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# BIMETALLIC Pt-Ni CATALYSTS SUPPORTED ON USY ZEOLITE FOR n-HEXANE ISOMERIZATION

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**Abstract** - Isomerization of linear alkanes has had considerable importance for the refining industry because the isomers formed in this reaction have high octane number. Most works reported in the literature studied the use of bifunctional catalysts, i.e., ones that have acid sites and metallic sites. In this study, bifunctional monometallic (Ni or Pt) and bimetallic catalysts (Pt-Ni), using HUSY zeolite as the support, were prepared in order to verify the role of the metal content and composition on the catalytic properties for n-hexane isomerization. The method used for metal dispersion in the zeolite was competitive ion exchange using ammine complexes [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> and [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> as precursors. Four series of catalysts with constant atomic metal content had total metal amounts between 130 and 280 µmol M/gcat. Catalysts were characterized by temperature programmed reduction (TPR) and subjected to catalytic evaluation for n-hexane isomerization at 250 °C and 1 atm using  $H_2/C_6 = 9$  molar ratio. TPR results show an easier reducibility of  $Ni^{+2}$  cations in the presence of Pt, which was evidenced by the displacement of the reduction peak of those cations towards lower temperatures in bimetallic catalysts. The bimetallic catalysts presented a higher activity in the isomerization of n-hexane when compared to the monometallic ones, as well better stability as the Pt content in the solid increases. The results of the activity as a function of the Pt content in the bimetallic catalysts show a maximum value around 50% of Pt. An addition of Pt above this critical value leads to a small decrease of the catalytic activity.

Keywords: Isomerization; Bifunctional bimetallic catalysts; USY zeolite.

#### INTRODUCTION

The interest in improving gasoline efficiency for automotive engines has been consolidated in the last few years, leading to the development of new processes and new catalysts (Jordão and Cardoso, 2001). One of the most researched processes for this purpose is the isomerization of linear alkanes, which has considerable importance for the refining industry due to the discontinued use of tetraethyl lead and the reduced addition of aromatic compounds to gasoline to mitigate environmental risks (Barsi, 2005). Isomerization results in branched alkane products that have higher octane number compared to linear alkanes.

Bifunctional catalysts have been used by the oil refining industry to isomerize linear alkanes. Those catalysts are normally made from platinum (metallic function) and supported on alumina with acidic properties, including chlorinated or fluorinated alumina (Jordão and Cardoso, 2001).

It has also been reported that, by replacing amorphous supports with crystalline materials, such as zeolites, some significant advantages can be added to catalysts, such as higher activity during reaction, improved selectivity due to the higher density of acidic sites present in the zeolite, and additional resistance to poisoning by sulphur (Jordão and Cardoso, 2001).

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To obtain branched isomers, Pt catalysts were frequently supported on solid acids (Guisnet, 1991; Otten, 1994; Zhan, 1994; Alvarez, 1996; Lee and Rhee, 1997; Chica and Corma, 1999). In the studies undertaken in this laboratory, bimetallic Pt-Ni catalysts were supported on HUSY zeolite, and the insertion of a second metal onto the zeolitic support (forming bimetallic catalysts) has proven to cause a significant increase to catalytic activity and selectivity for the formation of branched isomers (Jordão and Cardoso, 2001; Yoshioka, 2005; Jordão, 2000; Jordão, 1999).

In order to identify the changes caused in the properties of these solids by the insertion of a second metal, some special characterization techniques were used, since they allow us to directly or indirectly correlate the changes in these properties with the catalysts performance. A widely used technique to characterize transition-metal-containing catalysts is temperature programmed reduction (TPR).

Because cation reducibility in the zeolite depends essentially on its reduction potential and on its interaction with the zeolite (Figueiredo and Ribeiro, 1987), from TPR profiles it is possible to infer the different degrees of reduction of metallic ions and their location in the zeolitic cavities. This information is important to know because it indicates whether the metallic ions are available for reduction and the resulting particles for n-hexane isomerization.

It was observed that, for Pt-Ni catalysts supported on Y zeolite, ions located in large cavities are even more easily reduced than the ones located in small cavities in this zeolite (Jordão and Cardoso, 2001). Additionally, easier Ni reduction takes place when Pt is present, evidenced by the shift of Ni<sup>+2</sup> reduction peaks to lower temperatures.

Most studies (Jordão and Cardoso, 2001; Jordão, 2000; Jordão, 1999; Melo, 2002) on bimetallic catalysts were undertaken at a constant mass content, which may lead us to misleading conclusions (Jordão and Cardoso, 2001) because, for the Pt-Ni pair, the atomic weights of the two metals are very different (195.09 versus 58.71). Previous results obtained in this laboratory (Yoshioka, 2005) using constant molar metal content and Y zeolite with Si/Al=11 showed that there is a maximum activity of these bimetallic catalysts when the Pt/Ni ratio approaches one.

Therefore, to continue our previous studies (Jordão and Cardoso, 2001; Yoshioka, 2005; Jordão, 2000) and also in the best interest of understanding zeolite supported Pt-Ni systems, the objective of this study is to assess the influence of the metal content

and its composition on the catalytic properties of n-hexane isomerization, using a zeolite with Si/Al = 4.6.

#### **EXPERIMENTAL**

#### **Starting Material**

The starting material used to prepare all the catalysts was HUSY zeolite, with a Si/Al framework ratio equal to 4.6 and a bulk Si/Al ratio of 2.7, supplied by Petrobras.

#### Ion Exchange

The zeolite was submitted to ion exchange at room temperature with NH<sub>4</sub><sup>+</sup> ion solution to change its protonic form (HUSY) to ammonium (NH<sub>4</sub>USY) zeolite. This prior ion exchange process was applied to increase efficiency during the subsequent competitive ion exchange process with metallic ions.

## **Monometallic Catalysts**

Precursors of Ni containing catalysts supported on NH<sub>4</sub>USY were obtained by competitive ion exchange involving metallic complex cations  $[Ni(NH_3)_6]^{+2}$  and  $NH_4^+$  ions. For this purpose, we prepared a 0.05 mol.L<sup>-1</sup> solution of the  $[Ni(NH_3)_6]Cl_2$ complex containing NH<sub>4</sub><sup>+</sup> ions to achieve a NH<sub>4</sub><sup>+</sup>/[Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>+2</sup> molar ratio equal to 20. To perform this exchange, this solution was added slowly (0.2 mL.min<sup>-1</sup>) under stirring and at room temperature to a NH<sub>4</sub>USY zeolite suspension with sufficient water volume to reach 0.005 mol.L<sup>-1</sup> as the final concentration of [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>+2</sup> cation. After the exchange period of 1 hour under stirring, the solid was filtered, washed with deionized water, and dried at 110 °C for 2 hours. To determine the actual content of these metals in the solid, the filtrate obtained from each catalyst exchange was collected and then a metal analysis of this solution was performed using atomic absorption spectrophotometry.

For precursors containing only Pt supported on NH<sub>4</sub>USY, we used the same methodology described before to obtain Ni containing catalysts. However, we used a solution containing NH<sub>4</sub><sup>+</sup> ions and  $[Pt(NH_3)_4]^{+2}$  at a NH<sub>4</sub><sup>+</sup>/ $[Pt(NH_3)_4]^{+2}$  molar ratio equal to 10.

#### **Bimetallic Catalysts**

To obtain precursors of bimetallic catalysts containing Pt-Ni, two solutions were initially

prepared: one containing the [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> complex and the other containing the [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> complex, which were simultaneously added to a NH<sub>4</sub>USY zeolite suspension in water using the same methodology used to obtain the monometallic catalysts described above. After stirring for 1 hour, the solid was filtered and washed with deionized water, and dried at 110 °C for 2 hours.

#### Calcination

After their preparation, the precursors were calcined to remove ligands coordinated to the metal and to decompose NH<sub>4</sub><sup>+</sup> cations of the ammonium zeolite (NH<sub>4</sub>USY), and also to achieve Brønsted (HUSY) acid sites using the same conditions employed by Jordão (2000). The samples were heated at 10°C.min<sup>-1</sup> between room temperature and 100°C under N<sub>2</sub> flow (100 cm<sup>3</sup>.min<sup>-1</sup>/g<sub>cat</sub>) remaining constant at the latter temperature for 1 h. Then, they were submitted to air flow (100 cm<sup>3</sup>.min<sup>-1</sup>/g<sub>cat</sub>) and the temperature was increased from 100°C to 500°C at 2°C.min<sup>-1</sup>. Once the temperature of 500°C was achieved, the samples were kept at this temperature under air flow for a period of 2 h. Thus, the calcination process was completed.

## **Catalytic Tests**

Before carrying out the catalytic experiments, 100 mg of the calcined precursor samples were reduced "in situ", using the same conditions as Jordão (2000): temperature of 500°C for 6 hours under 55 mL.min<sup>-1</sup> hydrogen flow, at STP and 2°C.min<sup>-1</sup> heating rate. The catalysts' stability and activity were measured during the period of 6 hours of reaction using a fixed bed microreactor. The reaction was n-hexane isomerization at 250°C and 1 atm pressure. Hydrogen and n-hexane were fed to the reactor at 55 mL.min<sup>-1</sup> and 2 mL.h<sup>-1</sup>, respectively, giving a molar feeding ratio of 9:1 hydrogen/n-hexane.

#### **Temperature Programmed Reduction (TPR)**

Before the TPR analysis, 150 mg of catalyst was pre-treated "in situ" in a Micromeritics Pulse Chemisorb, model 2705, heated up to 200°C, at the rate of 10°C.min<sup>-1</sup>, and then kept at this temperature for 1 hour under a nitrogen flow of 30 mL.min<sup>-1</sup>. After being pre-treated, the sample was allowed to cool to 25°C and then submitted to a gas mixture containing 5,1% of hydrogen (v/v) in nitrogen under a flow of 30mL.min<sup>-1</sup> and the temperature increased

to 1000°C at the heating rate of 10°C.min<sup>-1</sup>. The sample was kept at 1000°C for 1 minute.

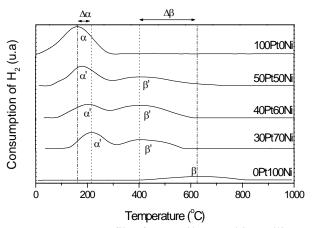
# **Transmission Electron Microscopy (TEM)**

The analysis was carried out in a Jeol model 2010 Transmission Electron Microscopy using the catalyst sample containing 50Pt50Ni with a total metal content of 230  $\mu$ mol M.g<sub>cat</sub><sup>-1</sup>. Before performing the analysis, the catalyst sample was reduced and transferred to an Eppendorf containing n-heptane.

#### RESULTS AND DISCUSSION

Figure 1 shows the profile of the Temperature Programmed Reduction (TPR) obtained for Pt-Ni/HUSY bimetallic catalysts with a total metal content in the solid of 280  $\mu$ mol M/g<sub>cat</sub> and at different Pt-Ni ratios.

In Figure 1, two different peaks obtained during TPR can be seen. Peak  $\alpha$ , found in the platinum monometallic catalyst (100Pt-0Ni), can be related to Pt<sup>+2</sup> cations that are predominantly found in the large zeolite cavity. Most of these cations reduce at approximately 200 °C. In the presence of Ni<sup>+2</sup>, this peak, indicated by  $\alpha$ ', moves to higher temperatures as the amount of this cation increases. This shift to higher temperatures is related to the reduction of these two cations in the large  $\alpha$  zeolite cavity: Pt<sup>+2</sup> and Ni<sup>+2</sup>, as explained in more details below (Jordão, 2007).



**Figure 1:** TPR profiles for Pt-Ni/HUSY bimetallic catalysts, with total metal content in the solid of 280 μmol M.g<sub>cat</sub><sup>-1</sup>, at different Pt/Ni ratios.

On the other hand, by comparing to the Ni monometallic catalyst reduction profile, the influence of the platinum content on bimetallic

catalysts can be clearly seen, since the platinum helps the nickel reduction process. This occurs because the platinum cation is easily reduced and creates metallic sites that dissociate hydrogen molecules into atomic hydrogen, as stated by Jordão (2007) and Feeley and Sachtler (1990), this latter in the case of metallic Pd. Atomic hydrogen, in turn, reduces  $\mathrm{Ni}^{+2}$  cations more rapidly than molecular hydrogen, thus decreasing the temperature (Jordão, 1999). Figure 1 shows the shift of  $\mathrm{Ni}^{+2}$  cation  $\beta$  peaks to lower temperatures ( $\beta$ '), as well as the shift of the  $\mathrm{Ni}^{+2}$  cation  $\alpha$ ' peak, which is located in the large zeolite cavity, as the platinum ratio in the solid increases.

The TPR curves in Figure 1 also show that, although the content of transition metal cations remains constant during the experiments (same mass of the precursor with 280 µmol M<sup>+2</sup>/g<sub>cat</sub>) the area of hydrogen consumption decreases with the increase of the content of Ni<sup>+2</sup>. As explained above (Jordão, 2007; Feeley and Sachtler, 1990), as the content of the more easily reducible cations decreases (Pt<sup>+2</sup> or Pd<sup>+2</sup>, respectively) the difficulty of reducing the Ni<sup>+2</sup> increases. Therefore, the reduction of the Ni cations is shifted to higher temperatures, which facilitates the migration of Ni<sup>+2</sup> to positions were they cannot

<u>0.2 μm</u>

**Figure 2:** Micrographs of sample 50Pt50Ni with total metal loading of 230 $\mu$ mol  $M.g_{cat}^{-1}$ .

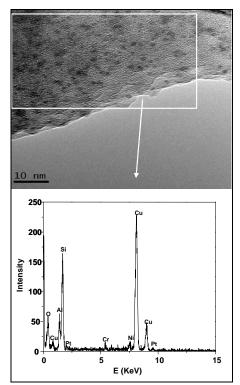
be reduced (sodalite cages and hexagonal prisms). Consequently, the hydrogen consumption decreases.

The same behavior was noticed for other total metallic contents used (130, 180 and 230  $\mu$ mol M/g<sub>cat</sub>). However, those results are not shown in this present work.

Figures 2 and 3 show micrographs obtained by high resolution electron microscopy of the 50Pt50Ni bimetallic catalyst with a metal loading of 230 µmol of M.gcat<sup>-1</sup>. Figure 3 also shows an EDX analysis in one region of the sample.

The metal particles found in Figures 2 and 3 present diameters in the range of 20Å that are very well distributed along the catalyst grain. This diameter means that the observed metal particles are outside the zeolite cavities, which in the FAU structure have the maximum value of 13Å. Nevertheless, in our opinion, it is likely that there are smaller metal particles, which are not detectable through TEM, inside of the cavities.

The chemical analysis of the region indicated in Figure 3, obtained with the help of EDX analysis, shows the presence of both metals, Pt and Ni. In this Figure, the signals of the metals Cr and Cu are formed from the sample holder and those of Si and Al from the zeolite.



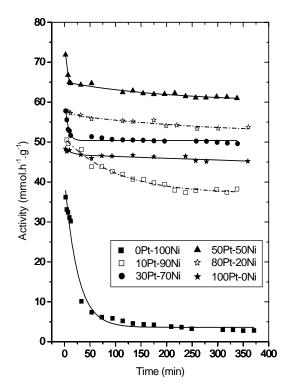
**Figure 3:** Micrograph and EDX analysis of sample 50Pt50Ni with a total metal loading of 230μmol M.g<sub>cat</sub><sup>-1</sup>.

Figure 4 shows the activities in the isomerization of n-hexane during 6 hours of Pt-Ni catalysts supported on HUSY zeolite with different Pt/Ni ratios and a total metal content of 180 µmol M/g<sub>cat</sub>.

Figure 4 shows that the nickel monometallic catalyst (0Pt-100Ni) presents low activity for n-hexane isomerization. This nickel monometallic catalyst behavior may be explained based on the greater difficulty to reduced Ni<sup>+2</sup> cations, that is, not enough nickel metallic sites may have been formed in the reaction.

Another hypothesis (Jordão and Cardoso, 2001) for such a low Ni monometallic catalyst activity would be the fact that the metallic nickel does not have a high dehydrogenating capacity and, since the isomerization includes a dehydrogenation step, there would be a limitation of the Ni monometallic catalysts activity for n-hexane isomerization.

Figure 4 also shows the catalyst stability versus reaction time. There is also an increased catalyst stability as the platinum content increases. The low stability for catalysts with higher nickel content may be explained by the Ni tendency to polymerize olefins and form coke (Jordão and Cardoso, 2001). This same behavior was also observed for the curves equivalent to other total metal contents (130, 230 and 280 μmol M/g<sub>cat</sub>).



**Figure 4:** The activity of catalysts with  $180 \mu mol M/g_{cat}$  during 6h reaction.

Figure 5 shows results of the initial activity,  $A_0$ , of Pt-Ni/HUSY catalysts with total metal contents of 130, 180, 230 and 280  $\mu$ mol M/g<sub>cat</sub>. These initial activities were estimated by the extrapolation of the activity curves (as shows in Figure 4) to zero time on stream using a second order exponential decay function, shown in Equation 1.

$$A_0 = y_0 + A_1 e^{-x/t1} + A_2 e^{-x/t2}$$
 (1)

The initial activity  $A_0$  is shown in Figure 5 as a function of the platinum fraction in the bimetallic catalyst. This Figure shows an interesting behavior of bimetallic catalysts when compared monometallic ones: nickel monometallic catalysts show low activity for n-hexane isomerization and this activity tends to increase with the platinum content. Therefore, it is expected that platinum monometallic catalysts would be the most active, but this is not what was actually observed. It is clear that the activity increases almost linearly with the platinum content in the catalyst of up to a maximum of 50% for the catalysts with more than 130 µmol M/g<sub>cat</sub>. For higher Pt percentage, there is a drop in the activity when more platinum is added to the catalyst. This behavior was noticed for every total metallic content studied (130, 180, 230 and 280 μmol M/g<sub>cat</sub>), but it is even more evident for catalysts having higher metallic contents.

This behavior has been reported in previous studies (Jordão and Cardoso, 2001; Yoshioka, 2005; Jordão, 2000; Melo, 2002) and, according to Jordão and Cardoso (2001), the presence of two metallic species supported on the zeolite leads to solids with a better catalyst performance than a monometallic catalyst. This is true even if the metal has a high activity, which is the case of pure Pt, evidencing that bimetallic catalysts have properties that are different from those of monometallic catalysts. These results indicate that bimetallic catalysts have high potential because they are more cost-effective than a catalyst made up of only one highly active noble metal.

Some hypotheses may be developed to explain the better activity of bimetallic catalysts compared to monometallic ones. One hypothesis is the fact that, for bimetallic catalysts, Pt particles helped reduce Ni<sup>+2</sup> cations, as observed through the characterization using temperature programmed reduction (TPR).

The presence of a maximum activity and its decline when the platinum content is increased above 50% may be also related to metal dispersion in the zeolite. As reported in previous studies (Jordão and Cardoso, 2001; Jordão, 1999), throughout the

reduction process, the formation of metallic platinum is influenced by the presence of nickel, leading to a reduction in the average size of the particles. For this reason, bimetallic catalysts Pt-Ni/HUSY have particles smaller than monometallic Ni/HUSY and Pt/HUSY, and they have better dispersion for metallic function, which would explain their higher activity for n-hexane isomerization.

Additionally, results reported by Jordão (1999, 2001) using different characterization techniques indicate that an interaction between the platinum and nickel atoms in the metallic particles is established, leading to changes in the physical, chemical, and catalytic properties. TEM (Transmission Electron Microscopy) results suggest the formation of bimetallic (Pt-Ni) particles, in which the nickel crystallographic parameters are preserved. As a result, it was concluded that platinum atoms, by accommodating in the nickel framework, will have higher surface energy, which could help them become more active in bimetallic systems (Pt-Ni).

Yoshioka (2005) also obtained similar behavior of activity as function of %Pt in the isomerization of n-hexane when using a FAU zeolite with lower aluminum content (Si/Al = 11), as shown in Figure 5. Using hydrogen chemisorption, it could be verified that the dispersion degree of the metallic particles reaches a maximum as the Pt content increases, which explains the activity behavior of both FAU catalysts.

Figure 5 also shows that, as expected, catalysts with total metal content of 180 µmol M/g<sub>cat</sub> are more active than catalysts with total metal content equal to 130 µmol M/g<sub>cat</sub>. Jordão (1999) suggests that this increased activity along with the metal content is due to the fact that there are a number of acid sites available in HUSY zeolite. Therefore, as the total metal content increases, the catalyst activity should also increase since the catalyst has a greater number of metallic sites up to the point where acid sites become limiting. In fact, increasing the metal content to 230 µmol M/g<sub>cat</sub> the catalyst activity does not increase significantly when compared to the catalyst with metal content of 180 µmol M/gcat. However, increasing the metal content to 280 µmol M/g<sub>cat</sub>, there is no difference between the activities if compared to the catalyst with 230 µmol M/gcat. Consequently, the catalysts with 280 µmol M/gcat should have an excessive amount of metallic sites, considering that the number of acid sites remains the same. Such behavior indicates that a catalyst with metal content of 230 µmol M/gcat reached a balanced proportion between the metallic and acid sites, as proposed by Alvarez (1996). Therefore, the n-hexane

isomerization step performed at acid sites becomes the limiting step to the process and, if the catalyst acidity could somehow be increased, this activity would also tend to grow.

Figure 6 shows the selectivity of bi-branched products as a function of the platinum proportion in the solid, for total metal contents of 130, 230 and 280  $\mu$ mol M/g<sub>cat</sub>, measured at low and approximately constant conversions (between 20 and 30%). As can be seen, bi-branched selectivity curves for metal contents of 130  $\mu$ mol M/gcat and 230  $\mu$ mol M/gcat are higher for Ni monometallic catalysts than Pt-Ni catalysts and this selectivity of the products of interest reduces as the platinum content increases in the solid.

On the contrary, increasing the metal content to  $280 \mu mol \ M/g_{cat}$ , the selectivity of bi-branched does not change significantly as the platinum content increases.

Comparing these catalysts with different metal contents, it can be seen that the selectivity of bibranched products increases with catalysts total metal content ( $280 > 230 > 130 \mu mol M/g_{cat}$ ). Such behavior was also found by Yoshioka (2005) for total metal contents of 130 and 180  $\mu mol M/g_{cat}$  using a USY zeolite with a higher Si/Al ratio (11.0).

Figure 7 shows the yield of bi-branched isomers for mono and bimetallic catalysts, at zero reaction time, as a function of the platinum content in the solid, for the total metal contents of 130, 180, 230 and 280 µmol M/g<sub>cat</sub>. The importance of this calculation is related to the higher octane number in these isomers when compared to mono-branched ones. Since the selectivity of dibranched hexanes does not change considerably with %Pt in the catalyst (Figure 6), the behavior of the yield in these compounds is similar to that of the initial activity (Figure 5).

As it can be seen in Figure 7, bi-branched yield is influenced by the total metal content in the solid and by the platinum to nickel ratio in the solid. The observed maximum yields at approximately 40-50 Pt % for all metal contents in the catalyst was also reported by Yoshioka (2005) and it means that the maximum yield occurs when the metals have similar molar proportions in the catalyst.

This maximum bi-branched isomer yield is very promising because there is a large difference between the octane number of bi-branched and the mono-branched isomers. As a consequence, although it was considered that there is no advantage in increasing a catalyst total metal content to achieve increased catalytic activity (Figure 5), it is worthwhile to increase it to achieve a higher yield of bi-branched isomers (Figure 7).

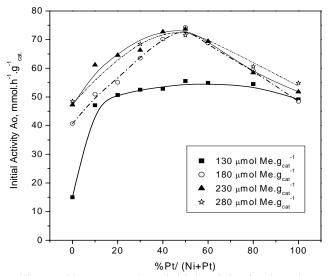


Figure 5: Bimetallic Pt-Ni/HUSY catalysts initial activity for the n-hexane isomerization.

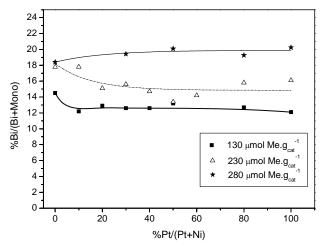
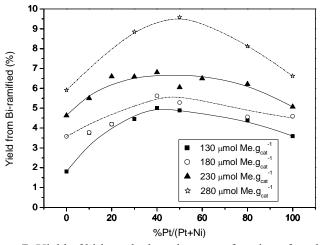


Figure 6: Selectivity for bi-branched products as a function of total cations and Pt ratio in the solid.



**Figure 7:** Yield of bi-branched products as a function of total metal content and Pt ratio in the solid, at zero time on stream.

#### CONCLUSIONS

The profiles obtained from TPR suggest that, for bimetallic catalysts, the presence of platinum facilitates the reduction of Ni<sup>+2</sup> cations. This occurs due to the fact that the platinum cation is reduced first, creating metallic sites that dissociate hydrogen molecules into atomic hydrogen.

The catalytic tests show that the presence of platinum in Ni-containing catalysts increased the catalytic activity, reaching the maximum value when Pt content is equal to or higher than 50%. On the other hand, the catalytic activity for n-hexane isomerization and the yield to bi-branched isomers is improved as the total metal content in the solid increases.

The nickel mono-metallic catalysts are more selective for bi-branched isomers, despite having a very low catalytic activity. When platinum is added to the catalyst, the maximum activity and good selectivity for bi-branched isomers are achieved.

Therefore, Pt-Ni bimetallic catalysts are better than mono-metallic catalysts because they have higher activity and better selectivity for bi-branched isomers.

#### **ACKNOWLEDGEMENTS**

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