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Characterization of Pt/HUSY and Pt-Ni/HUSY Catalysts by Transmission Electron Microscopy

Maura H. Jordão[a], *Eduardo Valencia*[b], *Vicemário Simões*[a], *Dilson Cardoso*[b*]

[a]*Departamento de Engenharia Química, Universidade Federal de São Carlos*
C.P. 676, 13.565-905 São Carlos - SP, Brasil
[b]*Universidad Central de las Villas, CUBA*

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Bifunctional catalysts formed by metals (nickel, platinum as well as an association of both metals) supported in an ultrastabilized Y molecular sieve (USY) were prepared. The samples were obtained using a competitive ion exchange method, followed by calcination and reduction of the transition metal under hydrogen atmosphere. The solids were characterized by ICP for their chemical composition, XRD, TEM and the catalytic properties evaluated in the isomerization of the *n*-hexane.

It was observed that the NH_4USY zeolite support presented better ion exchange efficiency in comparison to that of the zeolite HUSY, due to the decrease of the pH of the reaction medium in the last case. The TEM images of the catalysts, obtained in both bright and dark field, showed that the metal particles are dispersed almost inside the molecular sieve micro and mesopores. TEM images of the catalysts obtained in bright field showed that the average particle diameter were 64 and 108 Å for platinum and nickel respectively and about 70 Å when both metals are present.

In the mentioned reaction, platinum catalysts were more active and stable than the nickel ones and the catalysts formed by both metals (0,2%Pt + 0,8% Ni/HUSY) presented the highest activity.

Keywords: *platinum, nickel, zeolite, isomerization, TEM*

1. Introduction

The interest in improving the environmental protection and to promote the efficiency of the automotive motors encourages the formulation of new catalysts and development of new processes for gasoline production. Considering that branched-chain alkanes posses the greatest octane numbers, the use of gasoline containing higher content of these compounds is one alternative to obtain a fuel with the above characteristics[1,2]. Usually, they are obtained by isomerization reactions employing bifunctional catalysts formed by platinum supported over acid zeolites[3-11].

In view of the relative high costs of the platinum catalysts, the aim of this work is to compare the properties of bifunctional catalysts formed by Ni, Pt and Ni + Pt supported in an ultrastable Y molecular sieve (HUSY). Several methods for supporting a metal in the zeolite may be used, but the ion exchange method is the most appropriate since it performs a better metal dispersion, specially when compared to the impregnation method[12,13]. To understand the behavior of the largest activity of the bimetallic catalyst, also observed in other systems[14,15,16], the catalysts were observed by transmission electron microscopy. The objective was to distinguish the metallic particles in the support, in bright field as well in dark field, to determine their medium diameter and the volumetric fraction of the metallic particles on the zeolite support.

2. Experimental

2.1. Catalyst preparation

The supported metal catalysts were prepared starting from a zeolite HUSY (Engelhard, EZ-190P) with a global ratio of Si/Al = 6.0. The framework Si/Al ratio (Si/Al = 11), was calculated from XRD and ^{29}Si MAS-NMR data.

The dispersion of the metal in the zeolite pores was accomplished by competitive ion exchange of the metal complexes ions with NH_4^{+}[17], using the ratios NH_4^{+}/Ni^{+2} = 20 and NH_4^{+}/Pt^{+2} = 10^{18}. The method consisted in the slow addition of an aqueous solution of the metallic precursors to a zeolite suspension in water, with 48 h stirring. The precursors used were $Pt(NH_3)_4Cl_2.xH_2O$ and $[Ni(NH_3)_6]Cl_2$. The suspension was then filtered and washed for the elimination of the ions Cl^-. The chemical

* dilson@power.ufscar.br

composition of the filtrate was analyzed by inductively coupled plasma spectroscopy (ICP) to calculate the metal loading and the exchange efficiency. Samples were prepared with the following metal loading (weight %): 2% Ni; 0,1%Pt + 0,9% Ni; 0,2%Pt + 0,8% Ni and 1% Pt.

The obtained materials were submitted to calcination according to procedure described by Sachtler[19]: heating to a rate of 1 °C/min up to 500 °C and maintaining for 2 h under flow of synthetic air. Then, the metal cations M^{+2} were submitted to reduction process to M^0 under flow of hydrogen at 500 °C for 6 h.

3. Transmission Electron Microscopy (TEM)

3.1. Preparation of the samples

A few milligrams of catalyst powder with particles less 100 nm in size were dispersed in acetone ultrasonically. Then, a drop of this suspension was deposited on the standard grid (2 or 3 mm in diameter covered with a carbon film) and it was examined in the microscope after evaporation of the liquid in a vacuum chamber.

3.2. Analysis for TEM

Observations of the catalyst powder were carried out in a Philips CM-120 transmission electron microscopy with a EDAX CM-120 unit of detection, provided with a silicon detector inside a system submitted under high cryogenic vacuum, which possess a patron window of beryllium of 7.5 micrometers of thickness. The energy dispersive X-ray emission analysis (EDX analysis) were obtained inclining the sample 15-18 degrees in relation to the axis of the door-samples and the axis of the X-ray detector inclined in a constant angle of 20 degrees. The incident beam in each analyzed area had 10-20 nm in diameter and the time of count of the analysis was 100 s.

Bright field electronic micrographs were performed in order to analyze the morphology, particle size and dispersion. Some EDX analysis, corresponding to the particles indicated in the clear field images, accompany the figures.

For the sample 0,2%Pt + 0,8% Ni/HUSY, that presented the largest catalytic activity, a dark field image was obtained taking two reflections of the nickel structure, identified by the position of the objective aperture in the diffraction diagram. From the crystallographic point of view, the great majority of the particles illustrated in bright field belong to the nickel framework (Fig. 2b). As a proof of this statement, when the objective aperture is placed in positions that corresponding to the platinum framework reflections, these particles are not illuminated.

3.3. Catalytic tests

The *n*-hexane isomerization was accomplished in a fixed bed reactor, at 250 °C under atmospheric pressure, maintaining a molar relationship of $H_2/n\text{-}C_6H_{14}$ = 9. The catalysts were activated *in situ* under hydrogen atmosphere at 500 °C. The reaction products were analyzed *on*-line using a LM-1 capillary column (50 m and 0.25 mm i.d.), coupled to a gas chromatograph (VARIAN) provided with flame ionization detector.

4. Results and Discussion

4.1. Catalyst preparation

The ion exchange results showed a low efficiency when performing the exchange of the metallic complex using the zeolite in protonic form. It was observed that the low exchange efficiency was related with the reduction of pH of the reaction medium to the acid range. To reach a higher efficiency it was necessary to make a previous change of HUSY with a solution NH_4Cl (1M) to turn it NH_4USY. After the ion exchange the solids were calcined to remove the ammonium ions and reduced to the metallic form, as described before.

4.2. Characterization by Transmission Electron Microscopy (TEM)

Table 1 shows the metallic particle dispersion for the Ni, Ni + Pt and Pt catalysts. The dispersion was calculated assuming spherical particles, by the expression[20]:

$$D(\%) = \frac{11.57}{d(\text{Å})}\,100$$

It was observed that the average particle diameter of the metal particles was between 110 and 64 Å, and these values belong to the pure Ni/HUSY and Pt/HUSY catalysts, respectively. As the Y zeolite cavity has a diameter of about 13 Å, this indicates that the metallic particles are located not in these cavities, but either in the mesoporous formed during the hydrothermal dealumination of the Y zeolite or at the outer surface of the catalyst grains. Table 1 shows also that the average particle size diminishes as the platinum content increases and, as a consequence, the metal dispersion increases from about 10 to 20%.

From the TEM micrographs in the Figs. 1a, 2a and b and 3a it is possible to observe a significant increase in the number of metallic particles as the Pt content increases. This behavior is specially verified if it is taken in account that the metal content of sample in Fig. 1a (2% Ni/HUSY) is twice higher than the other ones. This indicates that the sample having only nickel was just partially reduced and

Table 1. Metal particle size and dispersion of the catalysts.

HUSY Sample	A	B	C	D
Metal loading	2% Ni	0,1%Pt + 0,9% Ni	0,2%Pt +0,8% Ni	1% Pt
d (Å)	108	77	69	64
D (%)	11	15	17	18

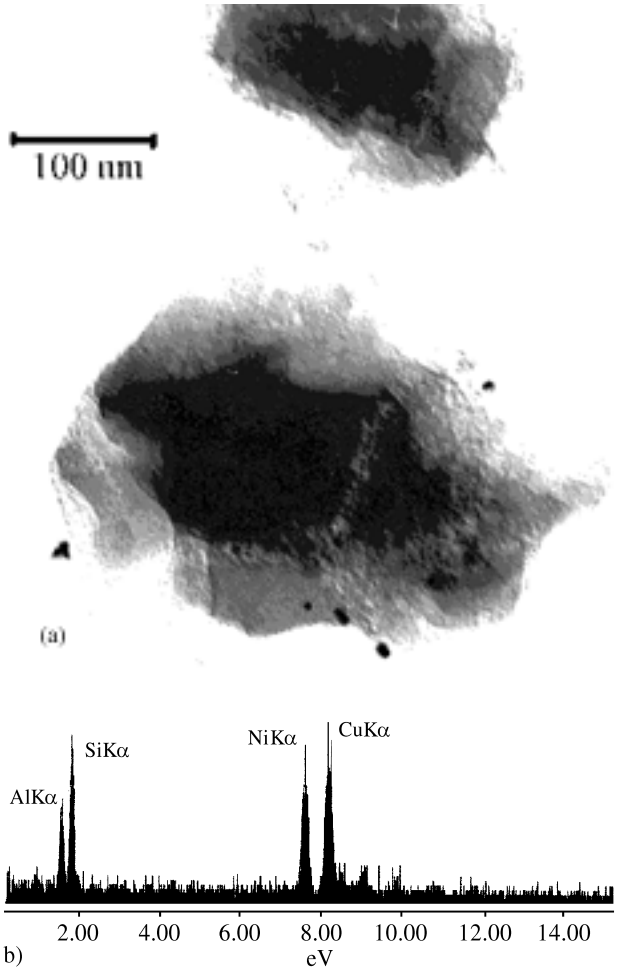

Figure 1. (a) TEM and (b) EDX analysis of 2% Ni/HUSY (sample A).

that the presence of platinum enhances its reduction. The EDX analysis in Figs. 1b and 3b confirms the presence of the nickel and platinum, respectively, in the analyzed particles. The EDX analysis of samples B and C are very similar to Fig. 1b, presenting no peak of Pt. This can be explained due the low intensity of the signal from L shell of this element, as showed by the EDX analysis of the Pt catalyst (Fig. 3b) as well to the low Pt content in these samples.

4.3. Catalytic tests

The activity of the Ni /HUSY catalysts for *n*-hexane isomerization decreases quickly in the first 2 h of reaction. Figure 4 shows the initial activity of Y zeolite catalysts in this reaction containing different nickel and platinum contents. Besides the lower stability, the nickel catalysts were much lesser active compared to the platinum ones: it is necessary about six times more nickel to obtain the same maximum activity as obtained for the platinum catalysts.

Contrarily to the pure nickel catalysts, the activity of those containing both nickel and platinum were very stable

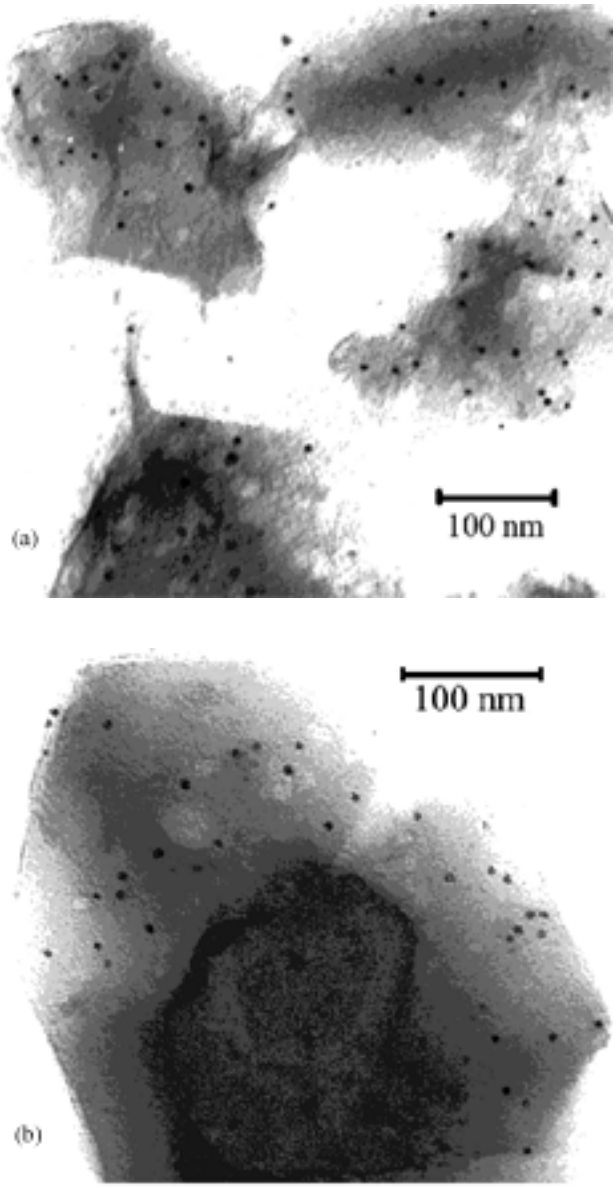

Figure 2. (a) and (b), TEM of samples B and C, respectively.

up to six hours under reaction. Figure 5 shows the initial activity for catalysts containing 1% of metal and different nickel and platinum proportions. The results reveal that the catalyst activity increases very sharply in the presence of small platinum content and the bimetallic catalyst formed by 20% of this metal produces is more active than the pure platinum one.

These results can be explained taking in account at least three factors. Firstly, as already discussed from the TEM results (Table 1), the presence of platinum enhances the reduction of the nickel cations forming more metal particles, decreases its particle size and hence increases the metal dispersion. Secondly, as the nickel particles are not very much active in the *n*-hexane isomerization, the sharp

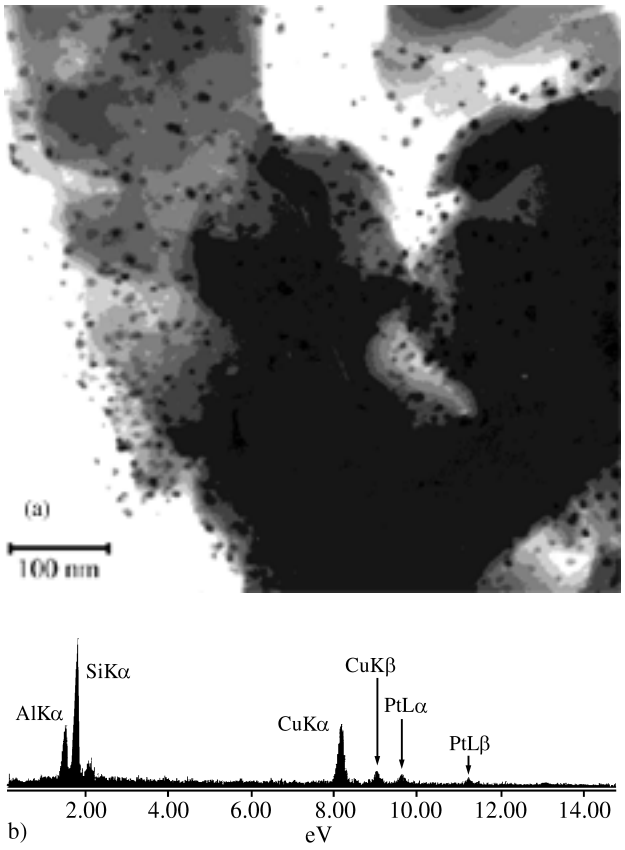

Figure 3. (a) TEM and (b) EDX analysis of 1%Pt/HUSY (sample D).

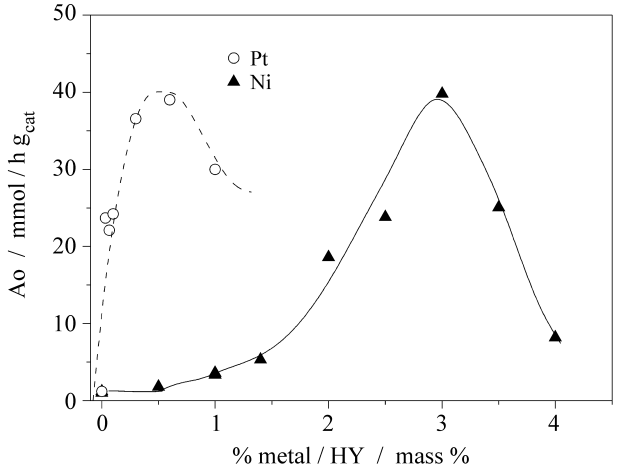

Figure 4. Initial activity (Ao) of catalysts Ni/HY and Pt/HY as a function of the metal content.

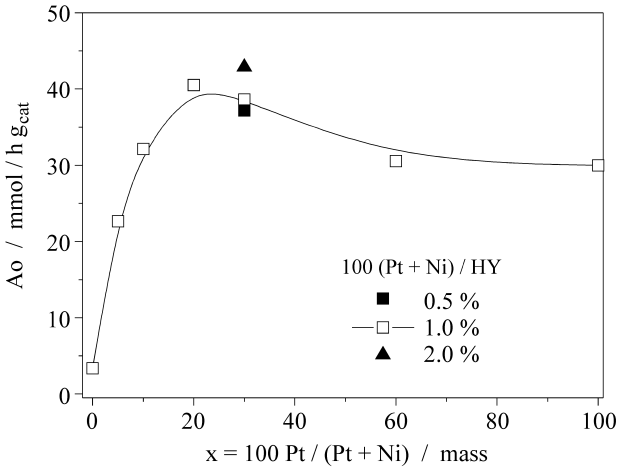

Figure 5. Initial activity (Ao) of catalysts 1% (Ni + Pt)/HY as a function of the platinum percentage.

increase due to the presence of small amounts of platinum suggests that probably this metal is located at the surface the metallic particles. In other words, the nickel particles are serving as support for the platinum atoms and these are responsible for the sharp increase in *n*-hexane isomerization. Finally, the observation that these superficial atoms are more active than the pure platinum catalyst can be explained by an increase of superficial energy in the case of the bimetallic catalysts. The higher superficial energy in the case of the bimetallic catalysts is probably generated due to the difficulty in accommodation of a platinum atoms in a nickel metal particle, considering the differences in their covalent radius (1.30 Å and 1.15 Å for Pt and Ni, respectively). In fact, the nanodifraction analysis of some particles of the bimetallic catalyst (0,2%Pt + 0,8%Ni/HUSY) showed a pattern characteristic for nickel structure, demonstrating that the Pt atoms are inserted in the nickel crystallites.

5. Conclusions

The NH_4USY zeolite presented a better ion exchange efficiency when compared with the zeolite HUSY, due to the stronger decrease in the pH of the reaction medium in the last case. The TEM analysis of Ni/HUSY catalysts reveals that they present very few metallic particles indicating that great part of the nickel cations were not reduced. The presence of small amounts of platinum in the bimetallic catalysts enhances greatly the formation of metal particles and reduces their sizes, pointing out that this metal enhances the nickel reduction.

The catalytic activity and stability of the Ni/HUSY catalysts are very much lower than the Pt/HUSY ones. The presence of small platinum amounts in the bimetallic catalysts enhances sharply both properties and produces catalysts more active than the ones formed by pure platinum. The results can be explained by the location of platinum atoms in the outer surface of the metallic particles. This segregation is probably originated from the covalent radius differences of both metals. These radius differences difficult the accommodation of platinum atoms in the nickel particles, producing energy excess which can be responsible for the higher activity compared to the pure Pt/HUSY catalysts.

Nomenclature

d: Metal particle diameter (Å)
D: Metal dispersion measured by TEM (%)
Ao: Initial activity (mmol h^{-1} g_{cat}^{-1})

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