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Electron Microscopy and Catalytic Studies of Pt-Sn/$ZnAl_2O_4$

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ABSTRACT

In this work, zinc aluminate ($ZnAl_2O_4$) spinel is used to support platinum-tin catalyst. Three different impregnation procedures are followed: in the first catalyst is first impregnated with platinum and, then, with tin. In the second catalyst, the order of impregnation is the other way round. These samples are compared with a third solid obtained impregnating the $ZnAl_2O_4$ with a platinum and tin solution (simultaneous impregnation).

In this study, the effect of these protocoles on the structure and on the catalytic performance (isobutane dehydrogenation) is discussed. The characterization techniques are atomic absorption, X-ray diffraction, hydrogen chemisorption and high resolution electron microscopy.

KEYWORDS

High Resolution Electron Microscopy, Pt-Sn particles, zinc aluminate, catalysis, H_2 chemisorption

INTRODUCTION

For low pressure operation in naphta reforming and for processes in which continuous regeneration is performed, stable platinum catalysts are required by petrochemical industry. If, instead of Pt/Al_2O_3 catalysts, bimetallic catalysts as $Pt\text{-}Sn/Al_2O_3$ are used, a better performance is observed. To improve these solids new preparation methods as sol-gel synthesis are tried [1,2].

Our choice has been to study the inhibition of particle growth and carbon deposition if the support is modified. Spinels of the type MAl_2O_4 where M=Zn,Mg,Cu... prevent, indeed, sintering. Furthermore, hidrofobicity, low acidity and mechanical strenght are some of the features of those materials; they are, hence, well suited to the high severity conditions imposed on the light paraffins dehydrogenation processes. As proposed by Pakhomov et al.[3], we have used $ZnAl_2O_4$ as support.

In a previous work [4], we presented the electron microscopy and catalytic studies of Pt/ $ZnAl_2O_4$ and we found that catalytic activity is more sensitive to platinum content than to metal dispersion. The purpose of the present work is to determine if the presence of tin alters this conclusion or modifies the catalyst structure. The effect or addition order of tin on the morphology and the catalytic properties is studied. The characterization

techniques are atomic absorption, X-ray diffraction (XRD), hydrogen chemisorption and high resolution electron microscopy (HREM). The test reaction used was the isobutane dehydrogenation.

EXPERIMENTAL

Catalyst Preparation

Zinc aluminate was prepared by coprecipitation from aluminum and zinc nitrates. The stoichiometric amounts of zinc and aluminum nitrates were dissolved in demineralized water under vigorouos stirring. 20 wt.% ammonium carbonate aqueous solution was added to the acidic mixed solutions, all the way up to pH 7..5, until precipitate was formed. The precipitate was carefully washed with demineralized water and, then, calcined at 800°C in air for 6 hours.Three different impregnation procedures were, then, followed as in [5] containing $SnCl_2$. The solid was dried, again, at 110°C. Sn/Pt/$ZnAl_2O_4$ (Sample I): this catalyst was obtained impregnating, first, the $ZnAl_2O_4$ support with an aqueous solution containing H_2PtCl_6. The solid was dried at 110¦C before a second impregnation with an aqueous solutioPt/Sn/$ZnAl_2O_4$ (Sample II): in this sample, the first impregnation was with an aqueous solution containing $SnCl_2$. After drying at 110°C the solid was impregnated with an aqueous solution containing H^2PtCl_6, and dried at 110°C.Pt-Sn/ $ZnAl_2O_4$ (Sample III): the support was impregnated with an aqueous solution containing, both, H_2PtCl_6 and $SnCl_2$. The solid was, then, dried at 110°C. All the samples were calcined at 500°C in air for 6 hours.

Characterization techniques

Chemical composition was determined by atomic absorption spectroscopy with a Perkin Elmer 2380 apparatus. Hydrogen chemisorption was performed on a volumetric home-made installation at 25°C. X-ray diffractograms were obtained with a Siemens D-500 diffractometer coupled to a copper anode tube Conventional Transmission Electron Microscopy (CTEM) observations were carried out in a side entry JEOL 100 CX electron microscope; bright and dark field images were obtained fron differents zones for each sample in order to detect and localize platinum and tin particles.Selected Area Electron Diffraction (SAED) patterns, were obtained for each sample in order to detect presence of zinc aluminate and the existence of individual platinum and tin particles or platinum-tin alloys.High Resolution Electron Microscopy observations were carried out in a JEOL-4000 EX electron microscope operated at constant voltage of 400 kV. This electron microscope is equipped with a high resolution pole piece (Cs=1.00 mm). Samples for electron microscopy studies were ground in an agate 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 to improve the visibility of small metal particles.

Catalytic activity

Catalytic test was the isobutane dehydrogenation performed in a conventional flow reaction system at atmospheric pressure and 550°C. The catalyst bed (100 mgs) received a constant flow (80 ml/min) of a mixture of isobutane and hydrogen (1:1).

RESULTS AND DISCUSSION

Table 1 compares the metallic surface and the composition of the various catalysts. If Sn/Pt/$ZnAl_2O_4$ and Pt/Sn/$ZnAl_2O_4$ catalysts are compared, both samples, contain the same amount of platinum but the amount of tin present in the Pt/Sn/$ZnAl_2O_4$ is 2.5 times higher. Hence the order of addition of the

metals determines the Pt/Sn ratio. Furthermore, if $ZnAl_2O_4$ is first impregnated by tin a layer of tin is expected to be formed on the surface before platinum impregnation. When on this $Sn/ZnAl_2O_4$ support, platinum is added the metallic surface is 38 m^2/g. But, if platinum is deposited first on $ZnAl_2O_4$ and, then, tin is added the metallic surface is only 29 m^2/g. It seems, then, that in the last case the addition of tin reduces the H_2 adsorbing metallic surface. A first interpretation could be the poisoning of a fraction of the platinum surface with tin. This hypothesis is confirmed by the sample B reported in our previous work [4(. Sample B is a $Pt/ZnAl_2O_4$ whose platinum content is 0.47 wt.% (very close to the one of $Sn/Pt/ZnAl_2O_4$ and $Pt/Sn/ZnAl_2O_4$ catalysts). Catalyst B was reported to have a particle size of 70Å. Hence, to impregnate $ZnAl_2O_4$ or $Sn/ZnAl_2O_4$ with platinum provides platinum particles with the same mean diameter. However, in $Sn/Pt/ZnAl_2O_4$ the metallic area is lower and the metal particle size derived from this measurement is 97Å. This mean diameter values does not mean that the platinum particles are 97Å but that they, probably, are, also around 70Å and tin is deposited on top them masking a fraction of their surface to hydrogen.

If platinum and tin are simultaneously deposited on $ZnAl_2O_4$, 0.85 wt.% tin is retained by the support, i.e. twice the value found when tin was deposited first on $ZnAl_2O_4$. Such a value can be explained if not only a layer of tin is deposited on zinc aluminate (around 0.46%) but if tin is forming bimetallic particles with platinum (around 0.4 wt.%). These bimetallic particles would have a composition close to 0.11 wt.% platinum and 0.4 wt.% tin. Still some hydrogen is adsorbed and the obtained metallic area is 12 m^2/g. Again, the diameter estimated from this metallic surface may be misleading. The catalyst seems to be constituted by bimetallic particles not chemisorbing hydrogen and *some Pt particles* which are reponsible of the reported 12 m^2/g.

To determine the compounds present in the catalysts, X-ray diffraction studies were proposed. Unfortunately, only the crystalline peaks of $ZnAl_2O_4$ were observed. It was not possible to determine if platinum was alloyed to tin, if tin was found as an oxide or if any other compounds were present. The platinum and tin contents, as well as the metal particle sizes were too low.

However, by electron microscopy, Figures 2, 3,4 and 5, it was possible to estimate the metal particle sizes. In all samples the mean particle diameter was the same, In Table 2, size distribution of samples are presented. Note in HREM images, that the particle contrast varies;this might be due to that two types of particles are present: high contrast, low contrast. Probably the first ones (high contrast) are platinum particles and the second ones (low contrast) are bimetallic particles. In the sample $Pt/Sn/ZnAl_2O_4$ only higher content particles were observed, but in samples $Sn/Pt/ZnAl_2O_4$ and Pt-Sn/ $ZnAl_2O_4$ both types were found. The appearance of transparency of supported metallic particles also is observed in other catalytic systems [6] and is consequence of image formation under high resolution conditions.

Table 3 presents the activity and selectivity of the three catalysts in the isobutane dehydrogenation (time=3 hours). Again, catalyst Pt-Sn/ $ZnAl_2O_4$ is different from the other two. This catalyst has the lowest activity as well as the lowest selectivity. Such a bad performance has to be attributed to the very low platinum content and the high tin content. Excess tin, instead of forming the catalyst, poisons it partially. The order of addition of platinum and tin (catalysts Pt/Sn/ $ZnAl_2O_4$ and $Sn/Pt/ZnAl_2O_4$) does not seem to be determinant for the performance of the catalyst in the chosen reaction.

CONCLUSIONS

Not only the addition of a certain amount of tin to Pt/$ZnAl_2O_4$ catalysts may modify the structure and the catalytic performance of the catalyst but the order of addition of the metals. If the support is simultaneously impregnated with platinum and tin (Pt-Sn/$ZnAl_2O_4$) the obtained catalyst has a high Sn/Pt ratio but a low activity and selectivity in the dehydrogenation of isobutane. As it was shown by hydrogen chemisorption and HREM the particles seem to be bimetallic, probably platinum occluded by a thick layer of tin oxide or alloyed platinum tin. If tin is added first to the $ZnAl_2O_4$ support the platinum particles formed (Pt-Sn/ $ZnAl_2O_4$) seem to be a small and catalytically as active as if tin is added to a platinum impregnated support. However in this last case a samll fraction of the particles are probably bimetallic.

RESUMEN

En este estudio se utiliza la espinela de aluminato de zinc ($ZnAl_2O_4$) como soporte de un catalizador de platino-estaño. La impregnación se llevo a cabo de tres maneras: el primer catalizador se obtuvo impregnando primero con platino y luego con estaño; en el segundo catalizador, el orden de impregnación fue el contrario al primero. Estas dos muestras se comparan con una tercera obtenida impregnando el soporte con una solución de platino y estaño (impregnación simultánea). En este trabajo, se discute el efecto del modo de impregnación sobre la estructura y las propiedades catalíticas (en la deshidrogenación de isobutano). Las técnicas de caracterización usadas fueron: absorción atómica, difracción de rayos X, quimisorción y las microscopias electrónicas convencional y de alta resolución.

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Table 1. Atomic absorption and H_2 chemisorption results

	$Sn/Pt/ZnAl_2O_4$	$Pt/Sn/ZnAl_2O_4$	$Pt\text{-}Sn/ ZnAl_2O_4$
Pt(wt%)content	0.43	0.43	0.11
Sn(wt%)content (wt.%)	0.18	0.46	0.85
Metallic area (m^2/g)	29	38	12
Particle size (Å)	97	74	230

Table 2. Particle diameter determined by HREM

Sample	$Sn/Pt/ZnAl_2O_4$	$Pt/Sn/ZnAl_2O_4$	$Pt\text{-}Sn/ ZnAl_2O_4$
d (Å)	$12 \leq d \leq 65$	$9 \leq d \leq 70$	$23 \leq d \leq 55$

Table 3. Catalytic test results obtained with Pt-Sn bimetallic catalyst

	$Sn/Pt/ZnAl2_2O4_4$	$Pt/Sn/ZnAl_2O_4$	Pt-Sn/ZnAl2O4 $AZnAl_2O_4$
Activity (Conversion mol%)	12.0	10.0	2.0
Selectivity (Isobutylene mol%)	95	98	88

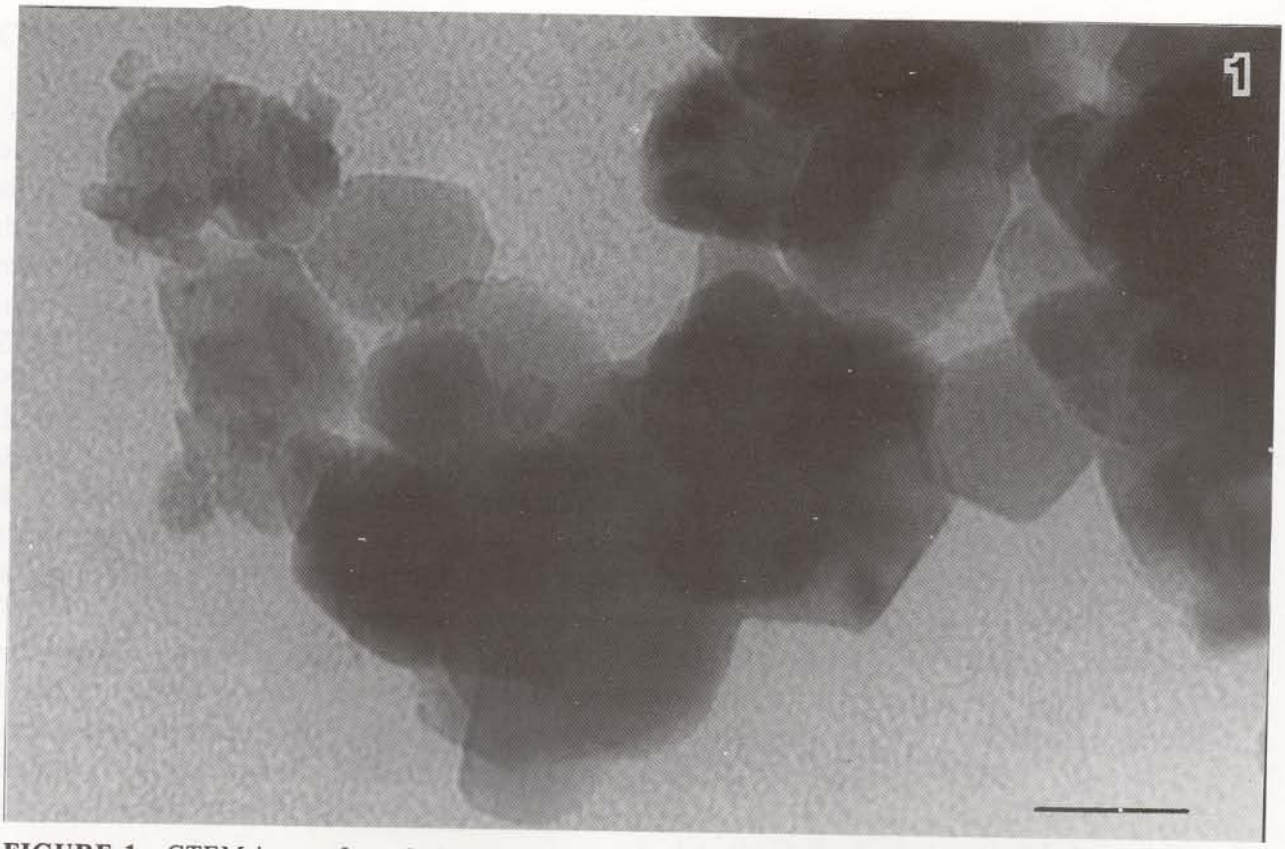

FIGURE 1.- CTEM image from Sn/Pt/$ZnAl_2O_4$ sample. Zinc aluminate faceted crystallites and arrowed metallic particle are observed in this image., which is a typical bright field image of the three samples studied in this work. Bar = 350 nm.

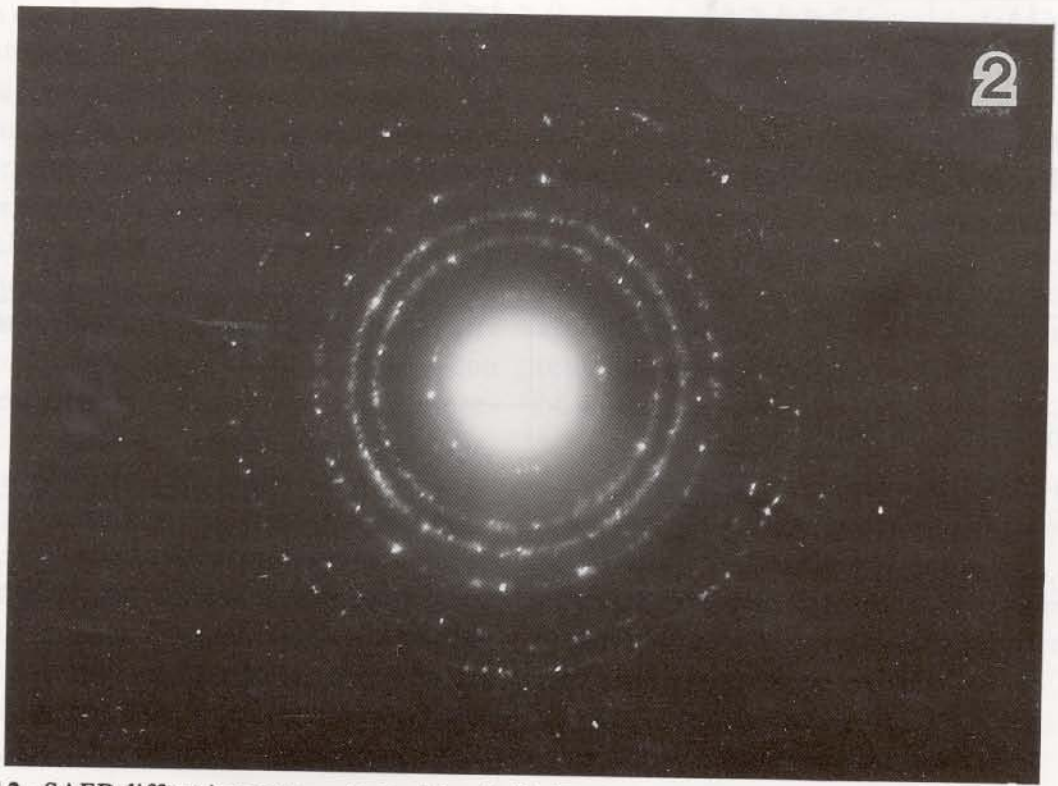

FIGURE 2.- SAED diffraction pattern obtained fron Pt/Sn/$ZnAl_2O_4$. Interplanar distances coming from $ZnAl_2O_4$ were detected after analysis. This pattern is typical for the three samples studied and in any case it was not possible to identify reflections coming from platinum or tin partciles.

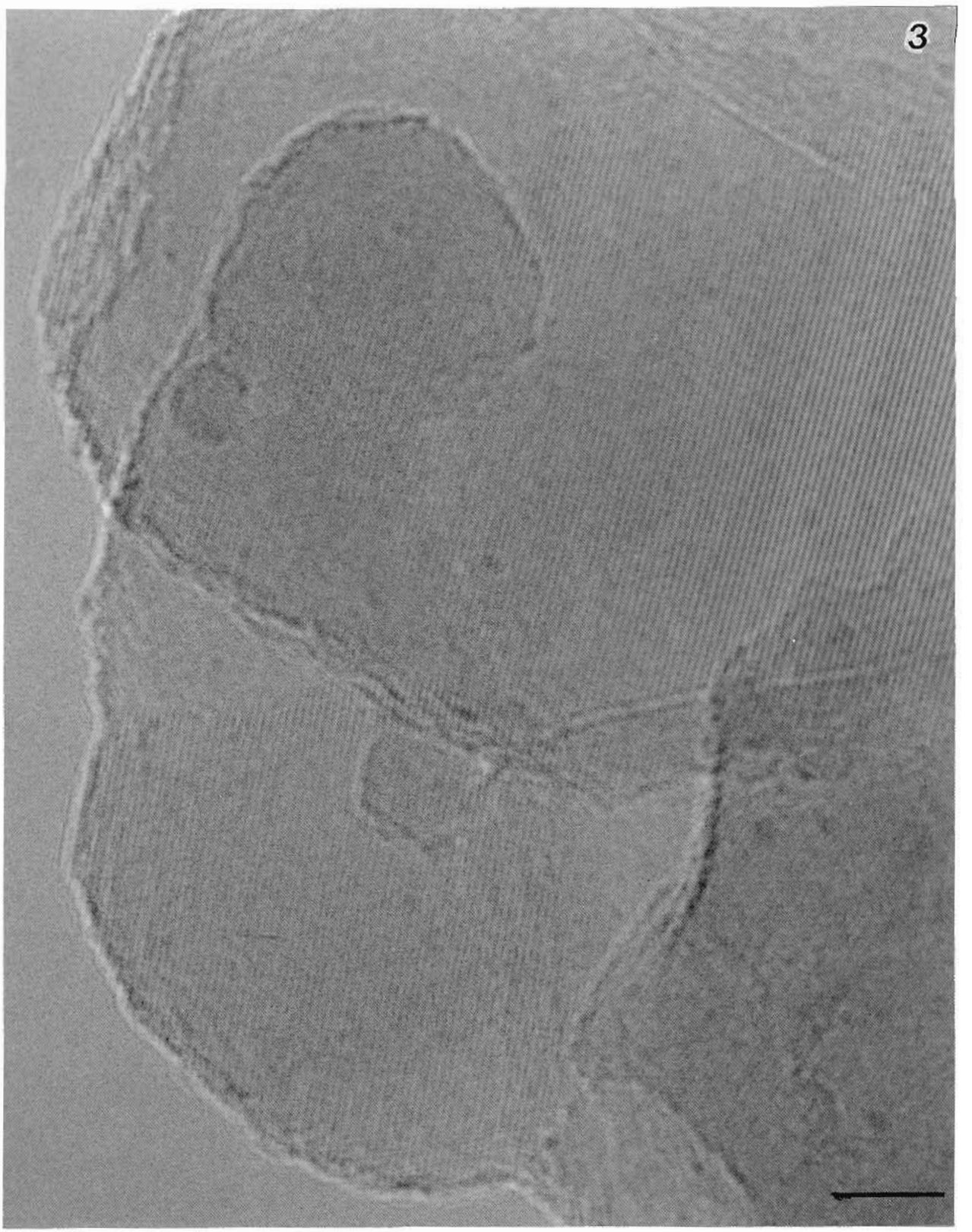

FIGURE 3.- HREM image from Sn/Pt /$ZnAl_2O_4$ sample. Lattice resolution in $ZnAl_2O_4$ crystallites and particle dispersion are observed in extended zones of this sample. Particles size detected in HREM images, runs from 1.2 to 6.5 nm. Bar = 8.5 nm.

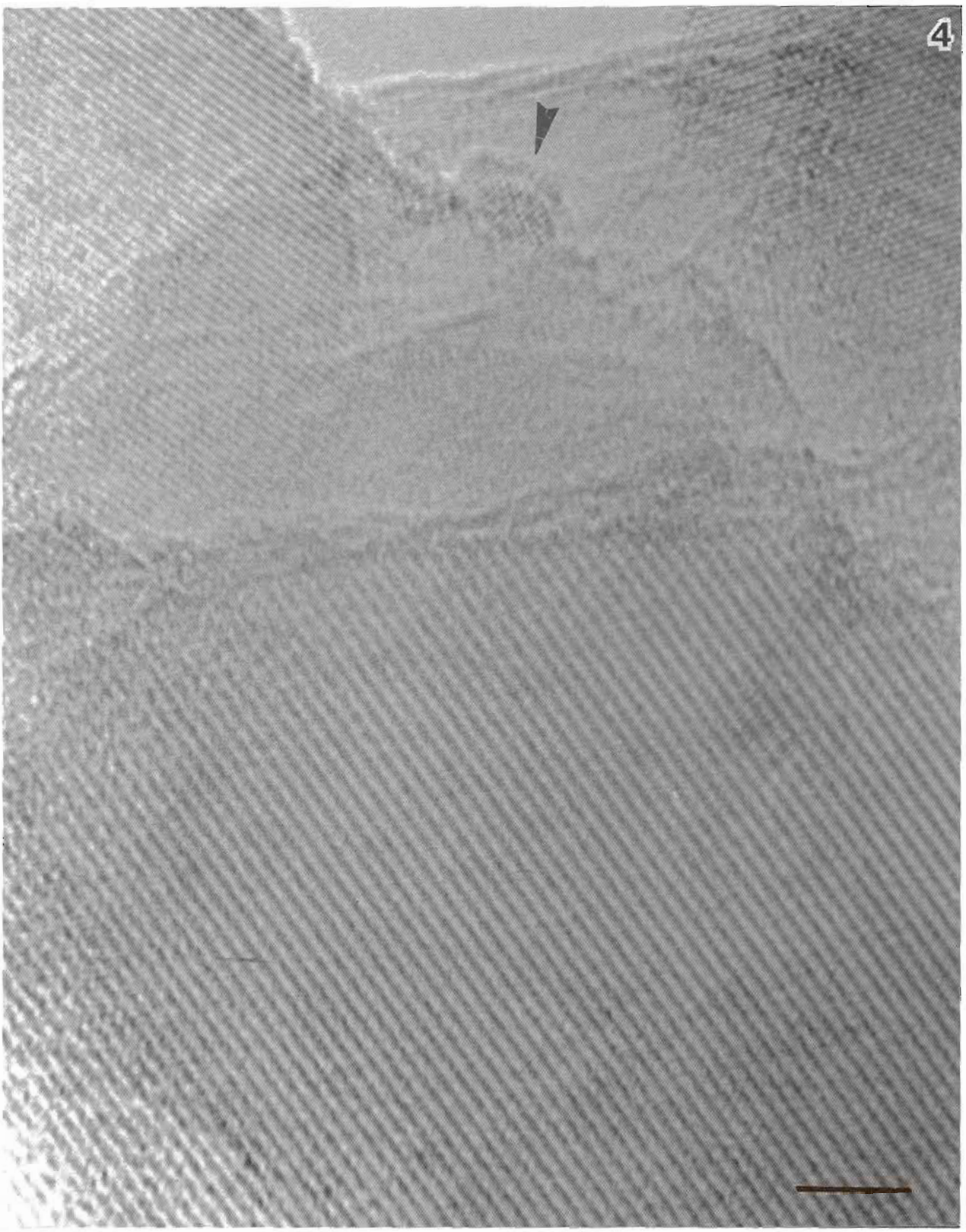

FIGURE 4.- HREM image from $Pt/Sn/ZnAl_2O_4$ sample. Lattice and atomic resolution in $ZnAl_2O_4$ crystallites are observed in this images. Low dispersion of metallic particles was observed in many HREM images. The arrowed big particle shows atomic resolution with interplanar distance d = 0.19 nm but it was not possible to determine if corresponds to aplatinum or a tin particle. Particles size measured in this sample runs from 0.85 nm to 7.0 nm. Bar = 3.2 nm

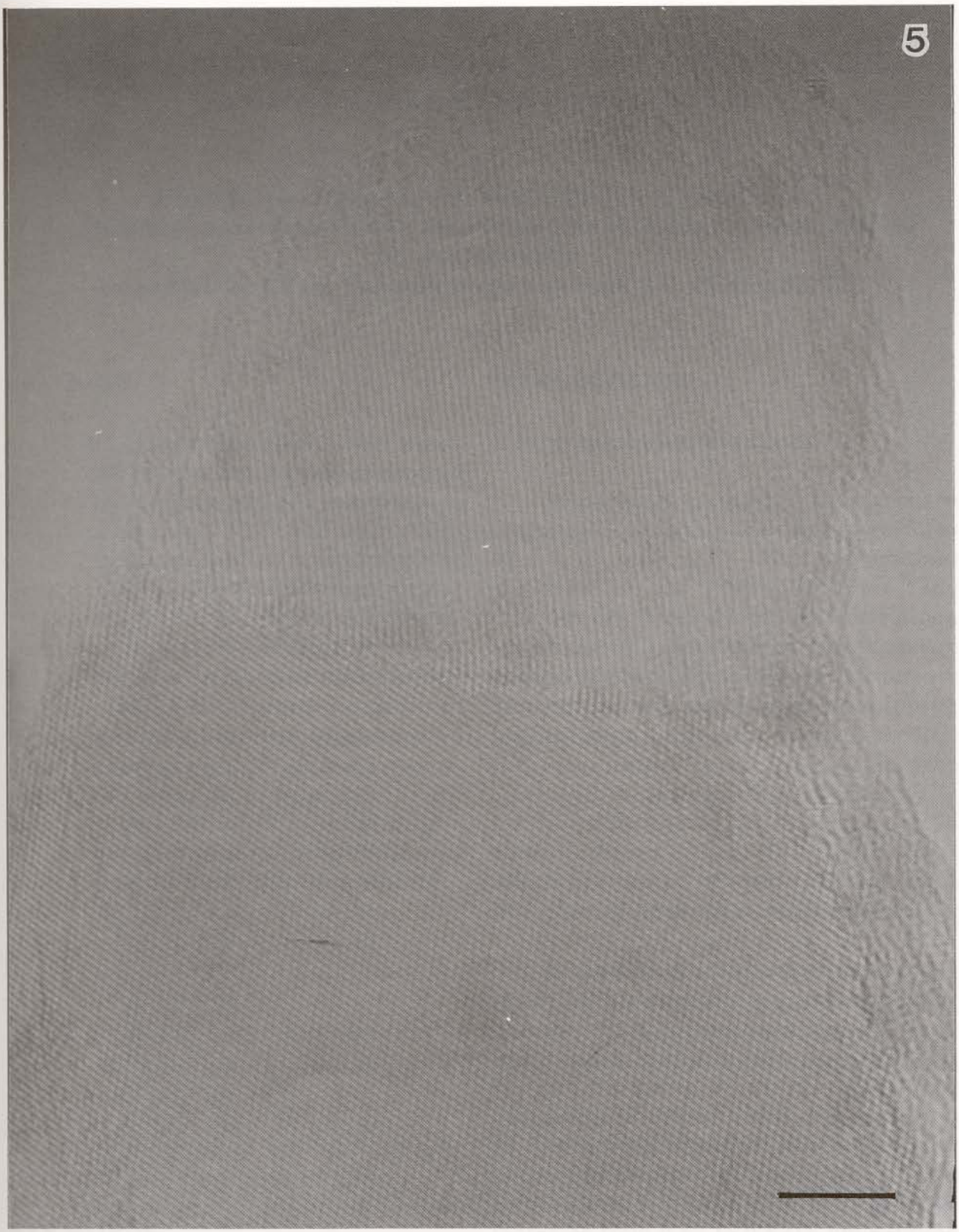

FIGURE 5.- HREM image coming from Pt-Sn/$ZnAl_2O_4$ sample .Lattice and atomic resolution can be observed in coalesced crystallites;dark patches observed over $ZnAl_2O_4$ lattice planes correspond to metallic particles with sizes between 2.3 and 5.5 nm. The transparency of metallic particles is due to image forming conditions.Bar 4.7 nm