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# STRUCTURAL AND CHEMICAL CHARACTERIZATION OF $Pt_x$-$Pd_{1-x}$ BIMETALLIC NANOPARTICLES SUPPORTED ON SILICA

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**Abstract.** Platinium-Paladium bimetallic nanoparticles ($Pt_x$-$Pd_{(1-x)}$) supported on amorphous silica ($SiO_2$) were prepared by wetness impregnation techniques at different concentrations of Pt and Pd ≈ 1 metallic wt.%. Physical properties like microstructure were studied by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and chemical properties were used to establish the activity of these nanoparticles supported in the cyclohexene isomerization reaction and its specific area by physisorption (BET). Influence of the chemical composition and particle size on the cyclohexene isomerization reaction was also studied.

## 1. INTRODUCTION

In many cases, the composition of bimetallic nanoparticles is different from those of macroscopic alloys, and the combination of different properties in one nanoparticle depends upon the combination and distribution of atoms in the alloy [1,2].Particularly, the interest in Pt-Pd bimetallic catalysts in skeletal reactions of hydrocarbons has been initiated by both, practical and theoretical reasons Pt-Pd supported catalysts and mass forms offer superior activity, higher selectivity and higher poison resistance than pure Pt or Pd catalyst in skeletal isomerization [3-6]. Metallic Pd was more selective toward $C_6$ products of a mixture of hexane isomers formation than Pt**.** The chemistry of $C_6$ linear and cyclic hydrocarbons on platinum surfaces is of special interest for those aiming to understand the reforming reactions that produce high octane gasoline [7].

The interest in the study and production of bimetallic nanoparticle is increasing nowadays. This kind of materials usually had different composition and properties than bulk materials. By the way, their property depends upon alloy composition [8]. Particularly Platinum Palladium ($Pt_x$-$Pd_{1-x}$) bimetallic materials are important because practical and theorical reason, as supported catalyst, the offer superior activity, higher selectivity and higher poison resistance than pure Pt or Pd catalyst for example in skeletal isomeriazation. By itself, Pd has proved to be more selective toward $C_6$ product of various hexane isomer formations than Pt.

The chemistry of $C_6$ linear and cyclic hydrocarbons on platinum surfaces is of special interest for those aiming to understand the reforming reactions that produce high octane gasoline [7] The purpose of our work was to study the influence of the composition and nanoparticle sizes on cyclohexene isomerization reaction.

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**Table 1**. Chemical composition of $Pt_x$-$Pd_{1-x}$ nanoparticles.

| Bimetallic sample | Composition, wt.% | | Composition, wt.% 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 |
| S3 $Pt_{80}$-$Pd_{20}$/ $SiO_2$ | 80 | 20 | 19.83 | 80.17 |

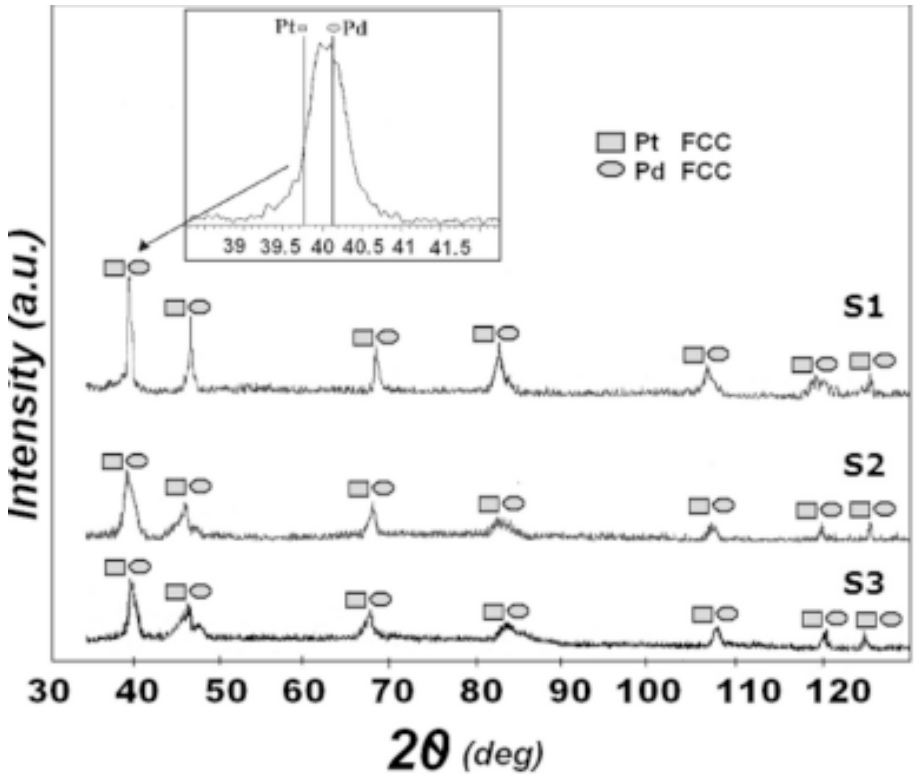


**Fig. 1.** X-Ray Diffraction patterns of Bimetallic Nanoparticles $Pt_x$-$Pd_{1-x}$ supported on silica.

## 2. EXPERIMENTAL

Bimetallic nanoparticles with different atomic concentrations of Pt and Pd ≈ 1% metallic weight was preparing by wet impregnation method. We used queous solutions of $H_2PtCl_6$ (Aldrich) and $PdCl_4$ (Aldrich) in varying concentrations. Amorphous $SiO_2$ (aerosil Ox.50) was used as support. In Table 1 chemical compositions of different $Pt_x$-$Pd_{1-x}$.nanoparticles are observed in wt.% concentrations. Physical properties like microstructure were studied by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and chemical properties were used to establish the activity of these nanoparticles supported in the cyclohexene isomerization reaction and its specific area by physisorption (BET).

## 3. RESULTS AND DISCUSSION

By X-Ray Diffraction (XRD) pattern in the range from 35 to 125 in 2θ angle were determined (Fig. 1). It is clear that the support was not observed because of its amorphous structure, but the presence of metallic platinum and palladium reflections made evident the presence of a bimetallic crystalline phase with face-centred cubic structure. For sample S1, the *a* lattice parameter was 0.389 nm,

**Table 2.** Results of samples the $Pt_x$-$Pd_{1-x}$ nanoparticles supported on silica.

| Bimetallic nanoparticle $Pt_x$-$Pd_{1-x}$ | Structure | Lattice Parameter (nm) | Bimetallic nanoparticles Diameter (nm) | BET [$m^2$ $g^{-1}$] | Conversion [%] |
|---|---|---|---|---|---|
| S1 $Pt_{20}$-$Pd_{80}$/ $SiO_2$ | FCC | *a*=0.389 | 3.40 | 37 | 80 |
| S2 $Pt_{50}$-$Pd_{50}$/ $SiO_2$ | FCC | *a*=0.390 | 3.72 | 39 | 85.6 |
| S3 $Pt_{80}$-$Pd_{20}$/ $SiO_2$ | FCC | *a*=0.391 | 4.20 | 38 | 93 |

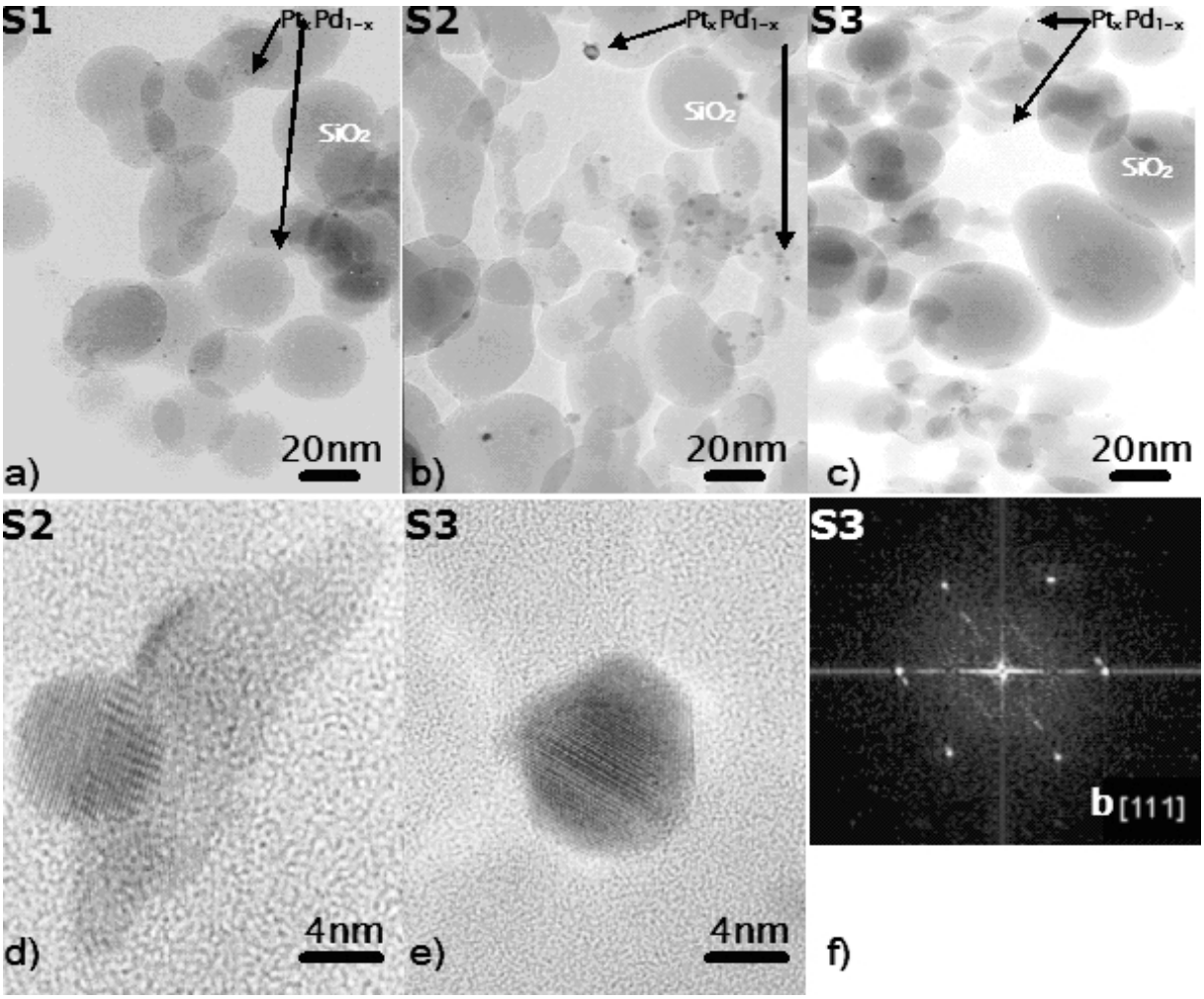


**Fig. 2.** $Pt_x$-$Pd_{1-x}$ bimetallic nanoparticles. (a) sample S1, (b) sample S2, (c) sample S3. In those micrographs bigger particles correspond to support. In (d) and (e) bimetallic particles: form, phase and crystallographic orientation are observed. In (f) micrograph a simulated electron diffraction pattern of the plane (111) from nanoparticle of micrograph (e) is observed.

0.39 nm for S2 and 0.391 nm for S3, according to the chemical composition of the samples, both metals with fcc structure.

By TEM, it was observed bimetallic nanoparticles $Pt_x$-$Pd_{1-x}$ and it was measured the nanoparticles diameters. In Fig. 2, it could be ob-

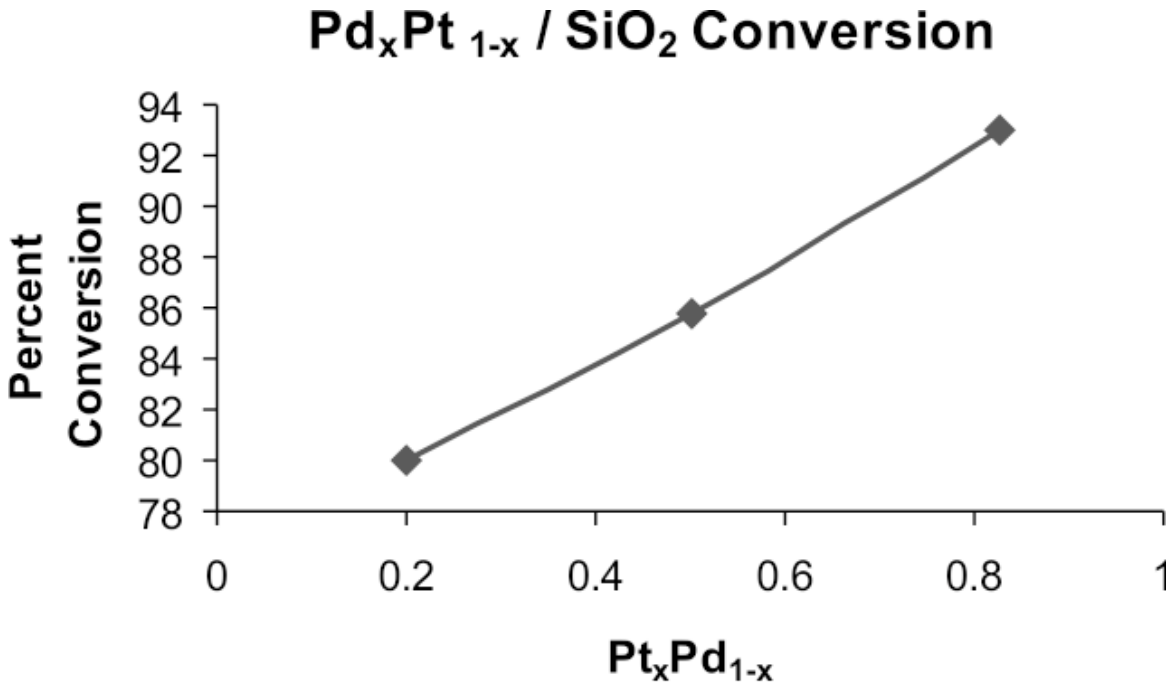


**Fig. 3.** Cyclohexene isomerization reaction behavior as a function of nanoparticle composition $Pt_x$-$Pd_{1-x}$ supported on $SiO_2$.

served as (a) bimetallic nanoparticles of the sample S1 with diameter of 3.4 nm, while in Fig. 2b it was observed bimetallic nanoparticles $Pt_x$-$Pd_{1-x}$ of the sample S2 with diameter of 3.72 nm, (c) belongs to the Sample S3, similar to sample S1 an S2 present bimetallic nanoparticles with diameters of 4.5 nm, in Fig. 2d HREM image of $Pt_x$-$Pd_{1-x}$ bimetallic nanoparticle was measured in the sample S2. This particle is compose of a single solid solution of Pt and Pd atoms and it mainly present a fcc packing, the $Pt_x$-$Pd_{1-x}$. While in the Fig. 2e, corresponding to S3 sample, it was observed the $Pt_x$-$Pd_{1-x}$ bimetallic nanoparticles. In this case, the particle was mainly composed of $Pt_x$-$Pd_{1-x}$ bimetallic particles with different phases; Pt-Pd bimetallic nanoparticles present cuboctahedral structures with fcc packing. Silica did not generate an electron diffraction pattern, which is characteristic of amorphous materials. But the metallic nanoparticle shows an electron diffraction pattern as observed in Fig. 2f corresponds to fast Fourier transform oriented along B(111) observe in $Pt_x$-$Pd_{1-x}$ bimetallic nanoparticle of Fig. 2e.

Fig. 3 shows cyclohexene isomerization reaction conversion as a function of chemical composition. Of the graph, it was observed that the highest selectivity for the isomerization reaction increases was obtained with S1 catalyst and its decreases for S2 and S3 samples, respectively. These results suggest that platinum in bimetallic $Pt_x$-$Pd_{1-x}/SiO_2$ is more selective to isomerization reaction. Although, the position and concentration of Palladium is important because of the distribution of products and the effect of the metal concentration influence the activity to methylcyclopentene.

BET surface area are presented in Table 2, in sample S2 it is possible to observe the maximum value, followed by sample S3 and sample S1.

In Table 2 it seems that platinum contents influence the conversion rate during isomerization reaction more than the BET surface area. It is possible that nanoparticle size has to do with these phenomena, possibly for this kind of reaction the best nanoparticle size is 4.20 nm. In order to understand if this phenomenon has to do with stability of nanoparticle because its size or lattice parameters, more experiments should be done.

## 4. CONCLUSIONS

By X- Ray Diffraction, platinum and palladium bimetallic reflections were observed and a bimetal-

lic crystalline phase with face-centred cubic structure was found. $Pt_x$-$Pd_{1-x}$ bimetallic nanoparticles forms with truncated cuboctahedral shape [9], with fcc packing were observed.

According to BET surface results, platinum amount influences the chemical selectrivity of our catalystsduring isomerization reaction. The selectivity to the cyclohexene isomerization over the $Pt_xPd_{1-x}/SiO_2$ bimetallic nanoparticles shows that catalytic activity increase with the platinum amount. It was also observed that S3 sample presents higher conversion in cyclohexene isomerization reaction. Finally, the most important parameters to control in cyclohexene isomerization reaction are nanoparticle sizes, chemical composition of nanoparticles and distribution of the metallic atoms in the particle surface.

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