

## Bimetallic Pd-Pt films prepared by MOCVD

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Bimetallic Pd-Pt films have been prepared on amorphous planar substrates by MOCVD using metal-acetylacetonate precursors. The effects of the MOCVD experimental conditions on the surface morphology, crystallite size and chemical composition of the bimetallic films have been analyzed. X-ray diffraction results show that bimetallic films consist of Pd-Pt solid solutions of variable composition depending on the initial metallic content in the inlet gases. Thus Pd-rich films can be obtained as preferred for the catalysts industry. The surface morphology of the bimetallic films varied from smooth to rough surfaces with the increase in total pressure. The crystallite size in the bimetallic films varies from 40 to 100 nm. Therefore, the MOCVD technique could be considered to be a viable alternative route for the preparation of bimetallic Pd-Pt films, which are in demand in the technology of supported bimetallic catalysts.

*Keywords:* MOCVD; thin films; bimetallic Pd-Pt.

Se prepararon películas bimetálicas Pd-Pt sobre sustratos amorfos por medio de la técnica MOCVD usando acetilacetatos-metálicos como precursores. Se estudiaron los efectos de las condiciones experimentales MOCVD sobre la morfología superficial, tamaño de cristal y composición química de las películas bimetálicas. Los resultados de difracción de rayos X muestran que las películas bimetálicas consisten de soluciones sólidas Pd-Pt de composición variable dependiendo del contenido metálico inicial en el gas de alimentación. De esta forma, se pueden obtener películas ricas en paladio, las cuales son requeridas en la industria catalítica. La morfología superficial de las películas bimetálicas varía de una superficie suave a una superficie rugosa con el incremento de la presión total. El tamaño de cristal en las películas bimetálicas varía de 40 a 100 nm. Así, la técnica MOCVD puede ser considerada una ruta alterna viable para la preparación de películas bimetálicas Pd-Pt, las cuales tienen demanda en el desarrollo tecnológico de catalizadores bimetálicos soportados.

*Descriptores:* MOCVD; películas delgadas; películas bimetálicas Pd-Pt.

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### 1. Introduction

The interest in bimetallic materials is increasing in both scientific and technological studies aiming to enhance the catalytic properties of single metals [1,2]. Bimetalization can improve the catalytic performance of the individual metals by the advantageous combination of their original intrinsic properties. In particular, bimetallic palladium (Pd) - platinum (Pt) catalysts have shown an improved sulfur tolerance in the hydrogenation of aromatics in petroleum feedstock containing sulfur compounds [3]. Typically, bimetallic supported catalysts are prepared by the simultaneous impregnation of two metal salts [4-6] or alternatively by ion-exchange [7]. In the

last decade, however, the metal organic chemical vapor deposition (MOCVD) method has been extended to the preparation of noble metal supported catalysts based on its favorable capacity to attain highly dispersed metallic nanoparticles in one single step [8-10]. Despite its valuable importance, the preparation of bimetallic Pd-Pt catalysts by MOCVD has scarcely been studied [11,12]. Thus as a first approach, this study reports on the preparation of bimetallic Pd-Pt films on amorphous planar substrates to establish the effects of the MOCVD experimental conditions on the surface morphology, crystallite size and chemical composition of bimetallic films.

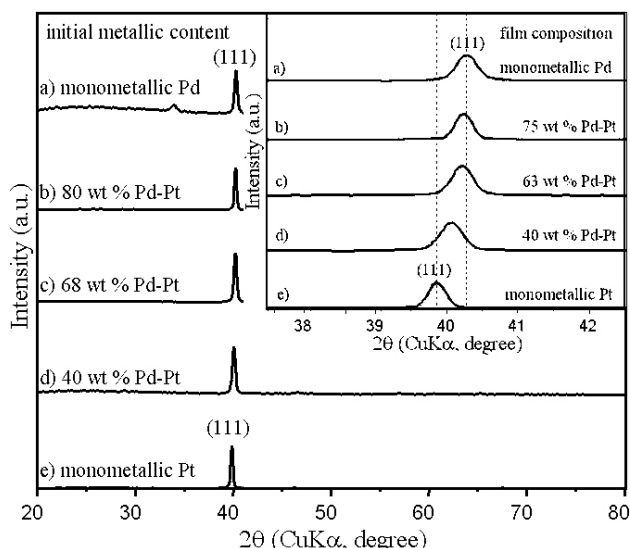


FIGURE 1. XRD patterns of (a) and (e) monometallic films and (b)-(d) bimetallic films prepared at  $T_{dep}=400^{\circ}\text{C}$  and  $P_{total}=1$  torr using various metal-precursor weight ratios.

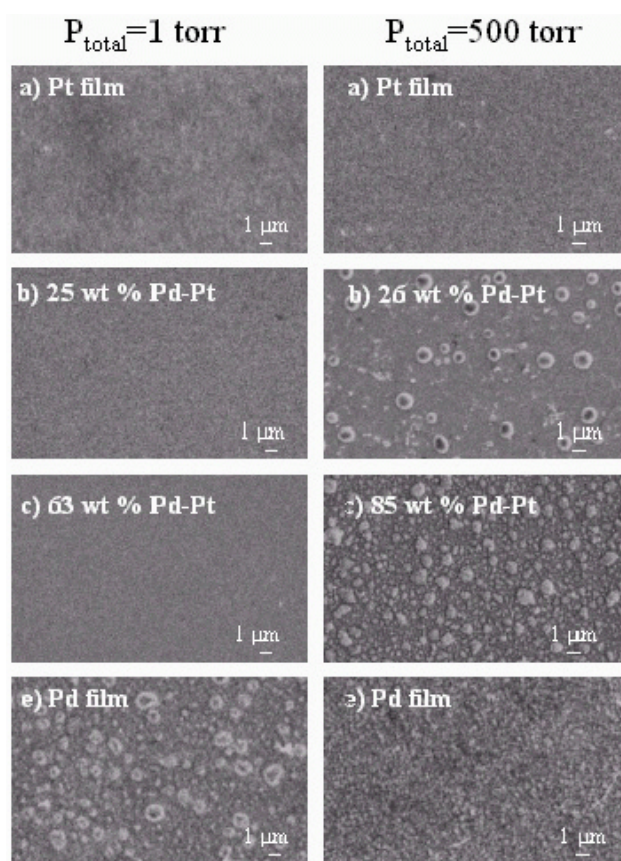


FIGURE 2. Influence of the total pressure ( $P_{tot}$ ) and Pd content on the film surface morphology.

## 2. Experimental

Monometallic and bimetallic Pd-Pt films were prepared on glass slide substrates in a horizontal hot-wall type

MOCVD apparatus which has been described elsewhere [13]. Metal-acetylacetonates  $[(\text{CH}_3\text{-COCHCO-CH}_3)_2\text{Pd}]$  and  $(\text{CH}_3\text{-COCHCO-CH}_3)_2\text{Pt}$  were used as the metal precursors. These precursors were mixed in various weight ratios to promote the variation in film composition. The initial metallic Pd content available for deposition was varied from 0 to 100 wt%. As the precursors have similar volatilities, they were evaporated together at  $180^{\circ}\text{C}$  to prepare the bimetallic films. The precursor vapors were carried to the reactor chamber with nitrogen gas at a constant flow rate of  $100\text{ cm}^3/\text{min}$ . The deposition temperature ( $T_{dep}$ ) was kept constant at  $400^{\circ}\text{C}$  and the total pressure ( $P_{tot}$ ) was controlled from 1 to 500 torr. Depositions were carried out for 15 min. The film morphology and the chemical composition were investigated by scanning electron microscopy (SEM) and EDS analysis, respectively. The formation of bimetallic films was verified by X-ray diffraction (XRD), and the crystal size was estimated from the widths of diffraction reflections (FWHM) using TOPASP software [14,15] and transmission electron microscopy (TEM). Thin bimetallic films were prepared for TEM observation (120 kV acceleration voltage); the films were mechanically removed from the substrate and suspended in acetone, and a small section of the film was taken using a copper grid.

## 3. Results and discussion

Figures 1b-1d show the XRD patterns of typical bimetallic films prepared at  $T_{dep}=400^{\circ}\text{C}$  and  $P_{tot}=1$  torr using various Pd/Pt weight ratios to modify the initial metallic contents. The XRD patterns of monometallic Pd and Pt films are shown in Figs. 1a and 1e as a reference. (111) reflections can only be observed in the monometallic films indicating a remarkable preferred orientation in the [111] direction. This implies that films tend to grow with the (111) plane parallel to the surface substrate. The (222) reflections are not observed because they are out of scale. The inset of Fig.1 depicts more clearly, in the  $2\theta$  range of  $37.5\text{--}42.5^{\circ}$ , that the monometallic Pd (111) reflection at  $2\theta=40.28^{\circ}$  and monometallic Pt (111) reflection at  $2\theta=39.78^{\circ}$  limit the angles at which the diffraction from the bimetallic films may occur. The intermediate reflections between those of Pd (111) and Pt (111) strongly suggest the formation of Pd-Pt solid solutions of particular lattice parameters depending on their chemical composition. It follows from this that the moderate deposition temperature used in these experiments ( $T_{dep}=400^{\circ}\text{C}$ ) leads to a sufficient surface diffusion for the formation of Pd-Pt solid solution films. The EDS analysis revealed that the composition of bimetallic Pd-Pt films can be controlled by varying the precursors' weight ratio. Thus, a higher initial Pd content will result in a higher Pd content of the film. The average crystal size of the bimetallic Pd-Pt films was determined by the specific growth conditions; this was estimated to be in the range of 70-90 nm.

Figure 2 illustrates the influence of the total pressure ( $P_{tot}$ ) and the Pd content on the film surface morphology.

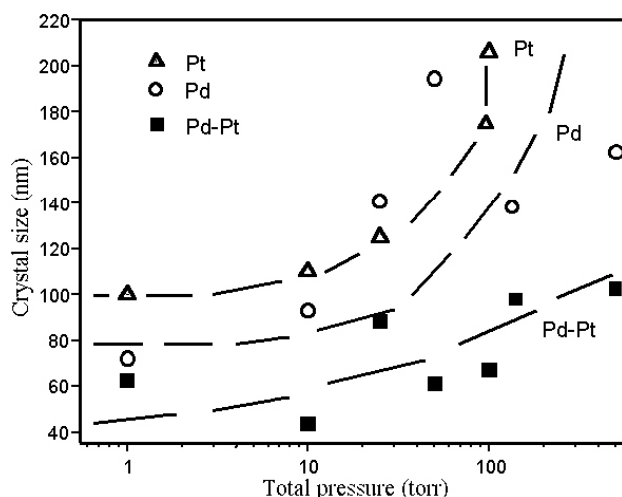


FIGURE 3. Variation of the crystal size as a function of total pressure.

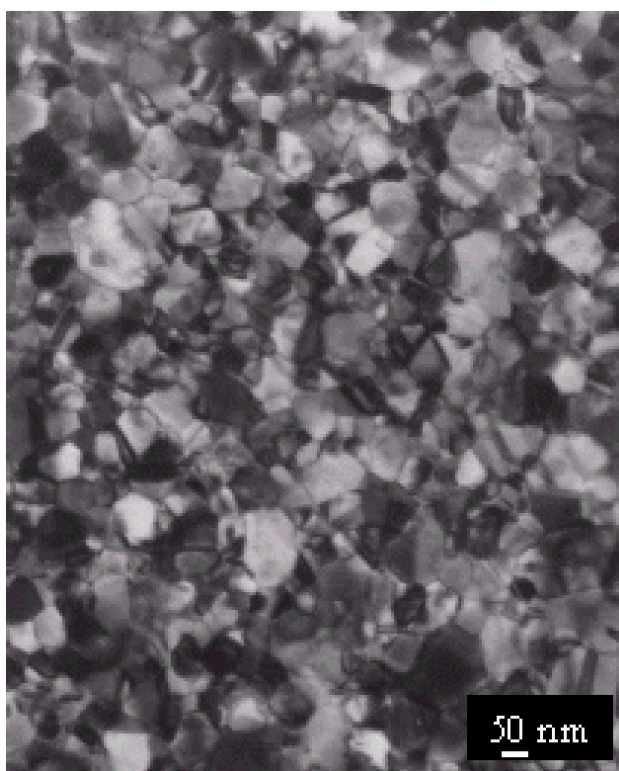


FIGURE 4. TEM image of a 63 wt % Pd-Pt film prepared at  $T_{dep}=400^{\circ}\text{C}$  and  $P_{total}=1$  torr.

At  $P_{tot}=1$  torr and Pd contents up to about 60 wt%, the bimetallic films exhibit smooth surfaces associated with small surface areas likely resulting from the minimization of their total surface energy under the particular growth conditions. As a result of the increase in total pressure ( $P_{tot}=500$  torr), the bimetallic films show rough surfaces regardless of the Pd content. This increase in surface area could be expected under high pressure conditions, for which the high

precursor gas concentration may promote nucleation of small metal particles in the gas phase. Monometallic films show intrinsic growth characteristics that cause them exhibit either smooth surfaces for Pt or rough surfaces for Pd, regardless of the total pressure.

As the total pressure ( $P_{tot}$ ) influences the bimetallic film surface morphology, its effect on the film crystal size was investigated. Figure 3 depicts the variation of crystal size as a function of total pressure. The crystal size increases with total pressure in a particular and non-linear fashion for Pt or Pd crystallites in the monometallic films. In contrast, the formation of Pd-Pt solid solutions results in a decrease in the crystal size, showing an almost linear dependency on  $P_{tot}$ . These differences are indicative of the attainment of bimetallic specific properties, which may represent a beneficial synergistic effect in the field of catalysis. Moreover, the smaller crystal size in bimetallic films can enhance not only the activity but also the selectivity in catalysts.

The TEM image of a 63 wt% Pd-Pt film prepared at  $T_{dep}=400^{\circ}\text{C}$  and  $P_{total}=1$  torr is shown in Fig. 4. The average crystal size revealed by this image is about 70 nm. This average crystal size is consistent with that estimated from the FWHM of the diffraction reflections. The crystal size in the film can be attributed not only to the intrinsic nature of the growth mechanisms, but also to the surface characteristics of the substrate material. Thus, the MOCVD conditions that promote either small crystal size or rough surface morphology on planar substrates could be considered important information in preparing dispersed nanoparticles on high surface area supports, which are widely used in catalytic applications such as hydrogenation of aromatics.

#### 4. Conclusions

In this study, it has been demonstrated that bimetallic Pd-Pt films can be prepared with an adequate control of their metallic contents and surface morphology by using the MOCVD technique. XRD results suggest that the bimetallic films consist of Pd-Pt solid solutions. Bimetallic Pd-rich films, as preferred for catalysts, can be obtained by an easy control of the metal-precursors' weight ratio. The crystal size in the bimetallic Pd-Pt films varies from 40 to 100 nm. These results represent important information in promoting the synthesis of bimetallic nanoparticles on high surface area substrates used in the catalysts industry.

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