

Synthesis and Catalytic Activity of Monodisperse Pd Nanoparticle Catalysts

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Introduction

Colloidal nanoparticle synthesis offers a great advantage over traditional catalyst synthesis from metal salts. Colloidal synthesis allows for a greater control over the nanoparticle size while providing a narrow size distribution, the surfactant protects the NPs from agglomeration, and can be easily removed to expose the surface for catalytic activity. Various techniques, such as the use of dendrimer encapsulation [1] or a surfactant (i.e., trioctylphosphine, (TOP)) to prevent particle agglomeration [2,3] have been developed in order to overcome this limitation. Both methods achieve nanoparticle separation by taking advantage of steric hindrance (figure 1a).

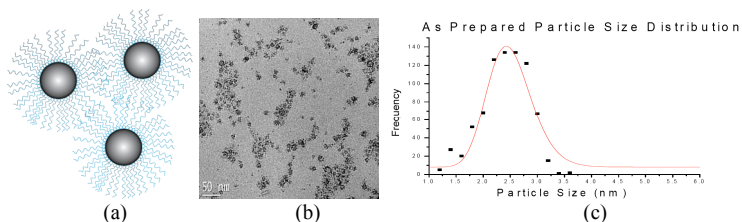


Figure 1. Ideological model of particles protected by surfactant (a), TEM image (b) and particle size distribution (c).

A key challenge is to ensure that the initial particle size distribution (figure 1c) can be retained when the nanoparticles are deposited on a support and used as a catalyst. In this work, we will present the results of the synthesis of colloidal (figure 1b) monodisperse Pd nanoparticles supported on aluminum oxide (Al_2O_3) that retain their size distribution after becoming catalytically active for CO oxidation.

Materials and Methods

To synthesize the palladium nanoparticles (Pd NPs), palladium mesityl ($\text{Pd}(\text{Mes})_2$ where $\text{Mes} = \text{C}_6\text{H}_3\text{Me}_3$ -2,4,6) was injected into TOP at 300 °C under an argon atmosphere. After reacting for 30 min., the flask was allowed to cool to room temperature, the precipitate removed by centrifugation, the NP washed with ethanol, and re-dispersed in hexane. The wash procedure was repeated twice before storing the product in hexane.

To characterize the NPs, a drop of suspension was placed on a carbon grid and examined using a TEM (figure 1b). As-prepared samples were mounted on Al_2O_3 and used for CO oxidation. The results were compared to a calcined sample prepared under otherwise identical conditions. The calcined samples were then re-examined using the TEM to determine

if any agglomeration had occurred. To complete the surfactant analysis, TGA was used to determine the surfactant removal temperature.

Results and Discussion

The NPs produced were found to be well dispersed, with an average diameter of 2.4 ± 0.4 nm (figure 1c). Supported particles (figure 2a) demonstrate good conversion to CO_2 (figure 2b) and good size stability after oxidation and calcinations (2.4 ± 0.4 nm (as prepared) $\rightarrow 2.6 \pm 0.7$ nm (after calcination), 2.9 ± 1 nm (after reaction), figure 2c). The calcined sample does show evidence of a few larger particles, but the majority remain close to the starting diameter. Up to 100% conversion can be seen with as-prepared samples, but this requires higher reaction temperatures (figure 2b). In contrast, the calcined sample is capable of achieving lightoff at 180 °C temperature, indicating that catalytic activity increases once the surfactant is removed. This suggests that the CO oxidation is not sufficient to remove the surfactant. TGA analysis indicates that heating the sample to 500 °C is necessary for surfactant removal.

Significance

The Pd NPs synthesized using this method maintain a narrow size distribution and provide easy removal of the surfactant and anchoring to the support. After surfactant removal, these particles are catalytically active in CO oxidation. Current research is aimed at synthesis of bimetallic PdZn particles to provide high reactivity and selectivity for methanol reforming.

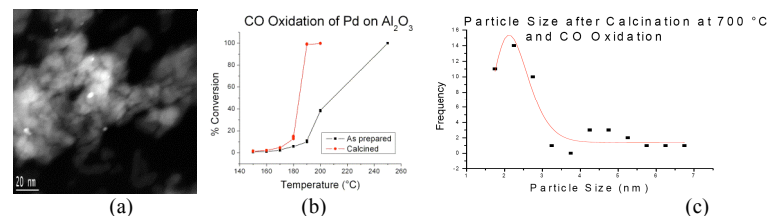


Figure 2. Image of as-prepared particles deposited on alumina support (a), conversion for CO oxidation (b) and particle size distribution after calcination and CO oxidation catalysis (c).

References

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