

Preparation and Microstructural Characterization of Pt-Pd Bimetallic Catalysts Supported on TiO₂

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ABSTRACT

Nanoparticles, specially metallic nanoparticles finely dispersed onto high surface area supports, play an important role in heterogeneous catalysis because the performance of a supported metal catalyst can be related to design, which is most crucial for the development of novel catalytic processes. It requires some understanding of the mechanism of the catalytic reaction, and knowledge of the crucial properties that determine the activity, selectivity and lifetime of the catalyst. Studies of the interrelationship between structural and chemical properties of solid materials and their catalytic properties. These studies are frequently carried out using specially prepared model catalysts, which are amenable to analysis with modern surface analytical methods providing structural and chemical information on molecular scale, as TEM attach with X-EDS. Various techniques and concepts of solid state and surface chemistry are applied for modifying and synthesizing catalyst materials with the required structural and chemical properties.

In this work, we prepared Pt-Pd bi metallic catalysts by impregnation with chloroplatinic acid and palladium chloride supported on TiO₂.

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

Our interest in Pt-Pd catalysts in skeletal reactions of hydrocarbons has been initiated by both practical and theoretical reasons. Both catalysts, in supported or unsupported forms, are active in skeletal isomerization, C5-cyclization, aromatization, and, to a lesser extent, hydrogenolysis. Of the two metal blacks, Pd was more selective toward C6 product formation from various hexane isomers than Pt[6].

It is well known that supported metal catalyst can exhibit drastically different performances depending on conditions of preparation and treatment.

Catalytic properties of Pt-Pd/TiO₂ for Metileiclopentene conversion (skeletal isomerization and hydrogen transfer) have been studied.

It has been shown that catalytic activity are increased on samples, but at the same time products of the hydrogen transfer reaction seem to be increased too, lowering the selectivity of the reaction: isomerization always predominates.

Keywords: Pt-Pd catalysts, TEM, X-RD, XEDS

1 INTRODUCTION

The physical and chemical properties of nanomaterials rely on their crystal and surface structures. By TEM is demonstrated for characterizing and measuring the thermodynamic, electric, and mechanical properties of individual nanostructures, from which the structure-property relationship can be registered with a specific nanoparticle/structure [1].

The wide application of supported platinum bimetallic catalysts in hydrocarbon conversions has led to intense research on this class of catalysts [1-3]. Compared to the catalysts containing only Pt, bimetallic catalysts are more stable, more selective, and showed higher activity in the conversion of hydrocarbons. A change of bond strength between chemisorbed hydrocarbons and Pt surface atoms due to electron transfer from the promoter to Pt (electronic effect) and a dilution of the Pt surface atoms to decrease the ensemble size by the second metal (geometric effect) have been proposed as reasons for the beneficial effect of the promoter.

Supported metal catalysts are generally comprised of small metal particles (1 – 100 nm in diameter) dispersed on high surface area carrier (e.g. silica). Modern catalyst formulations often include “active” metal (e.g. Pt) combined with other “less active” metals (e.g. Ru, Au, Pd). The second metal can enhance catalyst performance in several ways, such as promote desired reactions, prevent undesirable side reactions, or enhance catalyst longevity.

Titanium dioxide (TiO₂) plays an important part in research of metal oxide surfaces since it was found to be an efficient catalyst for the dissociation of water [45], and it is currently being used in a variety of applications, ranging from gas sensing to photocatalysis. Furthermore it is used as a support material in heterogeneous catalysis and it is

one of the components of the TiO₂-V₂O₅ catalyst that is being used for the reduction.

2 EXPERIMENTAL

Bimetallic catalysts were prepared via wetness impregnation techniques supporting on TiO₂. The TiO₂ was dried at 100°C for 12h prior to impregnation. A series of Pt-M (M = Pd) particles containing a controlled number of metal atoms at designated metal ratios (80, 50, 20% Pt).

We used are precursors H₂PtCl₆.6H₂O and PdCl₂ that, they were dissolved in just enough solvent to fill the pores of the carrier material, the support. The water is then evaporated, leaving only the metal salts on the support. The metal salts are then activated with high temperature treatments under flowing gas. These treatments serve to remove chlorine (a catalyst poison) and produce metal particles.

The impregnated catalysts were dried at 100°C for 12h. The catalyst samples were treated in flowing of O₂, for 2 hr at 400°C, and then reduced in flowing H₂ at the same temperature for 2 hr. After that, N₂ flow was employed. The total flow rate was of 60mL/min with the goal of getting high disperse metals to make them a good catalytic material.

To obtain suitable samples for TEM characterization the as obtained powders were dispersed in isopropanol by ultrasonication. A drop of the solution was then deposited onto a thin holey carbon film supported on a copper microscopy grid (400 mesh, 3.05 mm) and left to dry. The grains of powder containing the metallic particles are well separated and may thus be characterized by TEM. The determination of the size of the particles and their distribution over the supports was performed by TEM imaging, although TEM is unique in identifying and quantifying the chemical and electronic structure of individual nanocrystals. We used a high resolution electron microscope JEOL-2010 to measure the lattice parameters of Pt-Pd on Titania, attachments chemical composition of

these materials were obtained using X-Ray Energy Dispersive Spectroscopy (XEDS).

X-Ray Diffraction (XRD) spectra were obtained using Cu-Kα radiation (α = 1.54 Å). The (111) lattice spacing of the Pt Pd nanocrystals, step-scanning XRD were measured. The step length was 0.01, and the scanning range 2θ from 30 to 90.

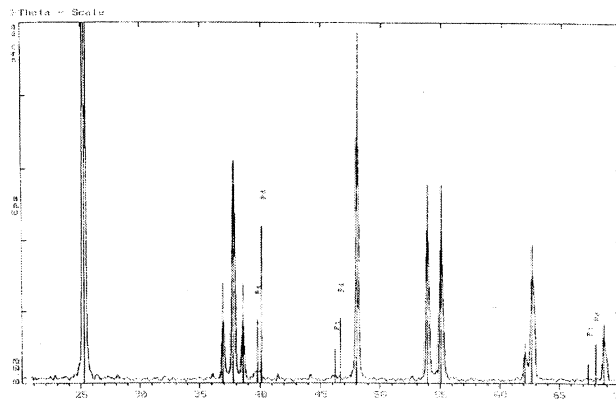


Fig. 1. Presents the XRD of the PtPd/TiO₂.

Catalytic properties of Pt-Pd/TiO₂ for Metilciclopentene conversion (skeletal isomerization and hydrogen transfer have been studied.

It has been shown that catalytic activity are increased on samples, but at the same time products of the hydrogen transfer reaction seem to be increased too, lowering the selectivity of the reaction: isomerization always predominates.

3 RESULTS AND DISCUSSION

The average surface area of the bimetallic catalysts was 46.59 m²/g. This values were measured using an "BET". But the highest area is sample M333, surface area is 89.07 m²/g. We had a good metal dispersion.

Sample	Composition		BET m ² /g	XRD	TEM Pt, Pd	CONVERSION
	Pt	Pd				
M331	20	80	21.32	Pt, Pd, TiO ₂ anatase	2-10 nm	100
M332	50	50	29.4	Pt, Pd, TiO ₂ anatase	2-12 nm	98
M333	80	20	89.07	Pt, Pd, TiO ₂ anatase	2-18 nm	96

Table 1. By X-Ray diffraction (XRD) spectra were obtained using Cu-Kα radiation (λ = 1.54 Å). We found that the starting sample includes anatase and a fraction of rutile phase, in the samples.

Grain size were measured from direct observation by TEM Pt-Pd small nanoparticles were 2nm to 20 and TiO₂ were 200nm. From this results and from HREM observations we concluded that since Pd is not surrounding the particles surface the formation of the oxides due to the treatments in oxygen and further reducing in hydrogen is modifying the active sites for the reaction. This change in morphology and chemical phases due to the treatments of

the particles can be observed in several of the micrographs taken in each step of the oxide-reducing treatments, these changes could explain the variations in catalytic activity of the catalysts.

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

Catalytic properties of Pt-Pd/TiO₂ for Metilciclopentene conversion (skeletal isomerization and hydrogen transfer) have been studied.

It has been shown that catalytic activity are increased on high Pt samples, but at the same time products of the hydrogen transfer reaction seem to be increased too, lowering the selectivity of the reaction: isomerization always predominates. The sample M333 were the most selective toward metilciclopentene in contrast to ciclohexene.

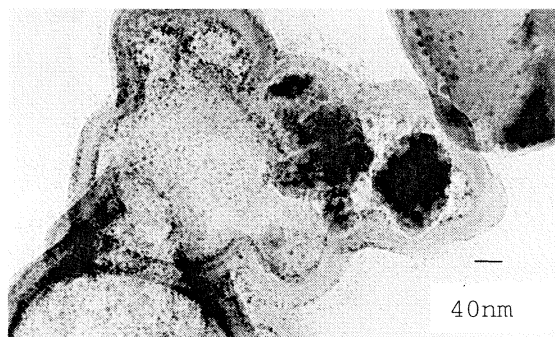


Fig. 2. By TEM Brigh field show TiO₂ around particles 200 nm and PtPd. .Particles around 10nm.

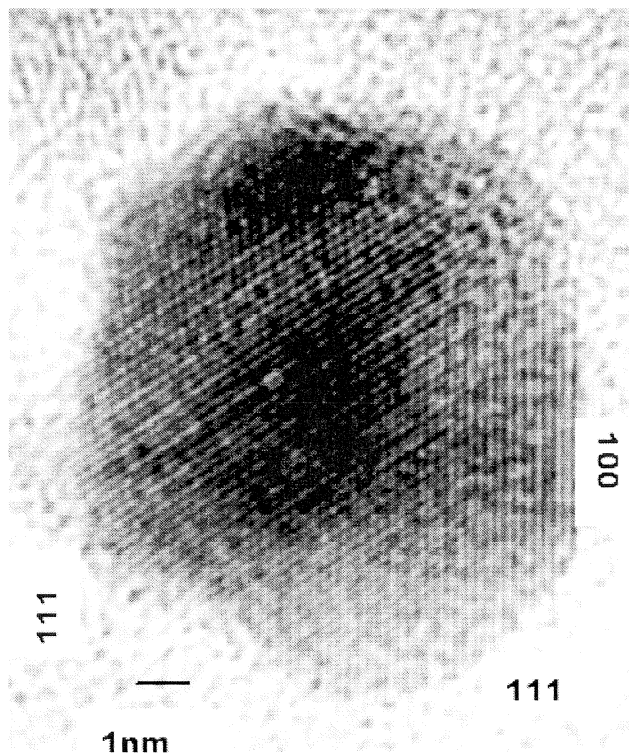


Fig. 3. The high resolution electron (microscopy) HRTEM images of Pt-Pd.

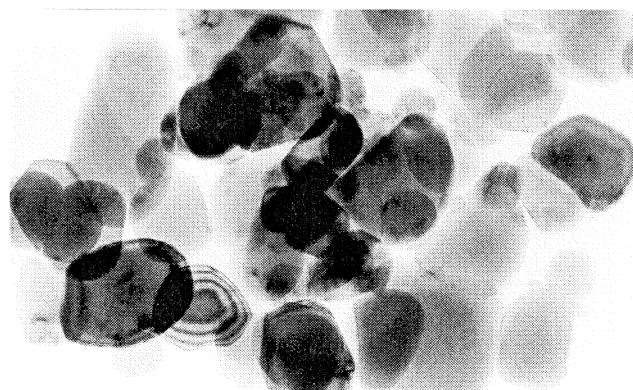


Fig. 4. TEM brigh field shows TiO₂ around particles 200 nm and Pt-Pd and small metallic (Pt-Pd) particles around 20 nm.

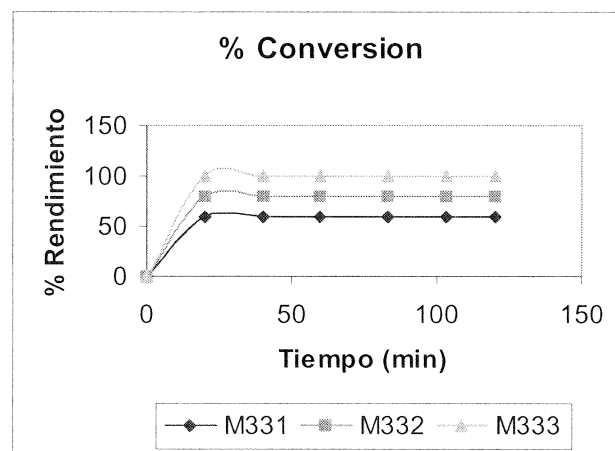


Fig. 5. Pt-Pd/ TiO₂ for Metilciclopentene conversion.

4 CONCLUSIONS

A catalyst that containing a noble metal is effectively catalyzes paraffin isomerization. Concentration of Pt is very active and selective Metilciclopentene conversion in the reaction. Although the position of the sample with composition of 0.8 Pt 0.2 Pd is the most selective in Metilciclopenteno, the second is the 0.5 Pt 0.5 Pd and the last is 0.2 Pt 0.8 Pd. So that Pt in the bimetallic Pt-Pd/TiO₂ catalyst is more selective in isomerization reaction.

Textural and morphological properties were correlated to explain catalytic behavior. Several possible explanations are possible to account for these variations on the activity. Among them are the following:

1. Variations in metal surface area. M331 is different of M332, and M333 to. Each sample had different surface area.
2. Variations in fractions of particular crystal planes produced by these treatments. The particle shapes are closely related to the crystallographic surfaces that enclose the particles. The {111}, {100}, and possibly {110} surfaces of face-centered cubic

structured metal particles. The tetrahedral Pt nanocrystals enclosed mainly by {111} facets have been found to be more stable than the {100} enclosed cubic Pt nanocrystals simply because of the difference in surface energies.[7]

3. Partially oxidized metals remaining after oxidation and low temperature reduction.
4. Variation in the composition metal and irregular surface. When TiO_2 (110) is annealed and the oxide becomes increasingly depleted in oxygen, the equilibrium shapes of islands and vacancy islands change, and one specific step direction becomes strongly favoured over the others. And it is possible in the sample M331 and M332, the nanocluster are formed so that decreased the surface area. The high selectivity and conversion in the sample M333 was for the chemicals and physics characteristics and the high surface area.

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