

Shape-controlled synthesis of Pd nanocrystals with exposed {110} facets and their catalytic applications

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Abstract: Palladium (Pd) nanocrystals with controlled shapes and their performance as catalysts have been widely investigated in various catalytic reactions. In this paper, we reported the use of glucose as a reducing agent for the shape-controlled synthesis of rhombic dodecahedral Pd nanocrystals, which enclosed by {110} high-energies facets with small grain sizes. The as-prepared Pd nanocrystals were loaded on CeO₂ to form the Pd/CeO₂-g catalysts and used in automobile emission reaction. The Pd/CeO₂-g catalysts showed high three-way catalytic activity.

Keywords: Pd nanocrystals, {110} facets, glucose, automobile emission.

1. Introduction

On the basis of the fact that surface energies of different crystallographic planes are in the order of $\gamma_{\{110\}} \gg \gamma_{\{100\}} > \gamma_{\{111\}}$, the metal-support interaction would be strengthened and catalytic activities of the catalyst would be improved by employing the Pd nanoparticles with high surface energies as the active centers. Recently, Zheng and co-workers[1] reported a facile synthetic strategy to prepare concave Pd nanocrystals enclosed by {111} and {110} facets. They synthesized the Pd nanocrystals using a solvothermal process in the presence of formaldehyde solution mixed with benzyl alcohol, which were not benefit to environment. Additionally, Xu and co-workers[2] reported a method for the synthesis of Pd nanocrystals with the {110} facets by using nontoxic ascorbic acid as a reducing agent. Unfortunately, the size of Pd grains reached up to 100 nm, which repressed the effective usage of the Pd catalysts. Hence, in this work, we investigated the possibility to employ the non-toxic glucose as an effective reducing agent to synthesis rhombic dodecahedral Pd nanocrystals enclosed by {110} facets with smaller grain sizes (labelled as Pd-g). Additionally, the Pd/CeO₂-g catalysts were used in automobile three-way catalytic reaction in comparison with catalysts by using ascorbic acid and citric acid as reductants (labelled as Pd-a and Pd-c), respectively.

2. Experimental

Pd-g nanocrystals: PVP and glucose were dissolved in D.I. water in a three-necked flask attached a reflux condensing tube and a heater in an oil bath at the oil temperature of 150 °C under stirring. The aqueous solution of Na₂PdCl₄ was then rapidly added into the flask. The mixed aqueous solution was kept in an oil bath at the temperature of 150 °C with reflux for 18 h. Then the product was collected by centrifugation, and washed with acetone and alcohol several times to remove excess PVP. The sample Pd nanocrystals prepared by using glucose as reducing agent was marked as Pd-g.

3. Results and discussion

The TEM and HAADF-STEM images of the Pd nanoparticles prepared by using the glucose as reducing agent were shown in Fig. 1A and B respectively. One can see that Pd nanocrystals showed the rhombic dodecahedral and an average grain size of 15-18 nm, far smaller than previous reports^[1, 2]. The high-resolution transmission electron microscopy (HRTEM) image (Fig. 1C) showed lattice fringes with an interplanar spacing of 0.140 nm, corresponding to (220) planes of the Pd nanocrystals^[1]. Fig. 1D displayed a typical SAED pattern of a flatly lying rhombic dodecahedral Pd nanocrystals along the [011] zone axis

obtained by directing the electron beam perpendicular to the upper face of the nanocrystal, which was consistent with Xu's report about Pd rhombic dodecahedrons nanocrystals^[2]. It proved that the synthesized nanocrystals were single-crystalline with the 12 well-defined {110} facets.

After the as-prepared Pd nanocrystals (1 wt%) supported on CeO₂ and calcined at 500 °C for 3 h, the Pd/CeO₂ catalysts were formed. Fig. 2 presented the conversions of CO, HC and NO under stoichiometric conditions over the Pd/CeO₂ catalysts which by using glucose, ascorbic acid and citric acid as reducing agents. It can see that the

glucose-Pd/CeO₂ catalyst exhibited the best catalytic activities for the three contaminations. It finish conversion temperature (T₉₀) for CO, HC and NO were 140 °C, 160 °C and 140 °C,

respectively. The glucose-Pd/CeO₂ catalyst showed the best catalytic activities. As the ascorbic acid-Pd/CeO₂ catalyst, the Pd nanocrystals exposed with {111} and {100} facets, and as the citric acid-Pd/CeO₂ catalyst, the Pd exposed with {111} facets. It known that surface energies of different crystallographic planes were in the order of $\gamma_{\{110\}} \gg \gamma_{\{100\}} > \gamma_{\{111\}}$, thus the interaction between Pd and CeO₂ of the catalysts were in the order of glucose-Pd/CeO₂ > ascorbic acid-Pd/CeO₂ > citric acid-Pd/CeO₂. From Fig. 6 A-C, it can see that the catalytic behaviors of the catalysts followed such a sequence: glucose-Pd/CeO₂ > ascorbic acid-Pd/CeO₂ > citric acid-Pd/CeO₂ for the three contaminations, corresponds with the above discussions, indicating that the active facets play a critical role in the three-way catalysts.

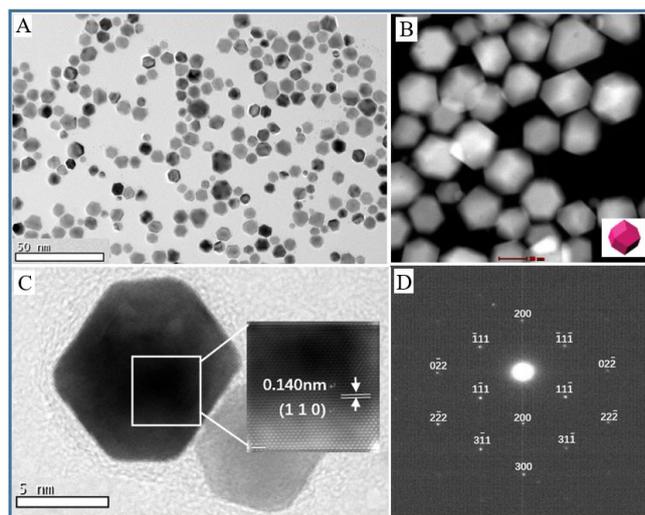


Figure 1. (A) TEM images, (B) HAADF-STEM images and (C) HRTEM images (scale bar, 1nm in the white box) of the Pd-g nanocrystals. (D) Corresponding SAED pattern of a single Pd-g nanocrystal recorded along the [011] zone axis.

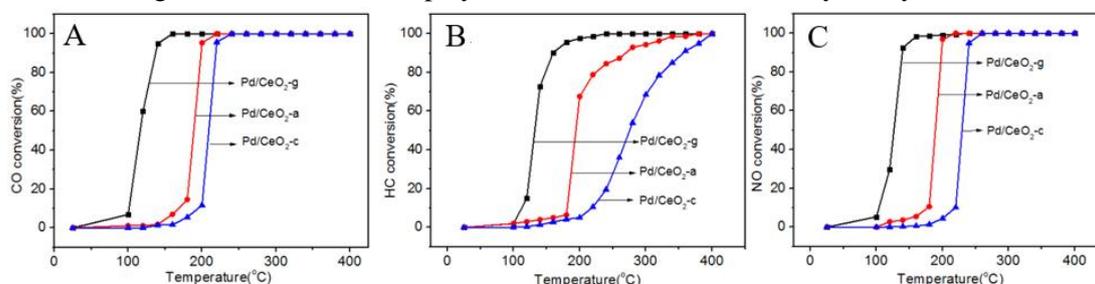


Figure 2. Catalytic activities of CO (A), HC (B), NO (C) over the Pd/CeO₂-g, Pd/CeO₂-a and Pd/CeO₂-c catalysts.

4. Conclusions

The catalytic activity evaluation revealed that the Pd/CeO₂-g catalyst showed high three-way catalytic activity in a comparison with the Pd/CeO₂-a and Pd/CeO₂-c catalysts. The Pd nanocrystals exposed with {110} facets was an important role to improve the catalytic activities for automobile three-way reactions.

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References

1. X. Huang, S. Tang, H. Zhang, Z. Zhou, N. Zheng, J. Am. Chem. Soc. 131 (2009) 13916-13917.
2. W. Niu, L. Zhang, G. Xu, ACS Nano 4 (2010) 1987-1996.