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Electron Microscopy and Catalytical Studies of Platinum Particles Supported in Zinc Aluminate

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ABSTRACT

Zinc aluminate was synthesized by coprecipitation and after calcination at 800 ° C was impregnated with chloroplatyinic acid to obtain 0.16, 0.47, 1.17 and 2.5 weight percentage of platinum catalysts. Samples were characterized by atomic absorption, nitrogen physisorption, X ray diffraction, hydrogen chemisorption, conventional and high resolution electron microscopy (CTEM y HREM respectively) and catalytic activity in isobutane dehydrogenation. Zinc aluminate showed a high crystallinity (spinel structure) and low surface area - 0.20 m / g. The highest dispersion (49%) was obtained with the 0.16% Pt catalyst diminishig sharply with the other platinun content catalysts. At low Pt concentrations (0.16 - 0.47) , was not possible localize and distinguish metal particles in HREM images . With the 1.17 % and 2.25 % Pt, samples with clear Pt aggregates with sizes around 2.0 nm could be seen. Catalytical activity was more sensitive to metallic content than to platinum dispersion.

KEYWORDS

Electron microscopy, platinum particles, zinc aluminate, catalysis.

INTRODUCTION

Platinum monometallic catalysts have been used for several decades in naphta reforming [1]. Another important application of the Pt catalysts is in the paraffins dehydrogentation [2]. As the global demand for olefins and derivatives is increasing,the installed capacity will be insufficient [3]. Traditionally light olefins have been obtained from steam cracking of naphta and from fluid catalysts cracking in oil refining [4]. Perhaps the most important olefin like-compound is isobutylene, because it is used as new material for MTBE [5], consequently it is necessary to produce more isobutylene by direct dehydrogenation of isobutane. At present time, Pt monometallic catalysts have been replaced in many cases by more active, selective and stable bimetallic catalysts [6].

There are two types of commercially important, dehydrogenation catalysts: The supported bimetallic Pt-Sn and the chromium alumina catalysts [7]. We have focussed our interest in the first group which consist in Pt-Sn/ Al_2O_3 (deflex process) [8] or Pt-Sn/Al_2O_4Zn (star process) [9] Although many works have been dedicated to study the system Pt-Sn supported on alumina little information is found in the literature about Pt and Pt - Sn system supported in zinc aluminate.

It is believed that catalytical behavior of the active phase is determined mainly by the following support features: surface acidity, thermal stability, texture, estabilization of active phase, dispersion and the chemical interaction with the active phase. In a previous work [10] we reported some metal support effects present in platinum supported in zinc aluminate. In present work we are showing additional information about the Pt/ Al_2O_4Zn system in conecction with its catalytical behavior.

MATERIAL AND METHODS

1.-Catalyst Preparation

Zinc aluminate was prepared by coprecipitation from nitrates; the required amount of zinc and aluminate nitrates were dissolved in demineralized water under vigorous stirring. The precipitation was performed at variable pH, adding a 20 % wt. ammonium carbonate aqueous solution to the acidic mixed solutions all the way up to pH equal to 7.5. The precipitate was carefully washed with demineralized water and then calcinated at 88 °C in air for 6 hours.The support (80 - 100 mesh) was impregnated by an incipient wetness technique using an aqueous solution of chloroplatinic acid to obtain Pt contents of 0.16, 0.47, 1.17 and 2.5 % weight. Catalysts were dried and calcinated at 500 °C for 4 hours.

2.- Characterization Techniques

Chemical composition was determined by atomic absorption spectroscopy in a Perkin Elmer 2380 apparatus. Textural properties were calculated from nitrogen physisorption data (Micromeritic ASAP-2000). The chemisorption measurements were carried out at 25°C in a vollumetric installation. X ray diffraction observations were performed with a Siemens D-500 X ray diffractometer, using the Cu K radiation and a nickel filter. High Resolution Electron Microscopy observations were carried out in a JEOL 4000 EX electron microscope working at 400 kV all the time and equipped with a high resolution pole piece (Cs =1.00 mm). Conventional and Analytical Electron Microscopy (CTEM and AEM, respectively) observations were performed in a side entry JEOL 100 CX microscope fitted with a goniometer stage and an EDS system (Tracor 5500). Samples for electron microscopy observations were ground in an agatar mortar and dispersed in distilled water in an ultrasonic bath. Some drops were deposited in 200 mesh copper grids covered with a carbon holey film. Focal series of images were obtained in high resolution conditions in order to improve visibility of small platinum particles embedded in zinc aluminate support

3.- Catalytical Activity

Isobutane dehydrogenation was carried out using a conventional continuous flow microreactor system operated at 550° C and atmospheric pressure. Measurement of isobutane conversion and the product distribution were made using on-line gas chromatographic analysis in all the experiemnts 0.05 g catalysts and a total flow rate of 2.4 l/h were used. Feed stream was an equimolar mixture of isobutane with hydrogen. Before the reaction test, catalysts were pretreated with hydrogen 1.8 l/h at 550 ° C for one hour. Reaction rate was calculated assuming differential behavior of the reactor.

RESULTS AND CONCLUSSIONS

Physico-chemical characterization and catalitycal activies are resumed in **Table 1** and **Table 2**. Also electron microscopy images are presented to show details of platinum supported particles on zinc aluminate.

Chemical composition of zinc aluminate showed a slight excess of aluminium with respect to the stoichiometry required. An Al /Zn atomic ratio equal to 2.12 was obtained. Nevertheless the spinel structure of zinc aluminate was corroborated by X rays diffraction (JCPDS card 5-699) and selected area electron diffraction patterns analysis. **Figure 1** shows the corrresponding X ray diffractogram with well defined peaks for zinc aluminate interplanar distances. The prepared catalysts are listed in Table 1 where the platinum content and chemisorption results are reported. From this table one can appreciate that platinum dispersion decreases sharply from 0.16 % Pt to 0.47% Pt and after that remains constant. The highest dispersion of the 0.16 % Pt catalysts has already been explained by a platinum atomic difussion mechanism into the oxygen vacancies in the spinel structure in locations like the ones showed in **Figure 2**.

Table 1. Physico-chemical parameters and hydrogen chemisorption results of Pt/Al$_2$O$_4$ Zn Catalysts.

Sample	Pt (%)	Dispersion (%)	Particle Size (nm)
A	0.16	49	2.2
B	0.47	16	7.0
C	1.17	12	10.3
D	2.50	10	11.3

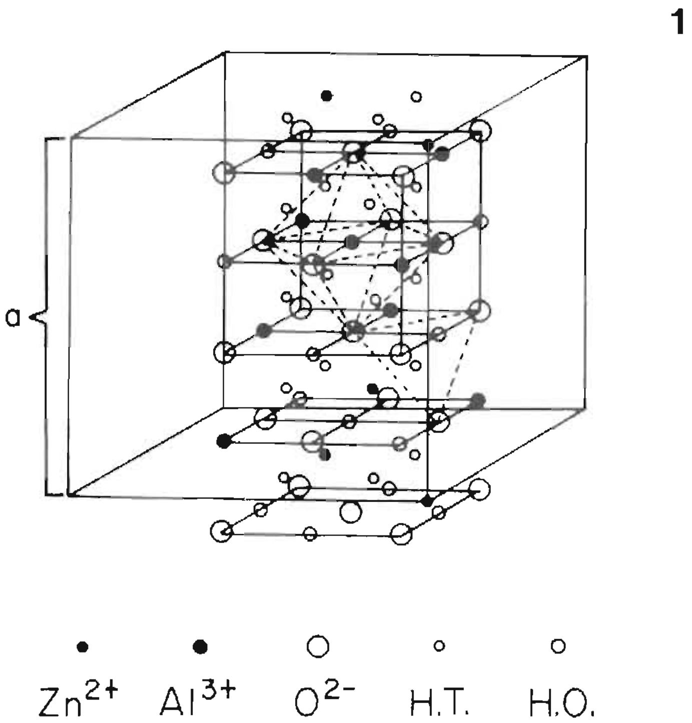

Figure 1. The spinel structure of zinc aluminate with tetrahedral and octaedral sites can be observed in this drawing. HO and HT empty circles indicates sites where Pt atoms could be accommodated.

On the other hand, for higher Pt loadings, it has been suggested that metal-metal interactions are dominant, leading to cluster or particles formation. In fact with the 2.25 % Pt we observe that Pt dispersion is decreased. From HREM observations [10] Fig. 4 it seems that Pt particles are embedded over zinc aluminate surface; for the lowest Pt concentration particles could not be observed even in atomic resolution images. This might be explained , for the first case, in terms of particle establization induced by the support in all the stages of catalysts treatment, and in the second case, particle diffusion to the bulk is expected, given that chemical composition analysis reveals the presence of plantinum in our sample. This behaviour is quite different when compared with platinum supported on alumina catalysts.

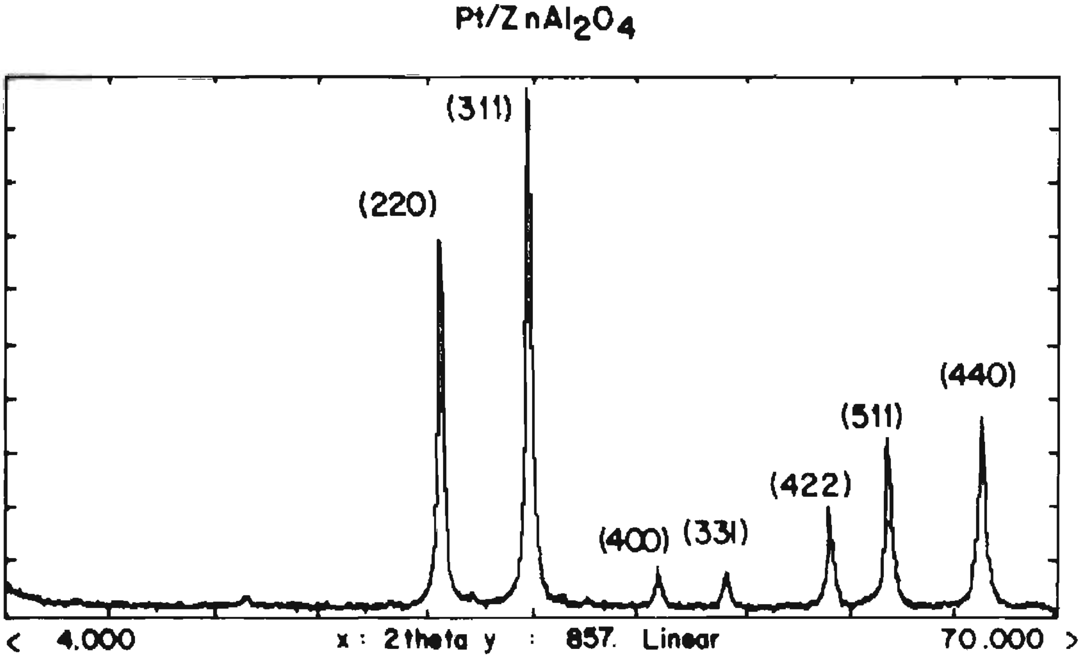

Figure 2. This is a x Ray diffractogram coming from sample C with a 1.17% Pt content. Peaks correponding to Pt do not appear in this diffractogram.

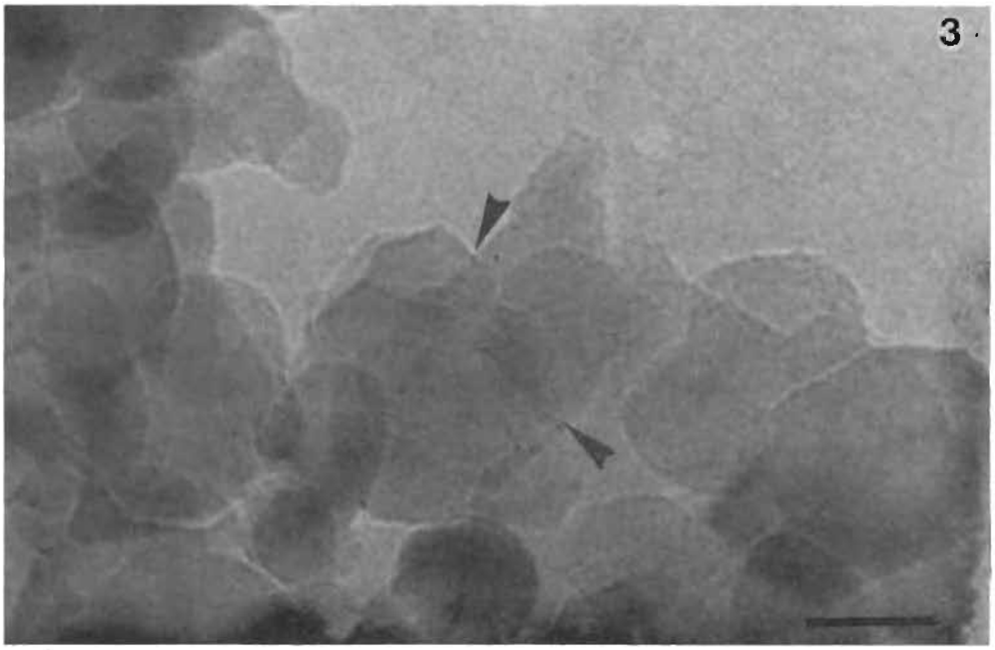

Figure 3.
CTEM image of sample C (1.17%). Crystalline zinc aluminate with plate configuration and platinum particles (arrowed) can be observed in this image. Bar = 31.4 nm

In **Table 2**, the catalytic activity results in the isobutane dehydrogenation are show presented. A clear increase of the reaction rate is observed as Pt contents is increased in the catalysts. Selectivity to isobutane practically remains constant and the lowest deactivation rate is found for the highest platinum content catalyst. From this results one can conclude that isobutane dehydrogenation is more sensitive to the amount of platinum in the catalyst than to high dispersion. Nevertheless selectivity did not change. This might be indicative that metal-support interaction with must be produced with any amount of platinum in the catalyst. Platinum particles were not detected by HREM, even in atomic resolution images for low Pt concentration. Lattice planes distortions were not detected in support. This suggest that platinum could diffuse into the zinc aluminate lattice occupying lattice sites in substitutional way. These results suggest that platinum on zinc aluminate might interact strongly

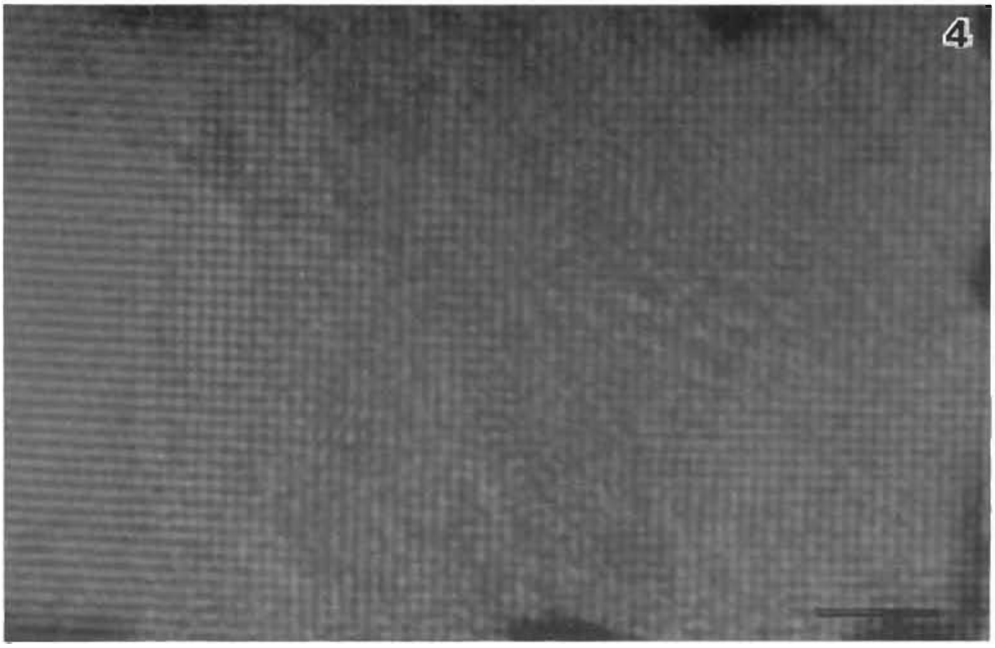

Figure 4.
Typical HREM image of sample A (0.16% Pt). Two overlapped zinc aluminate crystallites are observed but platinum particles are not detected.
Bar = 1.87 nm

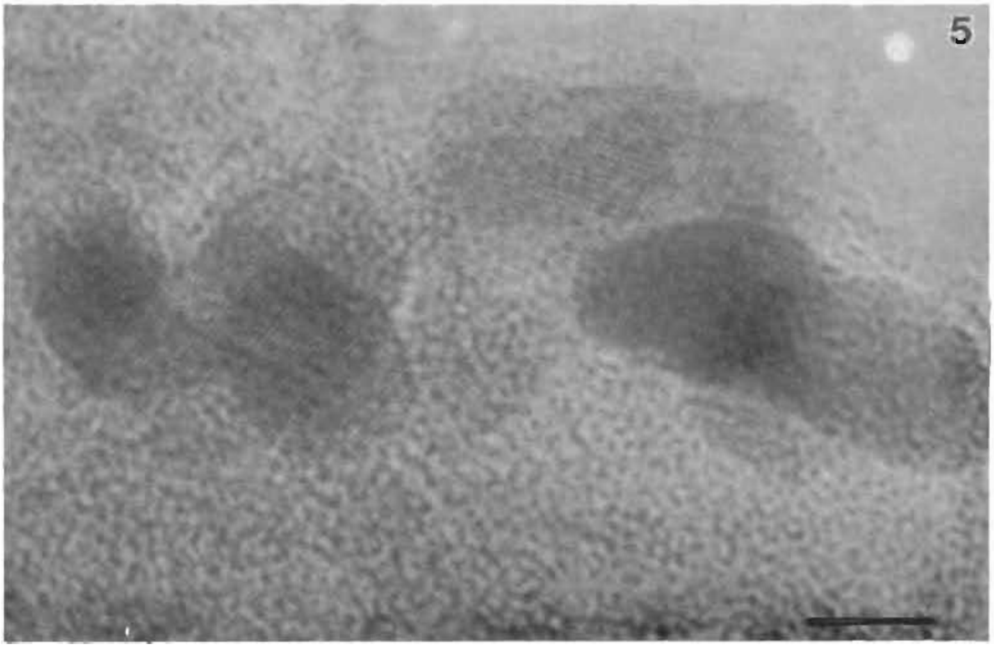

Figure 5.
HREM image of sample C (1.17%) Pt. Aggregates of platinum particles over an apparent amorphous zinc aluminate are clearly observed in this image. Bar = 4.42 nm

Table 2. Catalytic activity of Pt/Al$_2$O$_4$ Zn in isobutane dehydrogenation

Sample	$-r_{Ao}$	S(mol %)	kd x 10^4 (min^{-1})
A	22.5	91.7	30.0
B	26.5	97.5	22.8
C	34.9	96.0	29.1
D	41.8	97.3	15.0

$-r_{Ao}$ Initial rate reaction.

S Selectivity refered to isobutylene.

Kd First order deactivation constant.

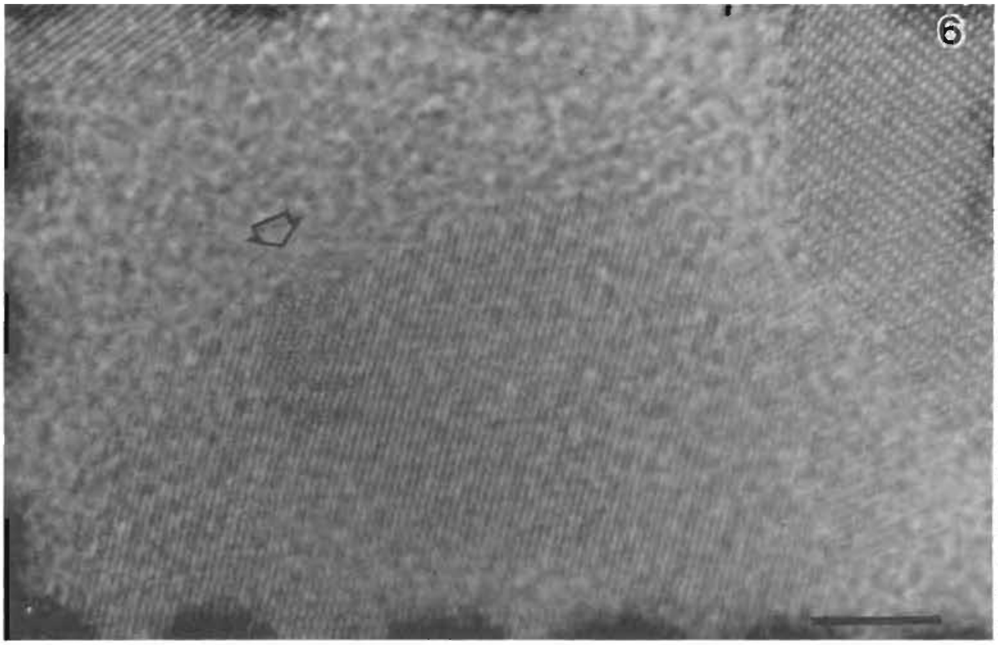

Figure 6. HREM image of sample D (2.25%Pt). In the right side a projected potential image of a zinc aluminate crystallite can be observed. Near the center a platinum particle (arrowed) embedded in a zinc aluminate crystallite is detected. Bar = 36.4 nm

with the support as evidenced by electron microscopy results.

RESUMEN

Se sintetizó aluminato de zinc por el método de coprecipitación y se calcinó a 800°C después de lo cual se impregnó con ácido cloroplatínico para obtener catalizadores con 0.16,0.47,1.17 y 2.5 %- de Platino en peso. Las muestras asi obtenidas fueron estudiadas por absorción atómica, fisisorción de nitrógeno, difracción de rayos X, microscopía electrónica convencional y de alta resolución y se probó su actividad catalítica en la deshidrogenación del isobutano.El aluminato de zinc presentó una alta cristalinidad y baja área superficial (0.20 m/g). La dispersión mas alta (49%) se encontró para el catalizador con 0.16% de Pt y disminuye abruptamente con otros contenidos de platino. A concentraciones bajas (0.16- 0.27 % Pt) no fue posible distinguir y localizar las partículas metálicas en imágenes de alta resolución. A concentraciones de 1.17 y 2.5 % de Pt se vió en las muestras, agregados de platino con tamaños alrededor de los 20 nm. Se observó que la actividad catalitica fué mas sensible al contenido metálico que a la dispersión.

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