows that Pt to Pd molar ratio is 0.22, 0.86, and 3.77 for PdPt14, PdPt11, and PdPt41 nanoparticles, respectively. The Z-contrast images of the samples (Figure S1, Supporting Information) suggest a narrow particles size distribution in all samples. The particle size distribution were obtained by running a circular diameter script for Digital Micrograph software (Gatan, Inc.) and is shown in Figure 1 for Pt, PdPt14, PdPt11, and PdPt41 nanoparticles on γ-alumina. The average Pt nanoparticle size of Pt/alumina sample is ~2.5 nm, and most of the particles are in the 0.5−4.5 nm range although there are some outliers. The bimetallic nanoparticles PdPt14, PdPt11, and PdPt41 also exhibit average particle size and particle

Figure 1. Size distributions of fresh Pt (top left), PdPt14 (top right), PdPt11 (bottom left), and PdPt41 (bottom right) nanoparticles from STEM analysis.
size distribution ranges of ≈2.5 nm and 0.5–4.5 nm, respectively. The Pd to Pt ratio does not appear to have an impact on average size of nanoparticles or particle size range.

In the following sections, we examine the impact of hydrothermal aging on PdPt14, PdPt11, and PdPt41 particles at 500 °C, 600 °C, 750 °C, and 900 °C to determine the impact of temperature and Pd concentration on growth behavior of Pd−Pt core−shell nanoparticles supported on γ-alumina. We find that Pd, even in relatively low loading (PdPt14), imparts hydrothermal durability to Pd−Pt particles because megaparticles of 400–500 nm normally observed for Pt after hydrothermal treatment at 900 °C are not seen in any of our samples (Figure 2). Furthermore, the average particle size of Pd−Pt in all three samples remains comparable after hydrothermal aging at 500 °C, 600 °C, 750 °C, and 900 °C despite some variations in particle size ranges.

On the basis of the results of hydrothermal aging at 500 °C and 600 °C, it became obvious that the growth of Pd−Pt core−shell nanoparticles is more complicated than the simple Lifshitz, Slyozov, and Wagner (LSW) model employed in catalysis to model particle growth behavior via Ostwald ripening. Because our sample contains Pd−Pt core−shell particles at 500 °C, core−shell particles and alloys at 600 °C and 750 °C, and alloys at 900 °C, simple average-diameter-based models will be misleading. To determine growth kinetics, it will be necessary to carry out both time- and temperature-dependent experiments at multiple temperatures to model growth of core−shell particles and alloy particles separately. The ongoing development of an in situ gas cell that can be used with AC-TEM will enable such an investigation in the near future, and our results will be presented in a future report.

3.1. Structure after Hydrothermal Aging at 500 °C. The Z-contrast images of samples after hydrothermal aging at 500 °C (Figure S2) do not show dramatic changes. The particle size distributions of the PdPt14, PtPd11, and PtPd41 nanoparticles are shown in Figure 3.

While the average size of PdPt11 nanoparticles does not change significantly in comparison to that of fresh samples (2.6 nm vs 2.5 nm), the distribution range increases to 0.5–6.0 nm, with the distribution being centered at 3.5 nm. The growth of PdPt11 nanoparticles is smallest of the three PdPt samples. The PdPt nanoparticles of PdPt14 and PtPd41 exhibit a slightly higher average size of ≈3.5 nm, but the particle size range is still the same for all three PdPt samples.

High resolution high angle annular dark field (HAADF) images show that the size of the PdPt11 core−shell particles on amorphous-looking supports varies from 1.0 to 6.0 nm after aging at 500 °C (Figure 2(a)). These results compare favorably to a high resolution electron microscopic study from Jose-Yacaman et al., which shows that unsupported Pt−Pd core−shell nanoparticles exhibit decahedral, octahedral, and triangular plate core−shell nanoparticles. An intensity boundary between core and shell could be seen for the particle in Figure 4(b) with heavier Pt in the core because heavier Pt atoms lead to higher intensity in HAADF images (so-called Z-contrast images). EEL spectrum images of an area of PdPt11 sample, marked by a green
box in Figure 4(c), and the corresponding elemental maps show that Pt exists mainly in the core of both particles. EELS elemental mapping on four randomly selected PdPt11 particles consistently exhibited core–shell features.

The EELS signal of Pd could not be obtained, probably due to the low Pd concentration and the interference from thick surrounding carbon (the carbon K-edge is at 284 eV is very close to the Pd M45-edge at 336 eV). In addition, the interaction with the electron beam tended to make the shells of the PdPt11 particles amorphous.

The merging of two PdPt11 nanoparticles on γ-alumina nanoparticles can be seen in the image shown in Figure 5. Both particles retain their core–shell structure, as the Pt map shows that Pt exists mainly in the core of both particles. Pt can also be seen in the center of the intersection of these two particles, suggesting that the shell has opened up a pathway for Pt of both particles to merge.

This merging of two particles can be schematically represented as follows (Figure 6) and suggests a pathway for the growth of core–shell Pd–Pt particles at moderate temperatures. In this pathway two core–shell bimetallic particles migrate until they come in contact. At this point, the shell merges and opens a channel to allow the cores to merge. The resulting particle retains its core–shell structure. In this model, Pt is bound by the Pd shell which prevents Pt particles from becoming very large.

3.2. Structure after Hydrothermal Aging at 600 °C. The Z-contrast images of samples after hydrothermal aging at 600 °C (Figure S3, Supporting Information) also do not show dramatic changes, but the average particle size increases to ~5.0 nm. The particle size distributions of the PdPt14, PdPt11, and PtPd41 nanoparticles are shown in Figure 7. The particle growth increases the particle size range to 0.5–10 nm for PdPt11 and to 0.5–15 nm for PtPd14 and PtPd4.

The high resolution images showed PdPt11 particles in 1–10 nm range (Figure 8(a)), and particles exhibited better defined lattice. For the particle shown in Figure 8(b), the interplanar spacings are ~0.23, 0.23, and 0.20 nm in three directions, suggesting (110) planes that show 111 and 200 spacings. The EELS elemental maps (Figure 8(c,d)) show that Pt exists in the core of the PdPt11 particles indicating a core–shell structure.

In addition to a less-defective lattice, the Pt-core area is larger than PdPt11 samples after aging at 500 °C. A weak Pd signal can also been detected on the edge of the particle. The spectral images of four randomly selected particles show that at least two have retained the core–shell structure. In the other two particles, Pt is well distributed across the particles. These results suggest that the transformation of core–shell structure to alloy structure is beginning to take place even at 600 °C.

3.3. Structure after Hydrothermal Aging at 750 °C. The Z-contrast images of samples after hydrothermal aging at 750 °C (Figure S4, Supporting Information) show extensive coarsening of metal nanoparticles. The impact of Pd fraction also becomes pronounced, the low Pd sample PdPt14 shows average particle size to be ~10 nm whereas higher Pd fraction samples exhibit average particle size to be ~15 nm (Figure 9).

The Z-contrast image in Figure 10(a) shows nanoparticles ranging from 1 to 20 nm for the PdPt11 sample. The triangle shape for the γ-alumina substrate suggests improved crystalline structure. The EELS of the area marked by the green box in Figure 10(b) shows Pt and Pd signals. The Pd and Pt distribution was examined for four particles (1–4) in Figure 10(c), and they all show variable Pt–Pd distribution. Most of the Pt is still localized in the center for particles 1–3, but it encompasses the whole particle 4. Conversely, the Pd encompasses whole particles 1–3 but exists only in the center of particle 4. We also found examples of particles that exhibit uniform distribution of Pt and Pd in entire PdPt11 nanoparticles (Figure 11(a–c)). Such a varying distribution of Pt and Pd suggests that the transformation of core–shell PdPt11 nanoparticles to alloy particles is becoming.

Figure 5. Z-contrast images of PdPt11 nanoparticles on γ-alumina after hydrothermal aging at 500 °C shows two merging nanoparticles (a) and Pt map of the particles (b).

Figure 6. Schematics of growth pathway for bimetallic core–shell particles.

Figure 7. Size distributions of hydrothermally aged PdPt14, PdPt11, and PdPt41 nanoparticles supported on γ-alumina at 600 °C.
rapid during hydrothermal aging at 750 °C although some of the particles still retain core–shell structure.

Most of the particles are not in major zone axes; therefore, it is not easy to see the atomic structure on them. But on the particle in Figure 11, we have observed clear alloy structure in atomic resolution. First, EELS spectrum images show that Pt and Pd both exist uniformly on the entire PdPt11 nanoparticle (Figure 11(a–c)). After being exposed to the beam, the edge of this PdPt particle started to rotate or reconstruct (Figure 11(d)). The high magnification image in Figure 11(e) shows interlaced columns.
of bright (red big circle) and weak (blue small circle) intensity. Because EELS shows the presence of only Pt and Pd elements on the shell, the bright and weak columns are likely Pt and Pd columns, respectively. The spacing and the face-centered structure features are consistent with PtPd alloy in the \([100]\) zone axis. The intensity of the weak columns is not uniform, and this structure is not stable under the electron beam, suggesting that there might be some vacancies or defects in the structure. Although the PtPd structure in \([100]\) zone might be formed under the beam radiation effect, it confirms the EELS result that the nanoparticle is composed of a mixture of Pt and Pd atoms.\(^{41}\)

3.4. Structure after Hydrothermal Aging at 900 °C. Hydrothermal aging at 900 °C leads to extensive particle growth of all PdPt core–shell nanoparticles, and average particle size increases to \(\sim 30 \text{ nm}\) (Figure S5 (Supporting Information) and Figure 12).

The suppression of formation of extremely large Pt particles by Pd shells in core–shell particles during hydrothermal aging at 900 °C, previously seen for bimetallic Pt–Pd particles, is also observed for core–shell Pd–Pt particles which are essentially alloys at this temperature. The high resolution images of the PdPt11 particles and the mapping of Pt and Pd (Figure 13) clearly show that the core–shell structure is completely transformed into an alloy structure after hydrothermal aging at 900 °C. This EELS result is consistent for other randomly selected particles, which all showed Pt and Pd across the entire particle.

4. CONCLUSIONS

We have shown that core–shell PdPt nanoparticles supported on γ-alumina retain their core–shell structure below 750 °C and grow by merging of particles. At 600 °C, alloying begins with concurrent loss of core–shell structure for the supported PdPt nanoparticles. The hydrothermal 900 °C treatment completely converts the core–shell structure to alloy structure. The suppression of formation of extremely large Pt particle by Pd during hydrothermal aging at 900 °C, previously seen for bimetallic supported Pt–Pd particles, is also observed for core–shell Pd–Pt supported nanoparticles.
REFERENCES


