Structural Study of Pt_x-Pd_{1-x} Nanoparticles Supported on Silica by High Resolution Electron Microscopy.

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ABSTRACT

Pt_x-$Pd_{(1-x)}$ nanoparticles supported on amorphous silica (SiO_2) were prepared by wetness impregnation techniques with choroplatinic acid (H_2PtCl_6) and palladium chloride ($PdCl_4$) with different concentrations of Pt and Pd at about 1% in overall metallic weight.

The structural and physic characterization of these samples were carried out by BET Surface Area, X-Rays Diffraction (XRD), Transmission Electron Microscopy (TEM), attach with X-Ray and Energy Dispersive Spectroscopy (XEDS). .

In this work, we observed the distribution of Pt and Pd in nanoparticles. By XRD Pt_x-$Pd_{(1-x)}$ Nanoparticles are made of a single solid solution of Pt and Pd atoms, and the particles diameter of about 4 nm was estimated by HREM and Bright field image. Energy dispersive X-ray spectrometry (XEDS) allowed to determine that Pt-Pd nanoparticles were found mainly to have cubeoctahedral shape with fcc packing and their values were found to be close to the stochiometric relative concentrations in weight of the metals, in the precursor aqueous solution.

Keywords: Nanoparticles Pt-Pd, HREM, TEM, X-RD.

1 INTRODUCTION

Through the last decade, metallic nanoparticles of definite size have received considerable attention because of their fascinating properties and potential applications in catalysts, optoelectronics, and magnetic materials, [1–2]. The range of properties of metallic systems can be greatly extended by taking mixtures of elements to produce intermetallic compounds and alloys. Bimetallic Nanoparticles are relevance since they may display structures and properties which are distinct from those of the pure elemental metals. Platinum and palladium are of interest because they are widely used as catalysts (often as finely divided metal particles, in elemental or alloy form) in a number of important reactions like hydrogenation, isomerization, and electrochemical reactions, many of these involving hydrogen transference. They are used, for example, in catalytic converters in automobiles, for the reduction of exhaust gases. Their preparation has been achieved by a number of methods, such as solvent extraction[3], alcohol reduction [4, 5,6], impregnation–reduction [7–10] and the synthesis of Pd/Pt bimetallic nanoparticles using microemulsion technique [11].

2 EXPERIMENTAL

Bimetallic nanoparticles were prepared with different atomic concentrations of Pt and Pd, at 1% metallic weight. They were prepared from aqueous solutions of H_2PtCl_6 and $PdCl_4$ (Aldrich) and amorphous SiO_2 (aerosil Ox.50), by following wet impregnation techniques. **Table 1** shows the different Pt_x-Pd_{1-x}.

Sample Bimetallic	Composition %Weight Pt	Pd
S1 Pt_{20}-Pd_{80}/ SiO_2	20	80
S2 Pt_{50}-Pd_{50}/ SiO_2	50	50
S3 Pt_{80}-Pd_{20}/ SiO_2	80	20

Table 1. Chemical weight Composition of Nanoparticles Pt_x-Pd_{1-x}. in solution**.**

The SiO_2 was dried at 100 degree centigrade for 12 hours prior to impregnation. After impregnation, the support was stirred for 4 hours at room temperature then evaporated and dried at 100 ºC for 12 hours. Then the samples were reduced by flowing hydrogen for 2 hours at 400 degree centigrade with a flow rate of about 60 mililiters/minutes. BET surfaces area were measured by N_2 physisorption at 77 Degree Kelvin in a micromeritics.
X- Ray Diffraction (XRD) pattern were recorded in a siemens D500 difractometer Cu-K_α using radiation (λ = 1.54 Å) in order to identify and to obtain details on the electronic structure of nanoparticles.

A HREM, JEOL-4000EX was employed to determine both the structural dimensions and chemical composition (XEDS) of Pt-Pd bimetallic nanoparticles to measured particle diameter were determined by TEM imaging bright field. TEM preparation samples were obtained dispersing powders in 2-propanol . A drop of solution was deposited on a thin carbon film supported on a copper grid (400 mesh, 3.05 mm) and then left to dry. The dispersed powder containing metallic particles was well dispersed allowing to be characterized by TEM. And HREM has allowed us to obtain fine details of nanostructural constitution of these bimetallic nanoparticles Pt_x-Pd_{1-x}.

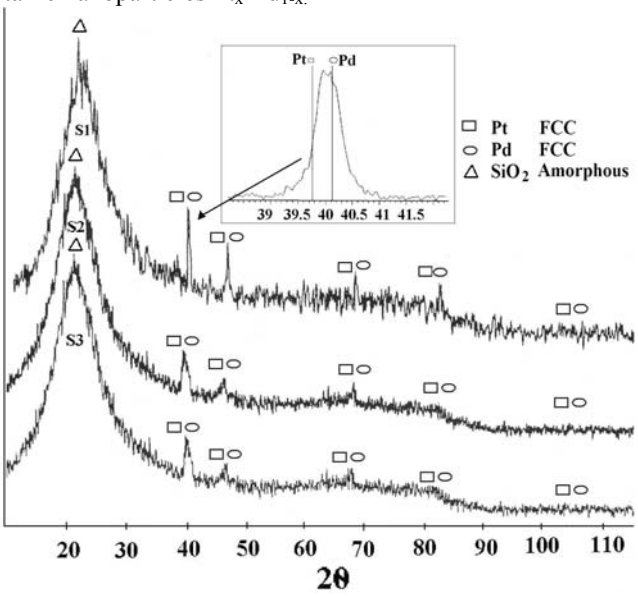
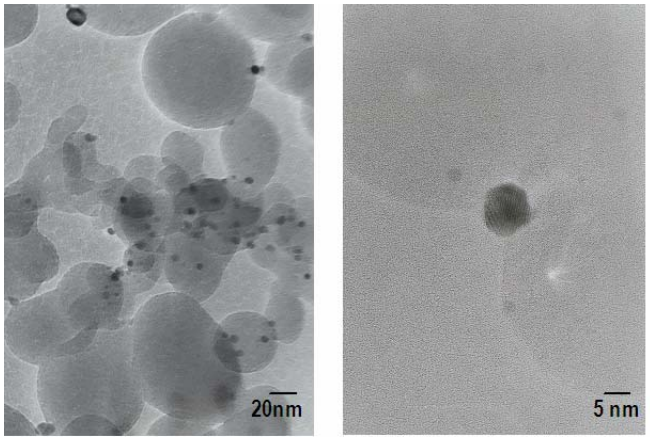
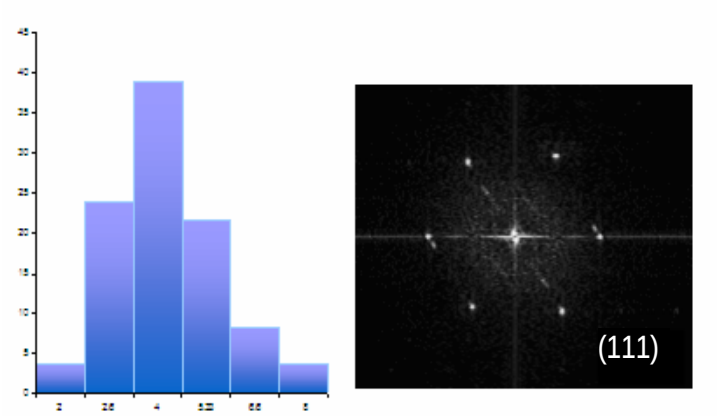


Figure 1. X-ray diffraction pattern of Bimetallic Nanoparticles Pt_x-Pd_{1-x} Supported on Silica .



a) **b)**

Figure 2. a) Pt_x-Pd_{1-x} Bimetallic nanoparticles supported on SiO_2,**b)** An amplification of the figure 2a) of Pt_x-Pd_{1-x} Bimetallic nanoparticles supported on silica.



a) **b)**

Figure 3. a) Average diameter of Pt_x-Pd_{1-x} Nanoparticles supported on Silica was measure to be of 4.2 nm of . **b)** electron diffraction pattern of Pt_x-Pd_{1-x} Nanoparticles Suported on Silica, oriented along (111).

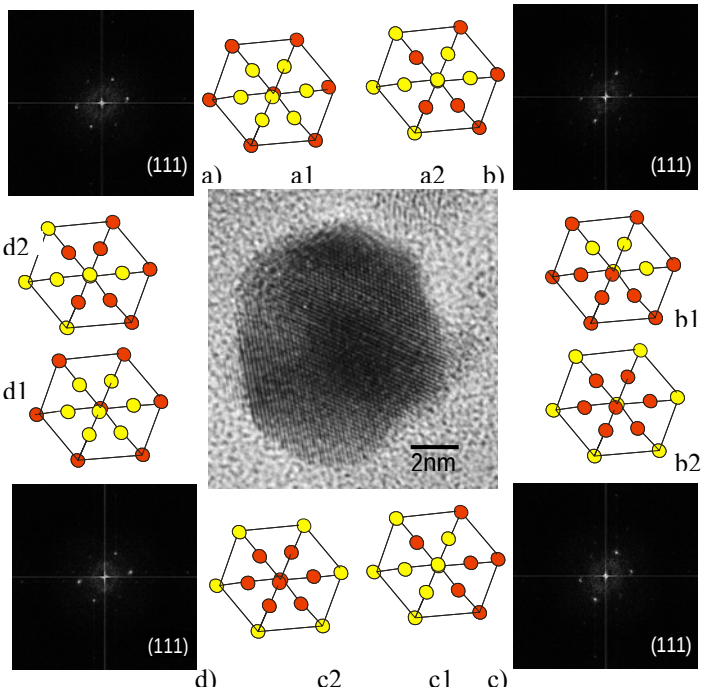
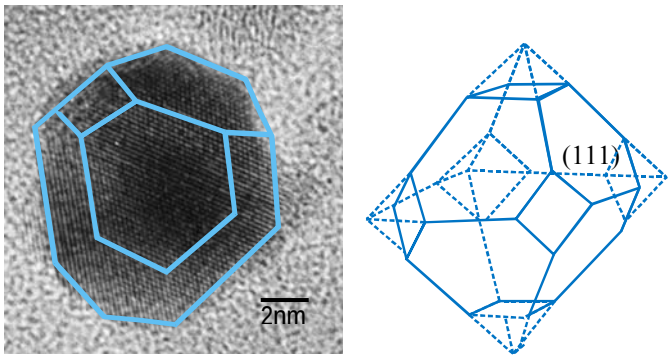


Figure 4. In the middle of the HREM image of Pt_x-Pd_{1-x} a bimetallic nanoparticle was measured in the figure 2b. 4a. Electron Diffraction Pattern with structure fcc oriented along (111), in 4a1 (Predominate Pd core Pt shell model) and 4a2(Predominate random model), 4b. Electon Diffaction Pattern, 4b1 (Predominate separate model) and 4b2 (Predominate Pt core Pd shell model) position of the Pt, Pd in the structure.4c Electon Diffraction Pattern. 4c1(Predominate random model) and 4c2 (Predominate Pt core Pd shell model) position of the Pt, Pd in the structure fcc. 4d Electon Diffraction Pattern. 4d1 (Predominate Pd core Pt shell model) and 4d2 (Predominate random model) position of the Pt, Pd in the structure fcc.



a b

Figure 4. **a)** HREM image bimetallic with a truncated octahedral shape of Nanoparticles Pt_x-Pd_{1-x} a. Oriented along (111). **b)** A Model of Cuboctahedral shape.

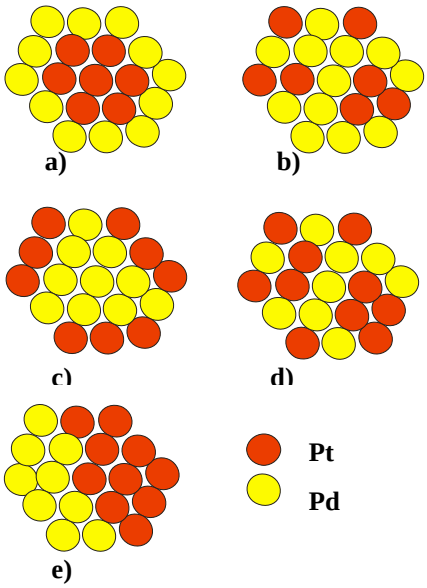


Figure 5. Cross section on the Pd/Pt bimetallic cluster model a) Pt core model, b) random model, c) modified Pt core model, d) random model, e) separate model[10].

Results and discussion

BET Surface area results were 37 m^2/g, in in the sample S1, 39 m^2/g in the sample S2and 38 m^2/g.. S3So that metal dispersion is similar for each sample.

By X- Ray Diffraction (XRD) pattern in the range from 0 to 130 in 2θ angle for the samples we observed the supported amorphous silica and the presence of metallic platinum and palladium reflections made it evident that a bimetallic crystalline phase forms with face-centred cubic structure.in the sample S1 the lattice parameter was a= 0.389 nm, in S2 b= 0.39 nm and S3 was 0.391 nm according to the composition of the samples both metals with fcc structure.

By X-EDS we found the conservation of the composition better in the metallic particles Pd than particles Pt similar to the composition.

Sample Bimetallic	Composition %Weight in solution		Composition %Weight XEDS	
	Pt	Pd	Pt	Pd
S1 Pt_{20}-Pd_{80}/ SiO_2	20	80	20.63	79.37
S2 Pt_{50}-Pd_{50}/ SiO_2	50	50	50.56	49.44
S2 Pt_{80}-Pd_{20}/ SiO_2	80	20	80.17	19.83

Table 2. Chemical weight Composition of Nanoparticles Pt_x-Pd_{1-x}. in solution and composition weight.

By HREM we observed bimetallic nanoparticles Pt_x-Pd_{1-x} and we measured the nanoparticles diameters. In the **figure 2** we observed in **a)** bimetallic nanoparticles of the sample S2 with diameter of 4.2nm, while in the figure **b)** we observed bimetallic nanoparticles Pt_x-Pd_{1-x} of S2 this shown a Bimetallic nanoparticles are made of a single solid solution of Pt and Pd atoms.and we found mainly to have

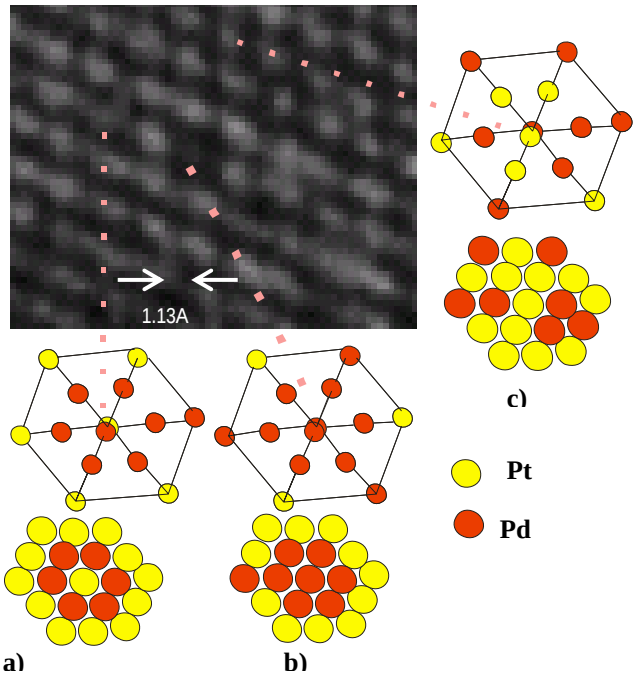


Figure 6. HREM image **a)** Image of Nanoparticles Pt_x-Pd_{1-x} (Pt core model), b) Pt core model and c) random model,.

3 RESULTS AND DISCUSSION

BET Surface area in the sample S1 was 37 m^2/g, in the sample S2 39 m^2/g and 38 m^2/g. in the sample S3. Due to the fact BET surface area does no vary between the samples, we consider that metal dispersion should be similar for each sample.

By XR Diffraction, it was observed that Pt-Pd alloys was formed in each sample with a fcc structure with the following lattice parameter a_1= 0.389 nm, for S1 a_2= 0.39 nm and for S2 and a_3= 0.391 nm for S3.

According to lattice parameters we found that nanoparticles characteristis are those in table 3.

Pt_x-Pd_{1-x}	BET [m^2/g]	Structure	Lattice Parameter [nm]	Diameter [nm]
S1	37	FCC	a=0.389	3.40
S2	39	FCC	a=0.390	3.72
S3	38	FCC	a=0.391	4.5

Table 3. Results of the samples Pt_x-Pd_{1-x} Nanoparticles Supported on Silica.

Bimetallic nanoparticles Pt_x-Pd_{1-x} were observed by HREM. Average diameter of nanoparticles were 4.2 nm observed in Figure 2a.

Chemical composition of nanoparticles was observed by XEDS, and it was established that it is similar to that osbserved by XRD.

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4 CONCLUSIONS

Pt and Pd alloys in form of bimetallic nanoparticles with 4.2 nm in diameter (average size) were produced via impregnation method.

Bimetallic nanoparticles presented an FCC structure, observed by XR Difraction Patterns and HREM.

Pt and Pd nanoparticles shape observed by HREM were cubo-octahedral.

The atomic distribution of Pt and Pd on the particle surface was studied by FFT, and it was established that follows a Pt core model, instead of a random distribution of Pt and Pd.

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