

The Stability and Catalytic Reactivity of Colloidal Palladium Nanoparticles on Al₂O₃ Supports

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Abstract:

Palladium nanoparticles were prepared using colloidal synthesis routes, and their stability was characterized with and without a surfactant. The catalytic activity of these nanoparticles was also determined after various treatments. The palladium colloidal nanoparticles were synthesized through a novel mesityl route, combining palladium (II) chloride with magnesium bromide mesityl to form palladium mesityl and magnesium bromochloride as a precipitate. The palladium nanoparticles formed were stabilized by the surfactant trioctylphosphine (TOP).

After being supported on alumina substrates, the colloidal nanoparticle samples were analyzed for catalytic activity for CO oxidation. Particle sizes were analyzed via TEM, STEM, light scattering and XRD. Samples were examined before and after thermogravimetric analysis (TGA), as well as before/after CO oxidation. The particle size distribution of the Pd/Al₂O₃ catalyst after reactivity measurements was very similar to that before removal of the surfactant (TOP) indicating that these nanoparticles are stable during CO oxidation. We conclude that the colloidal synthesis method allows for fine control over the Pd nanoparticles size and represents a novel approach to synthesize nanoparticle catalysts.

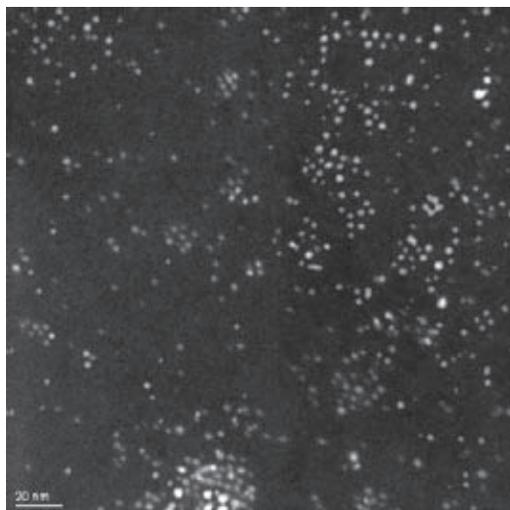


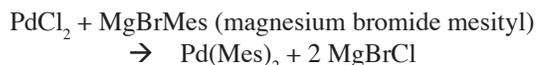
Figure 1: STEM of Pd nanoparticles suspended in solution.

Introduction:

Palladium nanoparticles are used in a wide variety of applications such as selective hydrogenation. In this project, our goal was to use these for the methanol steam reforming for H₂ production. By synthesizing the particles via colloidal synthesis, we can control the size as well as composition. The colloidal nanoparticles are covered with a surfactant to prevent agglomeration, but the surfactant must be removed prior to reaction. Hence, it is important to investigate the stability of these nanoparticles after exposure to reaction environments.

Experimental Procedure:

Synthesis: In these studies, we studied a novel synthesis route using organometallic precursors (mesityl compounds) to synthesize colloidal nanoparticles as shown in the reaction below:



The synthesis was performed under argon atmosphere at all times under a Schlenk line. The sample was refluxed at 300°C for 30 minutes before being exposed to air. The sample was washed with ethanol, centrifuged, and the supernatant was discarded. The nanoparticle suspension in hexane was also deposited on alumina supports via impregnation.

Transmission Electron Microscopy: Scanning and high resolution transmission electron microscopy (STEM and HRTEM) was performed on a JEOL 2010F FASTEM field emission gun STEM. Images were analyzed using Digital Micrograph™ to produce a size distribution. Light scattering was also utilized to produce an initial size distribution before TEM/STEM imaging.

Thermogravimetric Analysis (TGA) - Surfactant Characterization: Thermogravimetric analysis was performed using a TA instrument. These studies used ramp setting of 5°C/min from 25°C to 700°C or 900°C. Most samples ranged between 30.0-40.0 mg in size unless otherwise noted. Samples were run under either air or nitrogen gas at 100 mL/min. Samples were run as

prepared and after CO oxidation.

CO Oxidation: CO oxidation was performed to investigate the catalytic potential of the sample when it was fresh, as well as after we ran a sample through the TGA. CO oxidation was completed under 1.0% CO and 0.5% O₂ in balance helium. Samples of Pd/Al₂O₃ between 16.0-20.0 mg were used for these studies. A gas chromatograph was used to monitor CO/O₂ injections as well as the outlet concentrations of CO/O₂/CO₂. In accordance with literature values, the sample was run between 150°C and 200°C, the range at which Pd is known to become catalytically active. Data was collected in terms of CO₂ conversion. Samples were run as-prepared and after calcination at 700°C at a ramp rate consistent with the TGA experimentation noted earlier.

Results:

TEM and STEM: TEM and STEM imaging for different samples showed very similar particle size distributions. In Figure 1, we can see a wide distribution of particles, all with particles less than 4 nm. Size distributions were collected for the as-prepared sample, the sample after CO oxidation, and after calcination and CO oxidation. The as-prepared sample showed an average of 2.4 ± 0.4 nm, the CO oxidized sample showed 2.6 ± 0.7 nm and the calcination with CO oxidation showed 3.0 ± 1.0 nm.

TGA: TGA of the as-prepared Pd/Al₂O₃ sample showed the loss of surfactant (TOP) at around 500°C in both air and nitrogen environments (Figure 2). This data was then used for determining a calcination temperature of 700°C to use for preparing samples for CO oxidation after removal of TOP. TGA was also conducted on a sample after undergoing CO oxidation. These results showed there was still trace surfactant remaining that was again burned off by 500°C, but much less remaining compared to the original sample.

CO Oxidation: Figure 3 shows a comparison of two

18.4 mg samples, the as-prepared sample and one after calcination at 700°C in air. The as-prepared sample becomes visibly active on the graph at 190°C and reaches a maximum conversion of about 25%. However, the sample that was calcined shows a dramatic change in conversion after 180°C, reaching 100% conversion at 190°C and holding at 100% till 200°C.

Conclusions:

The surfactant stabilized colloidal palladium nanoparticles were active in their as-prepared state but were found to improve after removal of the surfactant trioctylphosphine, as well as retaining a small particle size throughout the process with no apparent signs of agglomeration. The particle sizes were all less than 3.0 nm, an ideal particle diameter size for nanoparticle catalysts. The TGA results indicated a complete loss of surfactant after 500°C.

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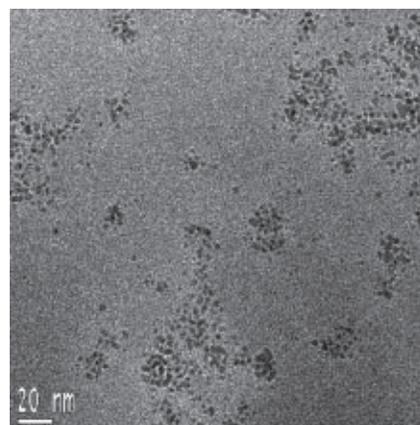


Figure 4: TEM image of Pd nanoparticles.

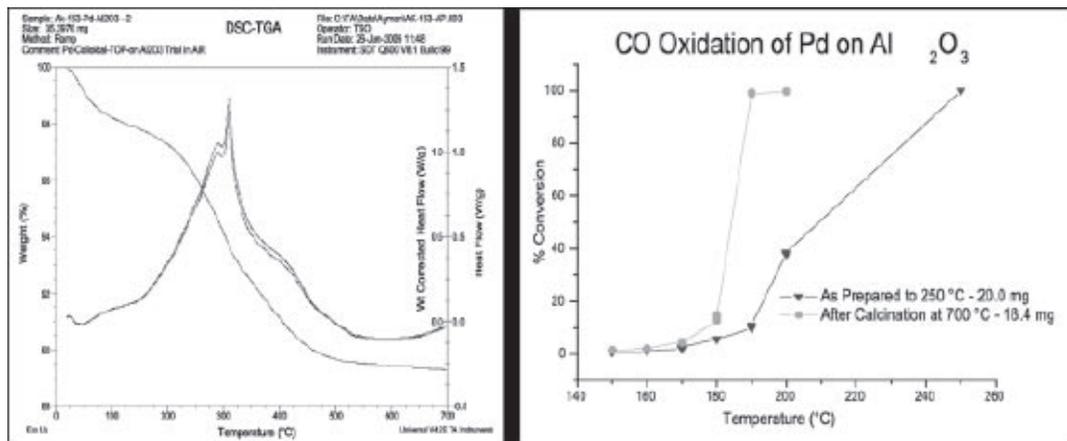


Figure 2, left: TGA curve in air to 700°C.

Figure 3, right: CO oxidation of Pd on Al₂O₃.