

ORGANIC AEROGEL SUPPORTED PLATINUM NANOPARTICLES PREPARED BY SUPERCRITICAL CARBON DIOXIDE DEPOSITION

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ABSTRACT

Supercritical deposition is a promising way to prepare supported nanoparticles which have numerous applications in optics, electronics and catalysis. The technique involves the dissolution of an organometallic (OM) precursor in a supercritical fluid (SCF) and the exposure of a substrate to this solution. After adsorption of the precursor on the substrate, the metallic precursor is reduced to its metal form by various methods resulting in supported nanoparticles. Resorcionol-formaldehyde aerogels (RFAs) are precursors of carbon aerogels (CAs) and are promising candidates for catalysis applications. In this study, platinum nanoparticles supported on polymer RFA8 (with 8 nm pore size) were synthesized. Effect of metal load on the average particle size of the supported nanoparticles was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The particle size of the nanoparticles was ranged between 2 and 4 nm depending on various platinum loadings (10 wt. %, 22 wt. % and 34 wt. %).

Models consisting of equilibria or kinetics of adsorption of the OM to the support material are critical for design, operation and control of large scale SCF deposition technology for synthesis of supported nanoparticles. Therefore, the thermodynamics of adsorption of the platinum precursor dimethyl (cyclooctadiene) platinum II (Pt(cod)me₂) on RFAs from supercritical carbon dioxide (scCO₂) was investigated using an experimental technique which consists of the direct analysis of the fluid phase.

INTRODUCTION

Supported metal nanoparticles have recently 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, shape and crystallographic orientation), metal dispersion, concentration and the electronic properties of the metal within their host environment [1]. In the preparation of supported metal nanoparticles, various types of inorganic or organic substrates are used as supports. Organic polymeric substrates are mostly used as catalysts for various types of reactions [2, 3, 4, 5]. Supercritical fluid deposition (SCFD) is a relatively new and promising method for preparation of supported nanoparticles. SCFD consists of a series of steps which involves the dissolution 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 technique has been used to incorporate various metallic nanoparticles on different types of polymers or carbon structured materials [6, 7, 8, 9].

RFA is a nanostructured polymeric matrix which can be synthesized to have controllable high surface area, (400 – 2000 m²/g), high porosity, controllable pore size in mesoporous range (2-50 nm), sharp pore size distribution and low mass density. RFA is used to carry sapphire spheres for astrophysical applications [10], and as a support for copper for catalytic and separation applications [11]. In this study, Pt nanoparticles supported on RFA were synthesized. The adsorption isotherms of PtMe₂COD were extracted using a newly developed experimental technique. The RFA support was synthesized with an average pore size of 8 nm and its pore properties and surface area was determined by using BET analysis. The total BET surface area of RFA8 was found as 759 m²/g. The total pore volume of RFA8 was found as 2.5 m³/kg. The preparation of Pt/RFA8 nanoparticles involved the adsorption of PtMe₂COD on RFA8 from scCO₂ solution and the subsequent thermal reduction of PtMe₂COD to Pt. The effect of metal load on the size and distribution of the Pt particles on RFA8 was investigated by using XRD and TEM measurements.

MATERIALS AND METHODS

Materials

Resorcinol (99 %) and sodium carbonate (99.99 %) was purchased from Merck. Formaldehyde (36 %) was purchased from Lachema. PtMe₂COD (99 % purity appears as white powder) was purchased from STREM Chemicals, Inc. and ethanol (99.9 % purity) was purchased from Merck. The chemicals were used as received. Water was distilled and deionized. Carbon dioxide (99.998 %) and Nitrogen was purchased from Messer Aligaz.

Experimental Methods

RFA8 was synthesized via a sol-gel route which involves the polymerization of resorcinol and formaldehyde in a basic environment along with water followed by a curing period which provides the cross-linking of the polymer. Afterwards, the gel is exposed to solvent-exchange (acetone ↔ water) and finally dried using scCO₂ in order to remove the solvent (acetone) and replace the pores with air to produce an aerogel.

Supercritical deposition experiments and the equilibrium adsorption measurements were carried out in the experimental setup presented in Figure 1. A 57-mL stainless steel custom made vessel was used as the deposition chamber along with two sapphire windows (2.5 cm in diameter, Sapphire Engineering, Inc., Pocasset; MA, and sealed with poly(ether ether ketone) O-rings, a T-type thermocouple assembly (Omega Engineering), a pressure transducer (Omega Engineering), a vent line, and a rupture disk assembly (Autoclave Engineers). For each experiment, a predetermined amount of organometallic precursor was placed in the vessel along with a stirring bar, and a certain amount of substrate. A stainless steel screen was also included in the vessel in order to separate the substrate and the stirring bar. The system was sealed and heated to 40°C by a circulating heater/cooler (Cole Parmer, Model 12108-15). The system was pressurized with CO₂ using a syringe pump (ISCO, 260D) up to a desired pressure and kept at these conditions for desired time. During this process, the organometallic precursor was dissolved in scCO₂ and adsorbed to the substrate from the fluid phase. After the deposition of the desired amount of precursor, the system was depressurized slowly (0.7MPa/min) using a needle valve (Autoclave Engineers). Subsequent to the deposition process, the substrate/precursor composite was removed from the vessel and placed in a custom made quartz process tube (with dimensions 3 cm of internal diameter and 57 cm of length) and the tube was placed into a tube furnace (model F1125 Thermolyne). The impregnated organometallic precursor was

reduced chemically at 200°C in the presence of H₂ gas with a flow rate of 100 cm³ min⁻¹ for 4 h. Later, H₂ was switched to N₂ and temperature was increased to 250°C in order to remove adsorbed hydrogen. Then, the system was cooled down to room temperature under flowing N₂. For the characterization of the synthesized Pt/RFA8 particles, XRD continuous measurements were carried out by using Cu K α source Huber G 670 Imaging Plate in a 2 θ range of 50-86.9150 with a scanning rate of 5.50 min⁻¹. The morphology of the supported catalysts was characterized by high-resolution TEM.

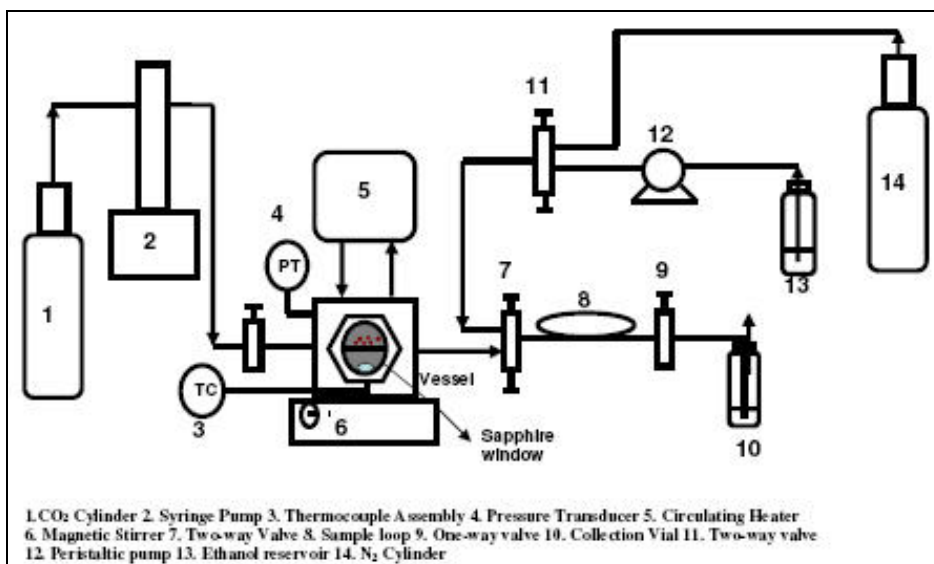


Figure 1. Experimental Setup

The amount of the precursor adsorbed was determined by analyzing the concentration of organometallic component in the fluid phase. For equilibrium measurements, crushed RFA8 particles were used. At a particular time, a small volume of the solution in the vessel was transferred and trapped in a sample loop by opening and closing the three-way valve (7). Subsequently, the sample loop was depressurized slowly by opening (9). The CO₂ was bubbled through an ethanol solution before being vented into the hood to trap any PtMe₂COD that may be in the gas stream. Then, the loop was flushed with ethanol using a peristaltic pump (Gilson, Model Minipuls 3) in order to collect PtMe₂COD that precipitated during depressurization. In order to determine the sufficient amount of ethanol needed to dissolve all the PtMe₂COD in the loop, the loop was flushed successively with approximately 5 ml solutions of ethanol. The solutions were collected in vials and analyzed in HPLC. About 15 ml of ethanol was sufficient to dissolve all the PtMe₂COD since no PtMe₂COD could be detected in additional washes. After each sampling, the vessel was charged with CO₂ to the original pressure to compensate for the pressure drop that occurred during sampling. In order to empty the sample loop for the next sample, the ethanol left in the sample loop was removed by passing N₂ through the loop. At each particular time, this procedure was carried out twice in order to first remove the sample left in the short tube between the three-way valve (7) and the vessel during the previous sampling. The PtMe₂COD concentration in the samples was analyzed using High Performance Liquid Chromatography (HPLC) (Agilent Technologies, 1200 Series).

RESULTS

The adsorption isotherms for PtMe₂COD on RFA at 20.7 MPa and 35°C and 60°C are shown in Figure 2. For both isotherms, a non-linear behavior is observed. Furthermore, at the same organometallic concentration and the same CO₂ pressure, it is shown that the uptake increases with increasing temperature. According to the retrograde adsorption phenomenon [12, 13]., there exist a cross-over pressure beyond which the amount adsorbed increases with increasing temperature at the same pressure and solute concentration. We do believe that the pressure and the density conditions in our experiments and 20.7 MPa is above the cross-over pressure.

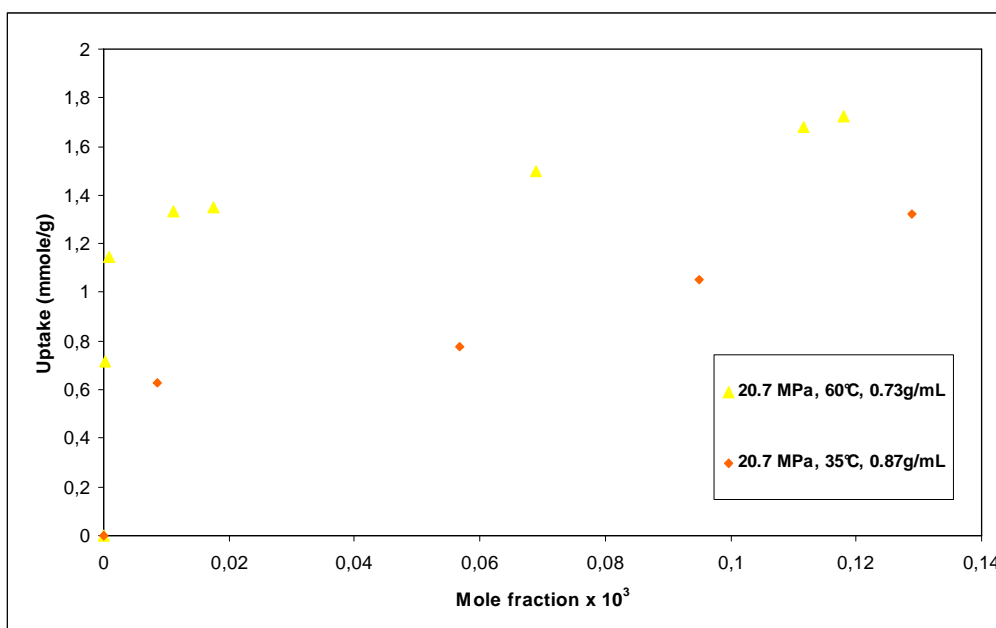


Figure 2. Adsorption isotherm for PtMe₂COD-RFA8 system at 20.7 MPa and at various temperatures.

Figure 3 shows the TEM images of RFA supported Pt nanoparticles synthesized by reducing the PtMe₂COD adsorbed on RFA. The reduction experiments have been conducted at 200°C under flowing H₂ for four hours. After reduction was completed, N₂ was passed through the reduced particles at 250°C in order to remove the H₂ adsorbed during reduction. Pt/ RFA8 particles with three different Pt loadings 10 wt. %, 22 wt % and 34 wt. % were synthesized. Figure 3 reveals clearly the particle size variation depending on the Pt loading of the samples showing our ability the control the nanoparticle size by manipulating the metal loading. A good dispersion of nanoparticles is also observed by the TEM images.

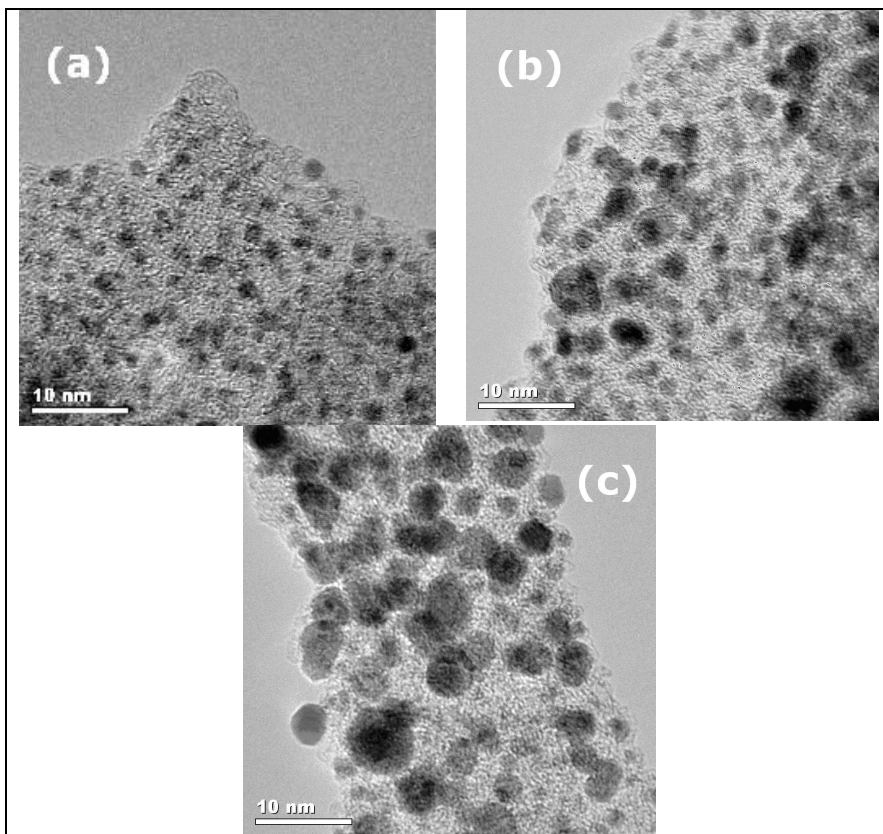


Figure 3. TEM images of RFA8 supported Pt nanoparticles. (a) 10 wt.% Pt. (b) 22 wt.% Pt. (c) 34 wt.% Pt.

The XRD spectra of the supported nanoparticles are given in Figure 4 indicating clearly the existence of the Pt in metal form. Furthermore, the average size of nanoparticles were calculated by the Scherrer's equation using the (111) peaks for each of the samples. The results were in agreement with the TEM images. The particle size increased with increasing metal loading; 2.3 nm, 3.1 nm and 3.9 nm for Pt loadings of 10.42%, 22% and 34%, respectively.

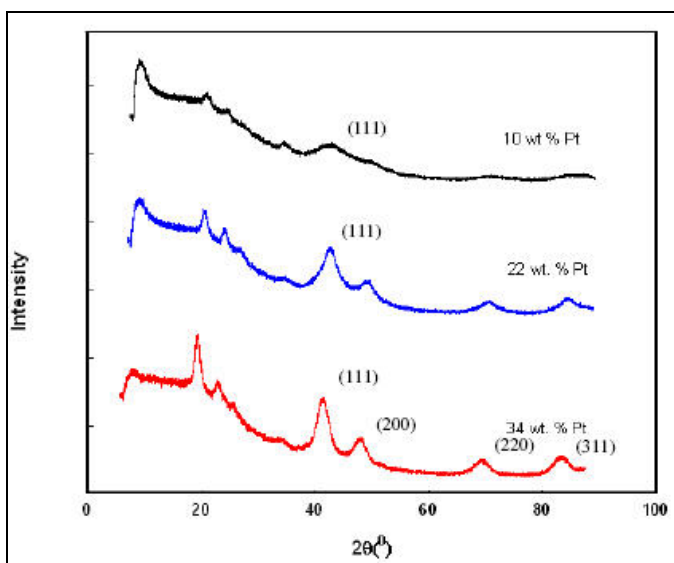


Figure 4. XRD spectra of different metal loaded Pt/RFA8 particles.

CONCLUSION

RFA8 supported Pt nanoparticles were prepared using scCO₂ route and adsorption isotherms of Pt precursor PtMe₂COD on RFA8 were investigated. It has been shown for the first time the possibility of incorporating nanoparticles on organic aerogels using SCFD. It was observed that metal loading could be a variable in controlling nanoparticle sizes in SCFD. The uptake amount of PtMe₂COD on RFA8 increased with increasing temperature at same pressure and solute concentration. The retrograde behavior is suggested to explain this phenomenon.

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