

# Carbon Black Supported Binary Pt-Pd Nanoparticles by Supercritical Deposition

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## Abstract

Supercritical deposition is an alternative and promising way to prepare supported metal nanoparticles. Such materials have potential applications in optical, electronic, magnetic devices and in catalysis. Supercritical deposition involves the dissolution of an organometallic precursor (OM) in a supercritical fluid and the exposure of a porous support to the solution. After adsorption of the precursor on the support, the metallic precursor is converted to its metal form by chemical or thermal reduction. This promising catalyst preparation technique results in small particle sizes and homogeneous dispersions. Even though the technique has been used to prepare a wide variety of supported single metal nanoparticles, there are very few studies on application of supercritical deposition to preparation of binary metal nanoparticles. In this study, the preparation of carbon black (BP 2000) supported single Pt, Pd and binary Pd-Pt nanoparticles by utilizing the supercritical CO<sub>2</sub> deposition method was investigated. Palladium (II) acetylacetonate (Pd(acac)<sub>2</sub>) and platinum dimethyl (cyclooctadiene) (PtMe<sub>2</sub>COD) were utilized as organometallic precursors. The support was first impregnated with precursors from supercritical CO<sub>2</sub> solution. The resulting composites were converted to their metal forms by chemical reduction in supercritical CO<sub>2</sub> with hydrogen. The catalysts were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-Ray spectroscopy (EDXS). The factors influencing the formation of the nanoparticles including reduction temperature and precursor loading and were investigated. The Pd particles were irregularly distributed and the size range of the particles was 3-100 nm, whereas Pt nanoparticles were homogeneously distributed with a size range of 2-4 nm. The particle size of the binary nanoparticles ranged from 2 to 10 nm. It was found that the addition of Pt increased the homogeneity and reduced the particle size on the support compared to single Pd nanoparticles.

## Introduction

A nanoscale composite material is defined as a material that has a structure such that at least one of its phases has one or more dimensions (length, width, or thickness) in the nanometer size range, usually ranging from 1 to 100 nm. Among these materials, supported metal nanoparticles have attracted a great deal of interest for microelectronic, optical and catalytic applications because of their unique properties which are directly related to the specific particle morphology (size and shape), metal dispersion, concentration and the electronic properties of the metal within their host environment [1].

Supercritical fluid deposition (SCFD) is a relatively new method for preparation of supported nanoparticles [2, 3]. SCFD consists of a series of steps which are the dissolving of a metallic precursor in a SCF, the exposure of a porous substrate to the solution, adsorption of the precursor on the surface of the support and finally the reduction of the precursor to its metal form. This method has been used to prepare nanoparticles of a wide variety of metals including Pt, Pd, Ru and Rh supported on various types of carbon substrates [4, 5, 6, 7, 8, 9]. Saqing et al. prepared Pt/carbon aerogel nanocomposites by SCFD and they investigated four different reduction methods in order to convert adsorbed PtMe<sub>2</sub>COD which was used as the precursor [4,5]. In a study by Bayrakçeken et. al. [6 above6], various carbon supported Pt electrocatalysts were prepared by SCFD and their electrocatalytic performance was investigated by cyclic voltammetry. Zhang et al. [7] prepared CA supported Ru nanoparticles by adsorption of Ru(acac)<sub>3</sub> or Ru(cod)(tmhd)<sub>2</sub> (cod(tmhd)<sub>2</sub>=bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5cyclooctadiene)) from scCO<sub>2</sub> followed by thermal reduction at atmospheric pressure under N<sub>2</sub> flow at temperatures between 300-1000 °C .

In this study, carbon black supported single Pd, Pt and bimetallic Pd-Pt nanoparticle catalysts were prepared by scCO<sub>2</sub> deposition using Pd(acac)<sub>2</sub> and PtMe<sub>2</sub>COD as the organometallic precursors. Black Pearl 2000 was used as the carbon support. The preparation of the single Pd, Pt nanoparticles involved adsorption of precursors from scCO<sub>2</sub> solution, followed by chemical reduction in a supercritical mixture of H<sub>2</sub> and CO<sub>2</sub>. The effect of reduction temperature and metal loading on the size of Pd particles was also investigated. In order to prepare Pd-Pt/BP2000 catalysts, the carbon support was exposed to a solution of PtMe<sub>2</sub>COD and Pd(acac)<sub>2</sub> dissolved in scCO<sub>2</sub> and both of the precursors adsorbed on the surface of the support simultaneously. Subsequently, the precursors were reduced to their metal form by chemical reduction in a supercritical mixture of H<sub>2</sub> and CO<sub>2</sub>. The prepared catalysts were characterized with XRD, TEM and EDXS measurements.

## Materials and Methods

### Materials

Palladium (II) acetylacetonate (99 %) was purchased from Aldrich. Dimethyl (cyclooctadiene) platinum (II) (99 %) was purchased from STREM. Black Pearl 2000 is a type of carbon black and was purchased from Cabot International. The chemicals were used as-received. Carbon dioxide (99.998 %) was purchased from Messer Aligaz.

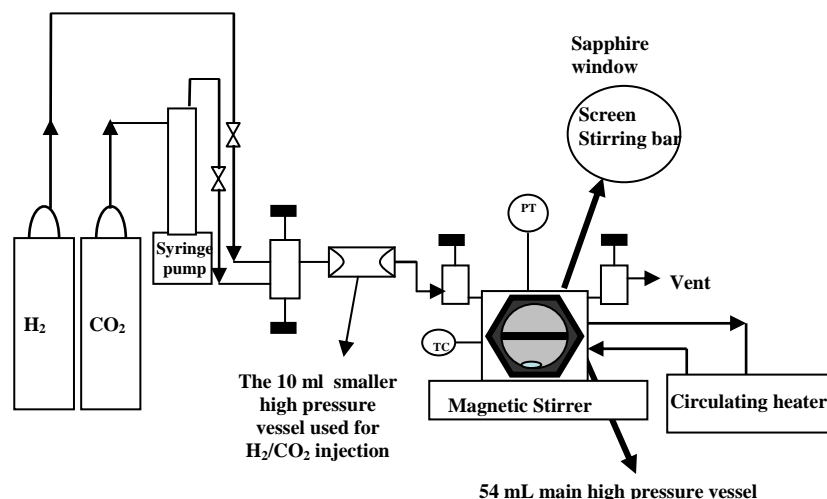
### Experimental Methods

A schematic diagram of the setup is given in Figure 1. The vessel used in adsorption experiments is custom manufactured from stainless steel and has an internal volume of 54-mL. It is equipped with two sapphire windows (1 in. in diameter, Sapphire Engineering, Inc., Pocasset; MA) and sealed with poly (ether ether ketone) O-rings. A thermocouple assembly and a rupture disk assembly (Autoclave Engineers) are also attached to the vessel.

For the preparation of Pd/BP 2000 catalysts, a predetermined amount of Pd(acac)<sub>2</sub> and BP 2000 in a pouch made of filter paper were placed in the vessel together with a teflon coated stirring bar. The vessel was sealed and heated to the desired temperature by a circulating heater/cooler (Cole Parmer, Model 12108-15). Subsequently, the vessel was pressurized quickly with CO<sub>2</sub> from a syringe pump (Teledyne Isco, Model 260 D) up to the desired pressure. The system was kept at these conditions until equilibrium was reached. After the system reached equilibrium, a 10 ml mixture of H<sub>2</sub> and CO<sub>2</sub> (P<sub>H<sub>2</sub></sub>= 0.8 MPa, P<sub>total</sub>= 27.6 MPa) was prepared in a vessel which was placed between the main vessel inlet and the syringe pump. The small vessel with a volume of 10 ml was first filled with H<sub>2</sub> at 0.8 MPa. Afterwards, the vessel was filled with CO<sub>2</sub> to a pressure of 27.6 MPa. Then, the high pressure H<sub>2</sub> and CO<sub>2</sub> mixture was injected into the main vessel containing the Pd(acac)<sub>2</sub>/BP2000 in scCO<sub>2</sub> solution at 20 MPa and at the desired reduction temperature. The selected reduction temperatures were 50, 60, 70 and 80 °C. The adsorption and reduction pressure, the amount of the substrate and the organometallic amount placed into the vessel were kept constant in each experiment for the investigation of the effect of reduction temperature on Pd particle size. Reduction was allowed to continue for 3 hours. After the reduction process, the vessel was depressurized slowly and allowed to cool down. The metal/substrate was taken away from the vessel. The metal loading of the composites was measured from the weight change by using an analytical balance. For the investigation of the effect of Pd loading (wt.% metal), the above procedure for the adsorption and reduction experiments were carried out, but this time the adsorption and reduction temperature were kept constant at 80 °C and the amount of Pd(acac)<sub>2</sub> placed in the main reactor vessel was varied for each run.

For the preparation of Pt/BP 2000 catalysts, a predetermined amount of PtMe<sub>2</sub>COD and BP 2000 was put in the vessel and all the procedure above is applied. The reduction was allowed to continue for 5 hours.

The preparation of Pd-Pt/BP2000 catalysts was carried out the same way as the single metal catalysts. The only difference was that both of the predetermined amounts of Pd(acac)<sub>2</sub> and Pt(cod)me<sub>2</sub> precursors were put in the vessel simultaneously.



**Figure 1.** Experimental Setup

XRD continuous measurements were carried out by using Cu K $\alpha$  source Huber G 670 Imaging Plate in a  $2\theta$  range of  $5^\circ$ -  $86.915^\circ$  with a scanning rate of  $5.5^\circ \text{ min}^{-1}$ . The morphology of the supported catalysts was characterized by high-resolution transmission electron microscopy (TEM).

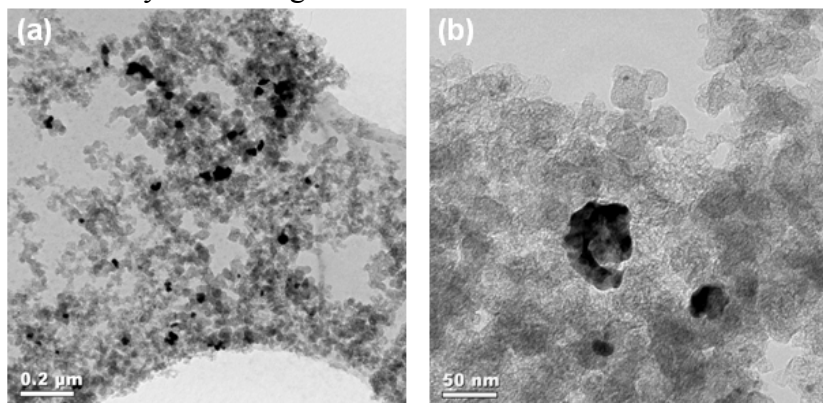
## Results

It was found that reduction of the Pd(acac) $_2$  precursor could be carried out by subjecting the Pd(acac) $_2$ /BP2000 to a supercritical mixture of H $_2$  and CO $_2$ . Before the injection of hydrogen to the system, Pd(acac) $_2$  is distributed between the scCO $_2$  phase and the BP2000 phase. The yellow colored solution with dissolved Pd(acac) $_2$  turned colorless a short time after H $_2$  was injected as observed from the sapphire window on the side of the vessel. The peaks for Pd in XRD spectra obtained from the catalysts indicated that chemical reduction of adsorbed Pd(acac) $_2$  was also occurring on the surface of BP2000.

The effects of reduction temperature and metal loading on the average Pd particle size were also investigated using XRD. The average Pd particle size increased as the chemical reduction temperature in scCO $_2$  was increased. The average size doubled from 7 nm to 14 nm as the temperature was increased from 50 to 80  $^\circ\text{C}$ . The most likely explanation for this effect is an increase in the mobility of the reduced palladium atoms with increasing reduction temperature, which results in more extensive particle coarsening during the reduction process.

Examples of TEM images obtained from the catalyst with 20 wt.% Pd loading prepared by chemical reduction in H $_2$ /scCO $_2$  at 80  $^\circ\text{C}$  are shown in Figure 2. Images such as Figure 2(a), which were obtained at lower magnifications, reveal clearly the structure of the BP2000 support and the sizes and distribution of the Pd nano-particles. The lighter features in such images correspond to the support, which consists of inter-linked homogeneous C particles 20-50 nm in diameter as expected for BP2000. The darker features superimposed upon the support are the Pd nano-particles which are distributed rather inhomogeneously. These Pd nano-particles are present in a wide range of different sizes ranging from 3 nm up to around 100nm. Higher magnification images such as Figure 2(b) show that the C particles that comprise the support consist of disordered carbon. Moreover, such images reveal that the larger Pd nanoparticles ( $> 20$  nm) have an irregular morphology suggesting that these may

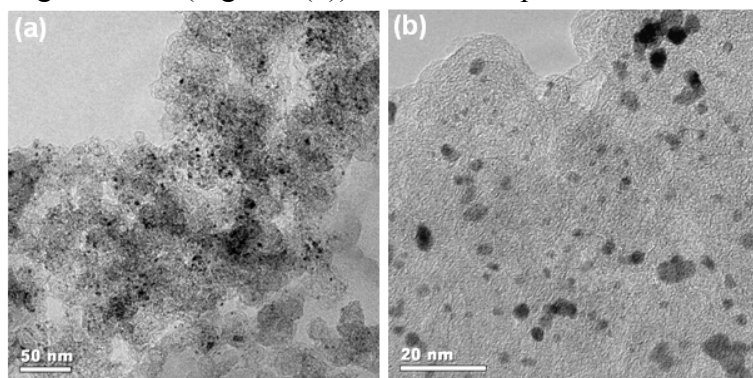
arise by the agglomeration of smaller nanoparticles migrating across the support surface instead of by coarsening due to the atomic diffusion of metallic Pd.



**Figure 2:** TEM images of the 20 wt.% metal loaded Pd/BP2000 catalysts prepared by chemical reduction in  $H_2/scCO_2$  at  $80^\circ C$ .

The effect of metal loading on the growth of Pd particle size was also investigated. In these experiments, the chemical reduction was carried out at  $80^\circ C$  in  $H_2/scCO_2$  ( $P_{H_2} = 0.8$  MPa,  $P_{TOTAL} = 27.6$  MPa) and the amount of organometallic precursor put into the vessel before the adsorption experiments was varied. The average Pd particle size increased with the metal loading of the Pd/BP2000 composites: the average size increased from 7.8 nm to 14 nm as the loading was increased from 3 to 20 wt. % Pd.

12 wt.% metal loaded Pt/BP2000 catalysts were prepared first by adsorption of a certain amount of  $PtMe_2COD$  onto BP2000 from  $scCO_2$  at 20 MPa and  $80^\circ C$ . Subsequently, the reduction of the prepared  $PtMe_2COD/BP2000$  composites was carried out in  $H_2/scCO_2$ . The XRD data obtained from the Pt/BP2000 catalysts revealed a much finer distribution of metal than that for the Pd/BP2000 catalysts, with a mean particle size of 2.8 nm. This is consistent with the TEM data and representative images are shown in Figure 3. The size and morphology of the Pt nanoparticles are revealed more clearly in images obtained at higher magnification (Figure 3(b)). These nanoparticles are in the range of 2 to 4 nm in diameter.

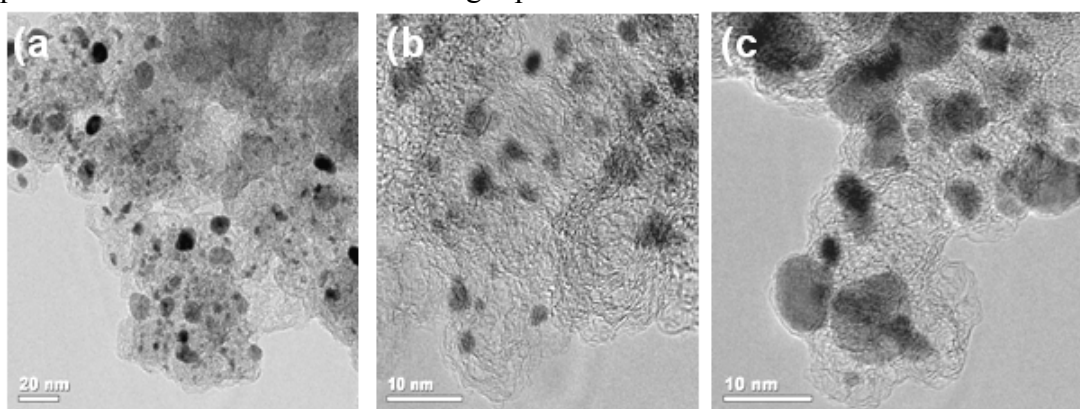


**Figure 3:** TEM images of the Pt/BP2000 catalyst

16 wt.% metal loaded Pd-Pt/BP2000 binary metallic nanoparticles were obtained first by simultaneous adsorption of a certain amount of  $Pd(acac)_2$  and  $Pt(cod)me_2$  from  $scCO_2$  at 20 MPa and  $80^\circ C$  onto the surface of BP2000. Subsequently, the precursors were reduced concurrently in a  $H_2/scCO_2$  mixture at 27.6 MPa ( $P_{H_2} = 0.8$  MPa) and  $80^\circ C$ . The molar ratio of Pt:Pd was 0.92 in the prepared catalysts and these showed much better control of

nanoparticle size than in the Pd/BP2000 catalysts. The average metal particle size of in the Pd-Pt/BP2000 catalyst calculated from the XRD spectra using Scherrer formula is 9 nm.

TEM images such as Figure 4 obtained from the Pd-Pt/BP2000 catalyst samples show metal nano-particles that are distributed more homogeneously than those in the Pd/BP2000 catalyst but less homogeneously than those in the Pt/BP2000 catalyst. Similarly, the particle size distributions are narrower than those for the Pd/BP2000 catalyst but broader than those for the Pt/BP2000 catalyst, with the diameters for most of the particles lying between 2 and 10 nm. Attempts to measure the chemistry of these particles by EDXS were complicated by the high particle density in these bimetallic catalysts, which meant that spectra acquired from a particular particle included contributions from adjacent particles. Despite this, a comparison of many such spectra from regions that contain predominantly larger or smaller particles (e.g. areas such as those shown in Figures 4(b) and 4(c), respectively) revealed that the smaller particles are less Pd-rich than the larger particles.



**Figure 4:** TEM image of the Pt-Pd/BP2000 with Pt:Pd molar ratio of 0.92

## Conclusion

The  $\text{scCO}_2$  deposition technique was used to prepare BP2000 supported single Pd, Pt and bimetallic Pd-Pt nanoparticles. The organometallics used for the study were  $\text{Pd}(\text{acac})_2$  and  $\text{PtMe}_2\text{COD}$ . It was found that the Pd precursor could be reduced in a  $\text{H}_2/\text{scCO}_2$  mixture. From the XRD data, it was found that increasing reduction temperature and Pd metal loading increased the Pd particle size. From the TEM images it was seen that Pd particles were not homogeneously distributed on the BP2000 support with numerous large particles with sizes ranging from 3-100 nm. In contrast to Pd nanoparticles, Pt particles were found to be homogeneously distributed with small particle sizes between 2-4 nm on BP2000. Binary metal nanoparticles of Pd-Pt on BP2000 could also be formed. It was found that addition of Pt increased the homogeneity and reduced the particle size on the support compared to single Pd nanoparticles. At the same experimental conditions, it was found that supported bimetallic Pt-Pd nanoparticle size was 9 nm whereas single Pd size was 14 nm from TEM data. From the EDXS results, it was seen that the smaller particles were less Pd-rich than the larger particles.

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