Thermal Wetting of Platinum Nanocrystals on Silica Surface

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Thermal stability of faceted Pt nanocrystals on amorphous silica support films was investigated using in situ transmission electron microscopy in a temperature range between 25 and 800 °C. The particles started to change their shapes at ~350 °C. Above 500 °C, the particles spread on the support film with increasing temperature, rather than becoming more spherical. Such temperature-induced wetting of Pt nanoparticles on silica surface can be attributed to the interfacial mixing of Pt and SiO₂ and the resulting negative interface energy.

For heterogeneous catalysis, both metal and metal−support interactions are crucial in determining catalytic properties.1−4 In particular, the thermal stability and shape evolution of active metal nanoparticles supported on different substrates at elevated temperatures need to be studied carefully.5−9 as many practical catalytic reactions utilized in industry take place at high temperatures.

It is a general tendency that the metal particles become spherical-like at high temperatures to lower the total surface area and the surface energy.10,11 Recently, Wang et al. reported a temperature-dependent shape transformation of the Pt nanoparticles on an amorphous carbon substrate. They showed that the particles were transformed into a spherical-like shape by surface melting and eventually agglomerated at high temperatures.5 However, in the present study, we observed by using in situ transmission electron microscopy (TEM) that the Pt nanoparticles spread on the amorphous SiO₂ substrates at temperatures above 500 °C. It indicates that for Pt nanoparticles on SiO₂, a typical heterogeneous catalyst, Pt tends to wet the SiO₂ surface instead of forming spherical particles.

Two different shapes of Pt nanoparticles (samples A and B) were produced by modified polylol process in the presence of poly(vinylpyrrolidone) (PVP).12 Briefly, 2.5 mL of ethylene glycol (EG) was refluxed for 5 min. A total of 0.5 mL of AgNO₃ solution was added to the boiling EG. Immediately, EG solutions temperatures need to be studied carefully,5 immediately, EG solutions were heated slowly from room temperature to 800 °C in 6−7 h to get the systems close to equilibrium. The temperature was measured using a thermocouple attached to the specimen cup. The analyzed areas were selected to be close to the Cu grid to minimize the temperature difference between the specimen cup and the sample areas.

The shape of the particles at room temperature was characterized.12 The cubic particles were enclosed by six {100} planes, of which the 12 edges were along {100} directions. The tetrahedral particles were enclosed by four {111} faces, and the six edges were along {110} directions. The cuboctahedral (also known as “truncated octahedral”) particles were enclosed by both {111} and {110} planes, with edges lying in {100} and {110} directions.

Figure 1, parts a and b, shows the in situ TEM images of samples A and B, respectively. For the particles with cubic and tetrahedral shapes (Figure 1a), the truncation started to develop at ~350 °C, consistent with the previous results of Pt nanoparticles on a carbon support by Wang et al.5 When the temperature increased to 550 °C, the shape of the particles was hardly identifiable between cubes and tetrahedra due to significant truncation. The particles became irregularly faceted at higher temperatures. In a few cases, the directions of the edges were derived from the relative orientations of the particles at high and low temperatures. For example, some tetrahedral particles possess a truncated rectangular shape at high temperatures, two of which are indicated by arrows in the snapshot taken at 800 °C. As schematically shown in Figure 1c, the short edges of the rectangles are parallel to the edges of the tetrahedral particles at low temperatures, which lie in {110} directions. The
Figure 1. In situ TEM images of the Pt nanoparticles recorded during the heating process, showing the temperature-induced change of shape and wetting of Pt on silica. (a) Mixed cubic and tetrahedral particles from sample A. (B) Cuboctahedral particles from sample B. Two tetrahedral particles transformed to truncated rectangular shapes at high temperatures are indicated by arrows in (a) and schematically shown in (c).
long edges are perpendicular to the short edges; they lie in (112) directions. As a comparison, we have also carried out the ex situ heating experiments. The Pt nanocubes were heated on silica grids under oxygen flow. After thermal treatment at 300 °C for 6 h, most of the particles still maintained their original shapes, although particle aggregation was observed under such conditions.

Because the cuboctahedral particles were truncated even at room temperature, the shape change (Figure 1b) was not as obvious as those of the cubic and tetrahedral particles. At room temperature, they were enclosed by small facets and looked like spheres. Similar to the cubic and the tetrahedral particles, the cuboctahedral particle shape was converted to irregular ones at higher temperatures.

Some particles shown in Figure 1, parts a and b, are bicrystals. There is no change in the length of the grain boundaries with increasing temperature (i.e., they extend to surfaces even at 800 °C), which suggests that surface melting did not occur for these Pt nanoparticles. It is also noted that no secondary phases such as platinum silicide formed at high temperatures. Figure 2 shows a selected-area electron diffraction pattern of sample A taken at 725 °C, exhibiting the sharp spots/rings only from metal Pt. This is in contrast to the reports that platinum silicides formed in Pt–SiO₂ systems. The reason for the difference is believed to be the treatment of the samples in reducing H₂ ambient for the latter cases.

The thermal stability of the polymer (PVP) layer enclosing the Pt nanoparticles is not available in the present study, mainly because the layer did not generate enough contrast from the SiO₂ substrate. It was demonstrated that, however, the polymer layer can be completely removed below 250 °C in the high vacuum environment of the TEM column. In ref 5, Pt particles attached at the edge of the grid were investigated using a TEM with a cold-field-emission gun, which generates a higher coherent electron beam than a thermal emission gun and thus higher contrast for the polymer layer.

Metal particles usually become more spherical-like at high temperatures to lower the surface energy. Thus, in TEM images, the projection area of the particles is expected to decrease with increasing temperature. However, in the present study, the projection areas increased with rising temperature as shown in, parts a and b of Figure 1. Statistical mean projection area of the particles is plotted against the temperature change in Figure 3. A critical temperature Tc around 500 °C is clearly observed, and the projection area (or the Pt/SiO₂ interface) below Tc remains almost constant with increasing temperature. Above Tc, the interface area increases rapidly with the increase of temperature. In the following, we will show that this temperature-induced wetting of Pt on SiO₂ can be attributed to the interfacial mixing and the negative interface energy.

Because the investigated particles were faceted at high temperatures, there was more than one contact angle between the particles and the substrates, and the accurate values were not generally available. However, by assuming a constant volume and spherical surface for the particles, the average contact angle can be estimated from the projection area (see the Supporting Information for details). Then the interface energy is obtained using the Young–Dupre equation

$$\gamma_{\text{int}} = \gamma_{\text{SiO₂}} - \gamma_{\text{Pt}} \cos \theta \quad (1)$$

where \(\gamma_{\text{int}}\) denotes the interface energy between Pt and SiO₂, \(\gamma_{\text{SiO₂}}\) is the surface energy of SiO₂, \(\gamma_{\text{Pt}}\) is the surface energy of Pt, and \(\theta\) is the contact angle. The work of adhesion is calculated using

$$W_{\text{ad}} = \gamma_{\text{Pt}} + \gamma_{\text{SiO₂}} - \gamma_{\text{int}} = \gamma_{\text{Pt}} (1 + \cos \theta) \quad (2)$$

The surface energies of Pt and SiO₂ are required in eqs 1 and 2. \(\gamma_{\text{Pt}}\) is 2.2 N/m at 1300 °C with a temperature coefficient of \(-0.60\) mN/mK; \(\gamma_{\text{SiO₂}}\) is 0.278 N/m at 1000 °C with a temperature coefficient of 0.035 mN/mK. The Pt/SiO₂ interface energy and the work of adhesion estimated using eqs 1 and 2 are given in Figure 4, where a negative interface energy at high temperatures is revealed.

The negative interface energies were reported for certain metal–metal systems, in which the heat of mixing was negative and interfacial alloying occurred through interdiffusion of metal atoms. In general, the stronger the interactions between mixing components are, the more energy that is gained by forming the interface, and thus the more negative the interface energy would be. For the Pt–SiO₂ system, the negative interface energy suggests a strong interactions between Pt and SiO₂. Since electron diffraction patterns shows no evidence of
alloying in Pt and SiO₂, the mixing could occur only at the Pt/SiO₂ interfaces.

There are several reports suggesting the strong Pt−SiO₂ interaction. By using X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) studies, charge transfer was detected between Pt and SiO₂, resulting in a partial reduction of Si(IV).¹⁷,¹⁸ Such an effect is much stronger for Pt than for other metals (Pd, Ag, and Au).¹⁷ A high-energy ion beam was also shown to be able to induce the mixing of Pt films on the SiO₂ substrate, and the mixing is much more significant than that of Pt films on other substrates (Al₂O₃, SiC, and MgO).¹⁹ In addition, the negative heat of interfacial mixing is expected to favor the surface diffusion of Pt on SiO₂ by Pt incorporation into the SiO₂ surface, consistent with the observation that the diffusion of Pt in SiO₂ was mainly through micropores or holes.²⁰,²¹

Very recently, by employing grazing incidence small-angle X-ray scattering technique, it was observed that the horizontal size of Pt particles (about 3 nm in diameter) on an oxidized Si wafer increased above 320 °C.²² The size increase was attributed to the agglomeration of the Pt particles.²² Base on the present study, however, it is quite likely that the Pt particles spread on the substrate in this study as well. If true, it may suggest a size-effect of the wetting temperature.

Due to the negative interface energy, the work of adhesion between Pt and SiO₂ was large, as shown in Figure 4. The large work of adhesion implies that the detachment of the Pt particles would not take place at the Pt/SiO₂ interface but rather in the SiO₂ substrate. From the Griffith criterion,²³ the energy required for the fracture from the SiO₂ substrate is two times the SiO₂ surface energy (~0.56 N/m), much less than the energy required for the fracture at the Pt/SiO₂ interface, i.e., the work of adhesion (~3 N/m). Cordill et al. measured the adhesion of Pt films on the SiO₂ substrate using nanoindentation.²⁴ The fracture energy was calculated to be 0.2 and 0.5 N/m for indentation blisters and spontaneous buckles, respectively. The values are close to the present estimation (~0.56 N/m) based on the Griffith criterion. In that work, however, the exact fracture position was not available.

In conclusion, the thermal stability of faceted Pt nanoparticles on silica support films has been investigated using in situ transmission electron microscopy. In addition to the shape changes, the particles’ wettability on the support films increased with increasing temperature above a critical temperature of about 500 °C. Such thermal wetting of Pt nanoparticles on the silica surface suggests a negative interface energy between Pt and SiO₂ at high temperatures, which is attributed to the interfacial mixing of Pt and SiO₂. This insight could have important implications in elucidating the actual catalytic process for Pt/SiO₂ heterogeneous catalysts, particularly at high temperature.

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Supporting Information Available: Estimation of average contact angle from the projection area of the nanocrystals on silica grid. This material is available free of charge via the Internet at http://pubs.acs.org.