

Synthesis of Palladium Nanoparticles for Methanol Steam Reforming Catalyst

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Introduction

There is a need for energy in remote corners of the world. An energy storage technology is needed that can last longer than current batteries and is easily transportable. One possibility is to use hydrogen to power a fuel cell. However, the trouble with hydrogen is that it is hard to store and is also highly volatile. Our approach to hydrogen production and storage is through methanol steam reforming (MSR). Steam and methanol produce three moles of hydrogen and one mole of carbon dioxide. Methanol offers a high conversion rate and produces less by-products than other hydrocarbon fuels. The challenge is to make stable catalysts that work at low temperatures.

Current MSR catalysts are made of a copper/zinc oxide alloy and are active at 230°C. The problem is that these catalysts deactivate quickly. A palladium/zinc oxide (Pd/ZnO) catalyst offers the possibility of high methanol conversion over a longer time but is active at a higher temperatures and a greater mass of catalyst. Since catalysis is a surface phenomenon, the Pd/ZnO alloy can be made more active by increasing the surface area. The optimal particle diameter is 6 nm.

Experimental Procedure

Palladium acetate was reduced with octylamine in hexadecanediol at 270°C for 30 minutes. As the organometallic decomposed, Pd metal precipitated out of solution. During this process, the amines coated the surface of the Pd to protect against interparticle agglomeration. The Pd nanoparticles were washed in chloroform and methanol to remove excess amine ligands. The final product was a suspension of black nanoparticles in chloroform. The solution precipitation route was effective in synthesizing nanoparticles of Pd of ~ 4.5 nm in all samples as transmission electron microscopy (TEM) and scanning electron microscopy (SEM) reveal.

Once the Pd particles are synthesized, they were impregnated on a ZnO support to make a catalyst.

In order to preserve the morphology of the ZnO powder, it was necessary to use an organic medium rather than an acidic environment, as other methods use. The method for attaching the Pd to ZnO was to perform a ligand replacement on the Pd. 12-mercaptododecanoic acid was mixed into the suspension of nanoparticles for 10 minutes. A theoretical amount of 10% of the thiol/acid ligand was added based on the mass of the

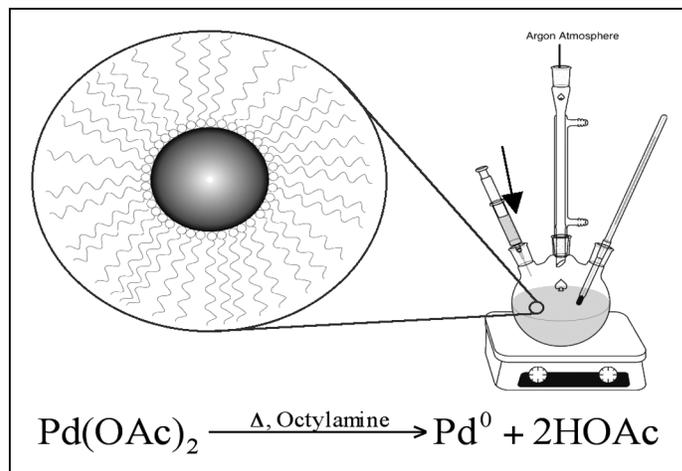


Figure 1: Solution precipitation.

nanoparticles. Infrared spectroscopy (IR) showed that a ligand substitution did take place. The theory of ligand substitution is that the thiol produces a stronger bond with Pd than an amine and the acid tail will bond with the surface of the ZnO. Pd will not agglomerate after amines are removed to reveal the Pd surface, because the particles will be anchored to the ZnO.

Problems in the synthesis came when depositing the Pd onto the ZnO surface. Several dispersion techniques were tested including incipient wetness, calcination at 80°C, mixing ZnO into the suspension, and a control of reducing palladium acetate on ZnO. (This is how the current Pd/ZnO alloys are formed.) The nanoparticles were prone to clump and form clusters rather than spread evenly onto the surface of ZnO.

Characterization

Pd decorated ZnO was partially formed. Spectroscopy measurements showed that ligand exchange took place. IR showed correct octylamine stretches before ligand replacement and clearly showed carboxylic acid stretches of the 12-mercaptododecanoic

acid after. X-ray diffraction showed that we had two crystalline phases of Pd and ZnO. Energy dispersive x-ray spectroscopy confirmed the composition.

Methanol is also capable of decomposing into hydrogen and carbon monoxide. Carbon monoxide (CO) binds to the Pd and deactivates the catalyst. However, this is not a problem as CO oxidation runs showed that the catalyst had a high selectivity to carbon dioxide (CO₂) over CO at reaction temperatures.

MSR was then performed on the catalysts. About 200 mg of catalyst was used in MSR and the average conversion was taken over four fifteen minute runs at 250°C. The control Pd/ZnO performed better because of the lack of ligands prohibiting the methanol interacting with the surface of the palladium. The best novel catalyst (Figure 2) had a methanol conversion of 41% and 35% selectivity towards CO₂. The best control catalyst was the 10% Pd:ZnO with 100% conversion and 87% selectivity.

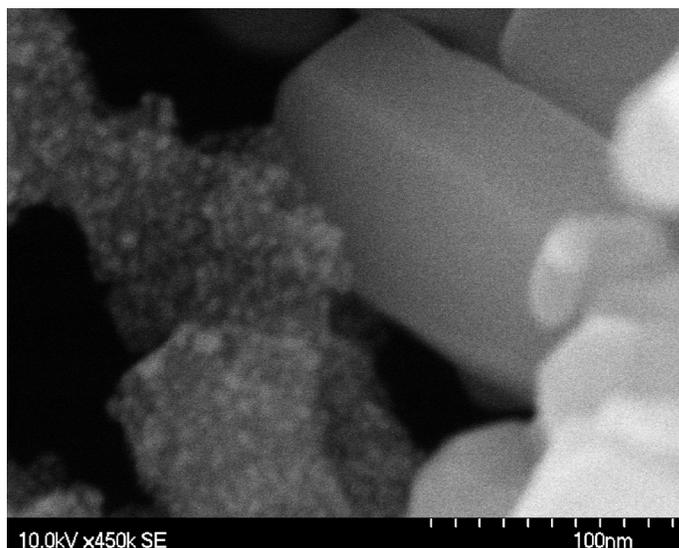


Figure 2: Pd/ZnO-incipient wetness.

Results

In this work, we have shown that it is possible to synthesize a catalyst from components of ligand-capped metal nanoparticles and metal oxide powders. The catalytic activity demonstrated by our catalysts using CO oxidation and MSR was low. The activity was hindered by residual ligands on the particles, resulting in a poor nanoparticle dispersion and overall powder coverage, as illustrated by TEM and SEM images.

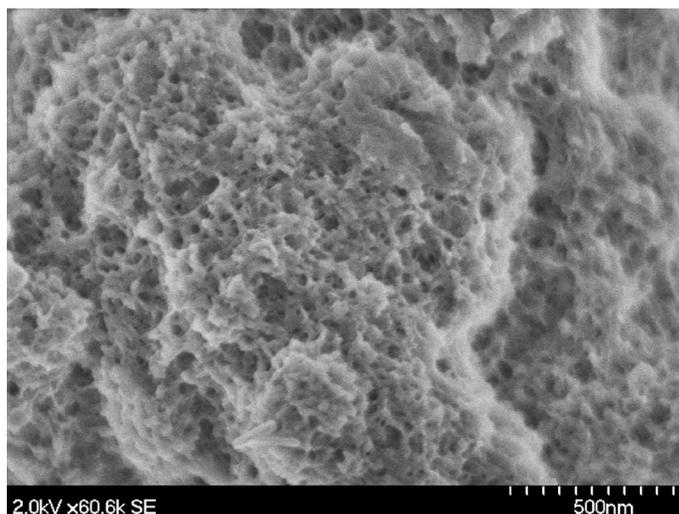


Figure 3: Pd/ZnO-ZnO doping.

Future Work

To improve our catalyst, it is necessary to enhance the particle dispersion over the oxide surface and remove excess ligands. Possible ways to coat the ZnO surface might be to functionalize the surface before adding nanoparticles or testing different ligands. Alternative deposition techniques also might need to be discovered. Even after coating with Pd, the amines need to be removed before any accurate MSR testing can occur. Possible techniques include an oxygen plasma etching process to gently remove excess amines. Although not yet perfect, this synthesis method offers a very promising way to collect hydrogen for fuel in the future.

Acknowledgments

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Sample (dispersion technique)	Methanol Conversion	Selectivity
2% Pd/ZnO (reduced on surface)	79%	90%
5% Pd/ZnO (reduced on surface)	5%	39%
8% Pd/ZnO (reduced on surface)	81%	95%
10% Pd/ZnO (reduced on surface)	100%	87%
15% Pd/ZnO (reduced on surface)	83%	96%
20% Pd/ZnO (reduced on surface)	75%	98%
Amine Coated Pd NPs (incipient wetness)	33%	53%
Thiol replaced Pd NPs (incipient wetness)	41%	35%
Thiol replaced Pd NPs (ZnO soaked in NP solution)	2%	37%

Figure 4: MSR conversion and selectivity.