

N-Hexane Isomerization on Ni-Pt/Catalysts Supported on Mordenite

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Received August 7, 2013; revised September 5, 2013; accepted September 17, 2013

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ABSTRACT

The aim of this work was to evaluate the catalytic properties for n-hexane isomerization of bifunctional monometallic (Ni or Pt) and bimetallic catalysts (Pt-Ni), using HMOR zeolite as support. The method used for metal dispersion in the zeolite was competitive ion exchange using ammine complexes $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ as precursors. The catalysts were characterized by X-Ray diffraction, X-Ray energy dispersion spectroscopy, temperature-programmed reduction and transmission electron microscopy. The n-hexane isomerization reaction using the catalysts was carried out to evaluate the catalyst activity. The reaction was carried out in a fixed bed reactor operating at 250°C, 1 atm, $\text{H}_2/\text{C}_6 = 9$ molar ratio. The profiles obtained from TPR suggest that, for bimetallic catalysts, the presence of platinum facilitates the reduction of Ni^{2+} cations. 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.

Keywords: N-Hexane; Isomerization; Mordenite; Nickel; Platinum

1. Introduction

Several factors determine gasoline quality. One of the key specifications of gasoline is the octane number, which corresponds to the fuel knocking (self-igniting) property in internal combustion engine. High octane numbers correlate to a low knocking intensity that is related to good engine performance [1].

Usually branched paraffins have higher octane numbers than corresponding linear paraffins. For example, linear hexane has an octane number equal to 25, while 2,2-dimethylbutane, an hexane isomer, has an octane number equal to 92. For that reason, isomerization of linear paraffins, a process in which straight-chain hydrocarbon molecules rearrange to form branched hydrocarbons, is used to improve gasoline quality [2].

Commonly, users of paraffin isomerization technology had the choice between robust zeolite based systems [3-8]. While zeolite catalysts are characterized by their outstanding tolerance of feedstock poison such as sulphur and water—this is particularly true for Sud-ChemieHysopar

catalyst that operates commercially at sulphur levels exceeding 100 ppm—the chlorinated catalysts suffer from extreme sensitivity to all kinds of feed contaminants [9].

The cases of Mordenite zeolite are employed in relatively high temperature (250°C) necessary to form the carbocationic isomerization reactions C5/C6 that the case of long paraffins such as n-heptane ends cracking occurring faster than favoring the formation of coke and avoids getting high fractions of branched isomers [10,11].

These catalysts are bifunctional, *i.e.* they consist of a metal supported on a zeolite, and since the reaction, and mechanism requires the dehydrogenation of the initial alkane to form an intermediate alkene. This alkene can then proceed through a carbocationic intermediate either to yield the isomerized products or to undergo cracking through a B-scission to give unwanted gaseous products [12,13]. For this kind of bifunctional catalysts, Guisnet *et al.* [14] estimated an optimum in the number of acid sites per available platinum atom 6. If this ratio is exceeded, the cracking reaction will be favored. Moreover, those catalysts without a proper balance between the metallic

and acid functions are expected to follow an alternative mechanistic pathway involving bimolecular intermediates [12].

The second ingredient of bifunctional catalyst is the hydrogenation/dehydrogenation site, being Pt and Pd very active in comparison with other transition metals.

According to Jordão *et al.* [16], they research with bimetallic catalysts Pt-Ni and Pt-Cu/HUSY in the isomerization of n-hexane, seeking a possible alternative for the decrease of the cost of the catalyst, doing a substitution from platinum to metals of low cost (Ni or Co). It was verified that the bimetallic catalysts presented a great activity when compared with the monometallic ones, even that the pure platinum. In this same perspective, it was analyzed that the proportions of the catalysts varied the percentage of platinum and nickel for the isomerization of n-hexane reaction.

Recent studies on Pt-Ni systems supported on H-USY zeolite and Beta zeolite [15-18] showed that these provided catalytic activities were higher than those of monometallic Pt catalysts.

Many studies [19-23] have been conducted using the Pt/Mordenite catalyst in the reaction of n-hexane isomerization, but the literature is sparse regarding the Ni-Pt/Mordenite catalyst.

Mordenite has an intrinsic activity for isomerization and the initial rate is rather lowered by the presence of Pt and hydrogen. Thus, the most important role of the metal component is to stabilize the catalytic activity and to offer higher selectivity for isomerization [24].

Mordenite consists of parallel 12-membered ring (MR) channels (0.67×0.70 nm) with 8 MR side pockets (0.34×0.48 nm) [25]. Due to the small size of the 8 MR, for most guest species, mordenite structure is generally considered as one-dimensional, which can induce diffusion limitations in catalysis applications [26].

The objective of this work was to investigate the effect of nickel on Pt/Mordenite catalyst in the reaction of n-hexane isomerization. The catalysts were prepared by competitive ion exchange and were characterized by X-ray diffraction, X-Ray energy dispersion spectroscopy, temperature-programmed reduction and transmission electron microscopy.

2. Experimental

2.1. Catalysts Preparation

The starting material used to prepare all the catalysts was commercial zeolite Mordenite (NH_4MOR , Si/Al ratio = 10), supplied by Zeolyst International.

Monometallic Catalysts: The platinum-containing catalysts were obtained by subjecting NH_4MOR zeolite to a competitive ion exchange [19] involving the cations of

the metal complex $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and NH_4^+ ions. For this, a solution of $0.05 \text{ mol}\cdot\text{L}^{-1}$ $[\text{Pt}(\text{NH}_3)_4]^{2+}$ containing NH_4^+ (to give an $\text{NH}_4^+ / [\text{Pt}(\text{NH}_3)_6]^{2+}$ ratio of 10) was used. To perform the exchange, the solution was added slowly ($0.2 \text{ mL}\cdot\text{min}^{-1}$, while stirring at room temperature) to a suspension of NH_4MOR that contained the volume of water required to give a final concentration of $0.005 \text{ mol}\cdot\text{L}^{-1}$ $[\text{Pt}(\text{NH}_3)_4]^{2+}$. After a period of 70 h, the solid was separated by filtration, washed with deionized water and dried at 110°C for 2 h.

For precursors containing only Ni supported on NH_4MOR , we used the same methodology described before to obtain Pt containing catalysts. However, we used a solution containing NH_4^+ ions and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ at a $\text{NH}_4^+ / [\text{Ni}(\text{NH}_3)_6]^{2+}$ molar ratio of 20 was used.

Bimetallic Catalysts: To obtain precursors of bimetallic catalysts containing Pt-Ni, two solutions were initially prepared: one containing the $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ complex and the other containing the $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ complex, which were simultaneously added to a NH_4MOR 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 [27].

Calcination: After the precursors were prepared, they were submitted to calcinations. This was done to remove the ligands coordinated to the metal and decompose the NH_4^+ cations presents in the NH_4MOR zeolite, thus, forming Bronsted acid sites (HMOR). The samples were heated at $10^\circ\text{C}\cdot\text{min}^{-1}$ rate from room temperature to 200°C , under N_2 flow ($100 \text{ cm}^3\cdot\text{min}^{-1}\cdot\text{gcat}^{-1}$) and the sample remained at this temperature for 1 h. Then, the samples were subjected to synthetic air flow ($100 \text{ cm}^3\cdot\text{min}^{-1}\cdot\text{gcat}^{-1}$) and the temperature was increased up to 500°C at $2^\circ\text{C}\cdot\text{min}^{-1}$. With the samples remaining under the air flow, the 500°C temperature was kept constant for 2 h, in order to complete the calcinations process.

X-Ray Energy Dispersion Spectroscopy (EDX): Elemental analysis was determined through energy dispersive X-Ray spectrophotometry, in a Shimadzu EDX-700 instrument.

X-Ray Diffraction (XRD): The powder method has been used, whereby the samples were sieved in an ABNT no 200 (0.074 mm) sieve and then placed in an aluminum sample door for the X-Ray diffraction, using a Shimadzu XRD 6000 equipment. Operational details of the technique have been set as follows: Copper $K\alpha$ radiation at 40 KV/30 mA, with a goniometer velocity of $2^\circ/\text{min}$ and a step of 0.02° in the range of 2θ scanning from 2° to 45° . The average diameter of the sample crystallites was determined by the Scherrer equation.

Analysis by Temperature Programmed Reduction (TPR): Calcinated samples were characterized by TPR

(Micromeritics-ChemiSorb 2705), under a mixed flow of H₂-N₂ (5% H₂ 30 mL·min⁻¹). Approximately, 150 mg of the sample were heated at a rate of 10°C·min⁻¹ in the range of 20°C - 1000°C. Before beginning data acquisition, the samples were subjected to a pre-treatment process that consisted of heating from room temperature up to 200°C (at 10°C·min⁻¹) and keeping this temperature for 1 h under N₂ flow (30 mL·min⁻¹).

Transmission Electron Microscopy (TEM): The analyses were performed on JEOL equipment Model JEM-1200 EX II Instrument with the technique of embedding in Araldite resin and then cut with Sorvall MT 5000 ultra micron.

2.2. 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 *et al.* [27]: temperature of 500°C for 6 hours under 55 mL·min⁻¹ hydrogen flow, at STP and 2°C·min⁻¹ heating rate. The catalysts stability and activity were measured during the period of 3 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⁻¹ and 2 mL·h⁻¹, respectively, giving a molar feeding ratio of 9:1 hydrogen/n-hexane. The reaction products were analyzed online using a LM⁻¹ capillary column (50 m and 0.25 mm i.d.), coupled to a gas chromatograph (VARIAN STAR 3400) equipped with a flame ionization detector.

3. Results and Discussion

The results of the elemental analyses obtained for mono and bimetallic catalysts are presented in **Table 1**. According to the data, it is possible to verify that the NH₄MOR zeolite showed high percentage of silicon oxide (SiO₂). After a competitive ion exchange the analyses performed by EDX revealed that a 100 wt% Ni (nickel monometallic catalyst), 100 wt% Pt (platinum monometallic catalyst), 60Pt40Ni/HMOR (bimetallic catalyst) and 40Pt60Ni/HMOR (bimetallic catalyst) were effectively incorporated in the Mordenite (MOR) structure.

Table 1. Chemical composition of NH₄MOR and catalysts.

| Sample | SiO ₂ (%) | Al ₂ O ₃ (%) | Ni (%) | Pt (%) | Impurities (%) |
|---------------------|----------------------|------------------------------------|--------|--------|----------------|
| NH ₄ MOR | 90.2 | 8.6 | - | - | 0.23 |
| 100Ni/HMOR | 89.0 | 8.5 | 100 | - | 0.82 |
| 60Pt40Ni/HMOR | 87.3 | 8.4 | 23.4 | 76.4 | 0.88 |
| 40Pt60Ni/HMOR | 87.3 | 8.4 | 76.9 | 23.1 | 0.94 |
| 100Pt/HMOR | 85.5 | 8.2 | - | 100 | 0.74 |

X-Ray diffraction pattern of the NH₄MOR zeolite, monometallic catalyst and bimetallic catalyst are presented in **Figure 1**.

NH₄MOR showed peaks at $2\theta = 22.24^\circ$; 25.68° ; 26.24° and 27.62° , a typical spectrum for the mordenite structure [28]. X-Ray diffraction profiles did not change significantly after competitive ion exchange with Ni, Pt and Ni-Pt (**Figures 1(a)-(e)**). It was found catalyst 60Ni40Pt/HMOR the presence of a peak at $2\theta = 39.74^\circ$ can be attributed to segregation of particles of PtO₂.

The average crystallite sizes are presented in **Table 2**.

It is important to note that after calcination and ion exchange, there was a small decrease in the average size of the crystallites. These changes are significant and can be attributed to the sizes of the radii of the embedded elements: nickel, platinum and nickel + platinum. The values of the radii of nickel and platinum are 1.25 Å and 1.39 Å, respectively, and are smaller in comparison with the ammonium ions.

Figure 2 shows the profile of the Temperature Programmed Reduction (TPR) obtained for 100Ni/HMOR, 40Ni60Pt/HMOR, 60Ni40Pt/HMOR and 100Pt/HMOR catalysts.

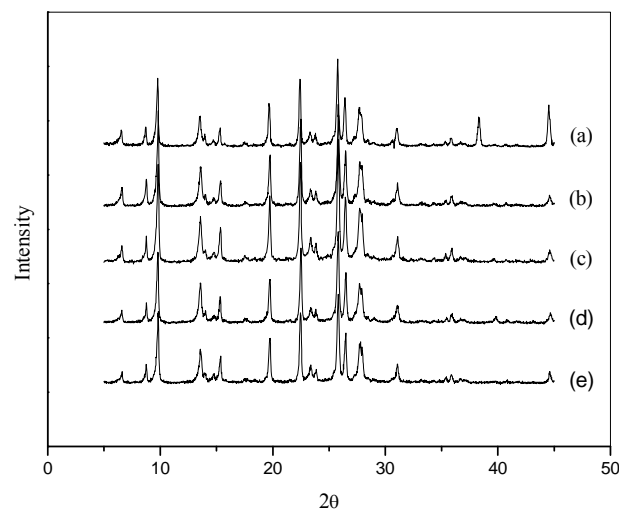


Figure 1. X-Ray diffraction patterns of zeolite (a) NH₄MOR, of mono and bimetallic catalysts (b) 100Ni/HMOR (c) 40Ni60Pt/HMOR (d) 60Ni40Pt/HMOR and (e) 100Pt/HMOR.

Table 2. Results of crystallites average size.

| Sample | Average size of crystallites (nm) |
|---------------------|-----------------------------------|
| NH ₄ MOR | 45.9 |
| 100Ni/HMOR | 42.3 |
| 60Pt40Ni/HMOR | 37.5 |
| 40Pt60Ni/HMOR | 45.2 |
| 100Pt/HMOR | 43.4 |

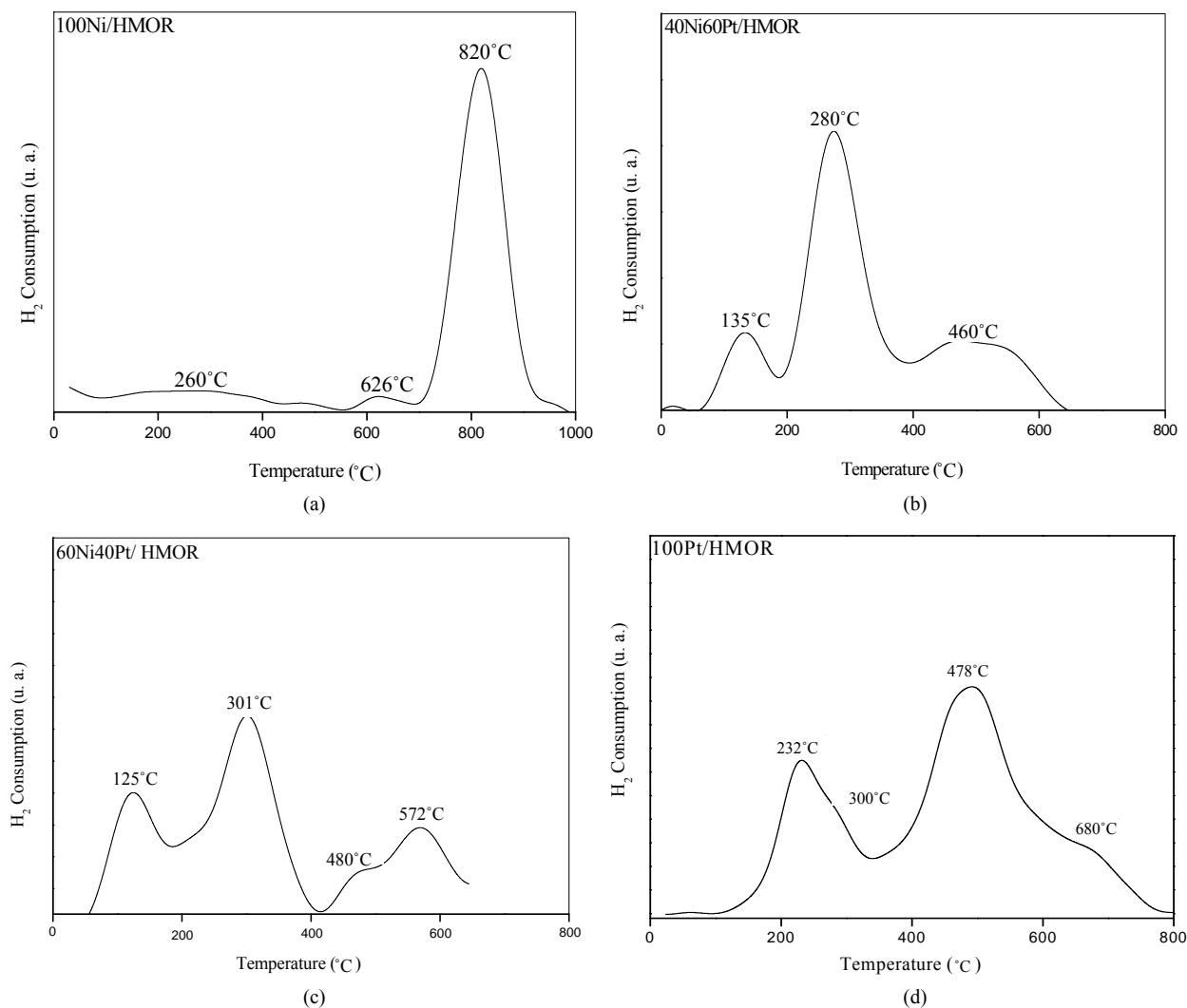


Figure 2. TPR of (a) 100Ni/HMOR; (b) 40Ni60Pt/HMOR; (c) 60Ni40Pt/HMOR; (d) 100Pt/HMOR.

It is important to note that the reduction profiles shown in **Figure 2(a)** exhibited three peaks reduction at 260°C, 626°C and 820°C. The first peak, at 260°C, can be related to a few particles of nickel (NiO) that lie freely in large channels (12 rings) of mordenite. According to Cardona *et al.* [29] the reduction of nickel oxide (NiO) at low temperature is believed to interact weakly with mordenite. The second reduction peak, at 626°C, equivalent to reducing the Ni²⁺ that are in positions exchange channel 12 rings, and the third peak at 820°C can be attributed to the presence of Ni²⁺ which is strongly interacting in lateral channels (8 MR) of the mordenite. Because of the great mobility of nickel, ions migration for the small mordenite channels (8 rings) may occur during heating, thereby increasing the reduction temperature of these species.

The profile of temperature-programmed reduction catalyst for 40Ni60Pt/HMOR shown in **Figure 2(b)** exhibited three peaks (135°C, 280°C and 460°C) and the catalyst 60Ni40Pt/HMOR proved four reduction peaks

(125°C, 301°C, 480°C and 572°C). This fact can be attributed to the increase in platinum content in the bimetallic catalysts that are totally reducing the nickel cations at 460°C.

According to Jao *et al.* [30] as the content of platinum increases, greater the possibility of interaction of Pt-Ni, explaining that the presence of the peak at 460°C can be attributed to the reduction of particulate nickel and platinum bimetallic catalyst 40Ni60Pt/HMOR, so it can be seen that nickel is forming “cluster” with platinum.

For 100 Pt/HMOR catalyst, three reduction peaks located at 225°C, 478°C and 680°C respectively, were observed. The first reduction peak at 225°C can be attributed to the presence of PtO₂ and some ions Pt²⁺ and Pt⁴⁺, which is not formed, and oxides which are in free channels, but which are exchanged on the surface.

The second reduction peak at 478°C and the third reduction peak at 680°C can be corresponded to the presence of Pt²⁺ ions, which are strongly interacting with the

channels (8 MR) of the mordenite, according Jimenez *et al.* [31].

Comparing the reduction profiles of monometallic and bimetallic catalysts, we observed a shift of peak reduction of cations to lower temperatures.

It may be noted that the addition of platinum alters significantly reducing the profiles, indicating that bimetallic catalysts, for the presence of platinum is facilitating the reduction of cations Ni^{2+} , decreasing reduction temperature of cations.

Yoshioka *et al.* [15] observed that this behavior occurs because initially the platinum is reduced causing metal sites that dissociate hydrogen molecules into atomic hydrogen, which reduce the Ni^{2+} cations present in the zeolite mordenite.

Representative TEM images of the catalysts after reduction are shown in **Figure 3**. The metal particles found in **Figures 3(a)-(d)** present diameters in the range of 8 - 18 nm that are very well distributed along the catalyst grain.

Figure 4 shows the activities in the isomerization of n-hexane during 3 hours of Pt-Ni catalysts supported on HMOR zeolite with different Pt/Ni ratios and a total

metal content of 180 $\mu\text{mol/gcat}$.

Figure 4 shows the results of the activities for the mono- and bimetallic catalysts. The catalyst 100 Ni/HMOR showed lower performance than the other catalysts (40Ni60Pt/HMOR, 60Ni40Pt/HMOR and 100Pt/HMOR).

This is due to the difficulty that the nickel particles have to reduce the temperature at which the reaction is performed (250°C) as was observed in the reduction profiles shown in **Figure 2(a)**. It is noticed that few nickel particles are reduced, and this implies that there are few metal sites formed.

There is an initial increase in activity with increasing platinum content as platinum assists in the reduction of nickel cations in the bimetallic catalysts, in such a way that these catalysts have higher activities. This fact can be explained with the dispersion of metals in the zeolite.

The formation of metallic platinum is influenced by the presence of nickel, resulting in a smaller average particle size. That is, Ni-Pt/HMOR bimetallic catalysts have metal particles with smaller diameter when compared to monometallic Ni/HMOR or Pt/HMOR. Therefore, the

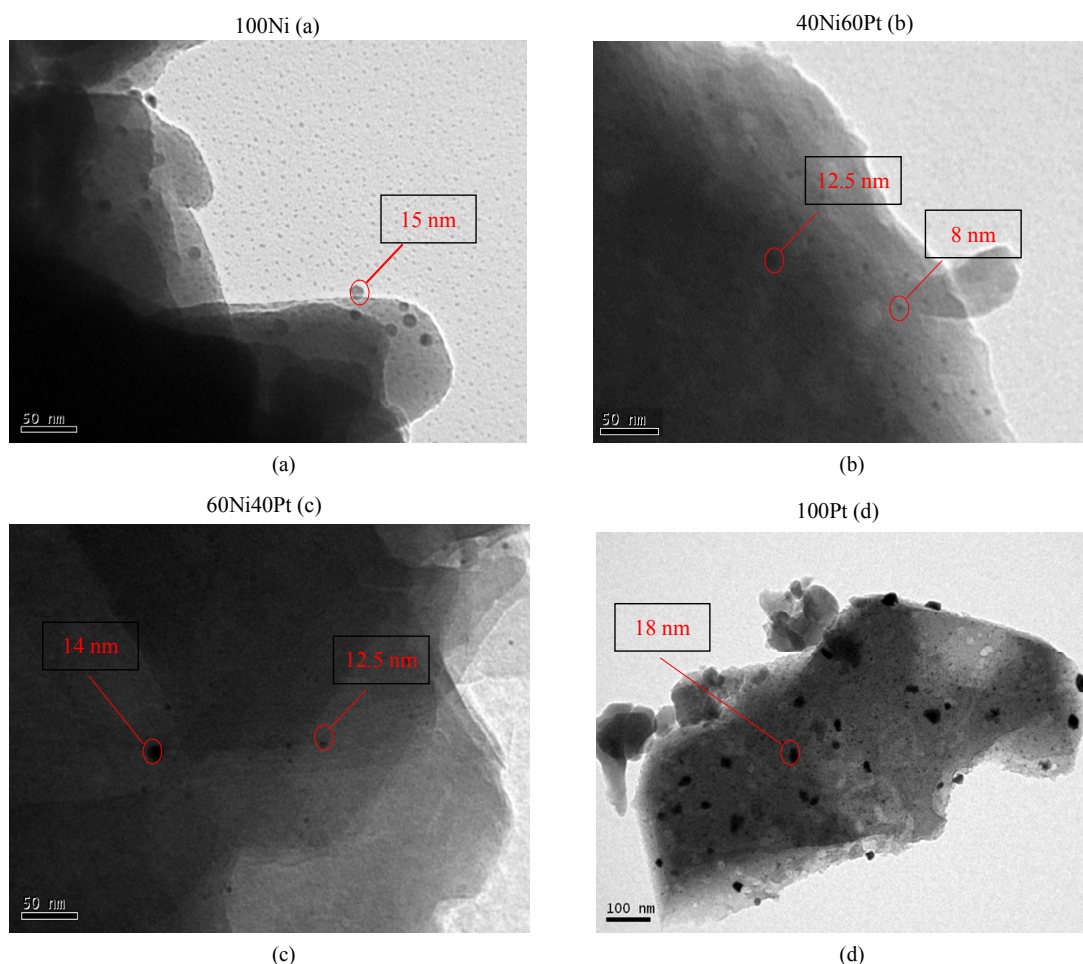


Figure 3. Micrographs of samples: (a) 100Ni/HMOR; (b) 60Pt40Ni/HMOR; (c) 40Pt60Ni/HMOR; and (d) 100Pt/HMOR.

bimetallic catalysts have higher metal dispersion for the function, thus presenting a greater activity in the isomerization of n-hexane.

The structure of mordenite shows a system formed by channels with large opening of 6.5 to 7 Å (12 ring members) connected by parallel channels of small dimensions from 2.7 to 5.7 Å (8 rings members). In view of the dimensions of organic molecules is important to note that the diffusion of n-hexane, whose diameter has dimensions of 4.3 Å and its isomers larger number octane (3-methyl-pentane, 2,2-dimethyl-butane and 2,3-dimethyl-butane) have diameters of 5 Å, 6.2 Å and 5.6 Å diffusion occurs only in the large channels of mordenite 12 members. However, because of its one-dimensional porous system, mordenite is susceptible to deactivation due to blocking of its channels by deposition of coke formed during the course of the reaction.

Figure 5 shows the selectivity of mono-branched products as a function global conversion.

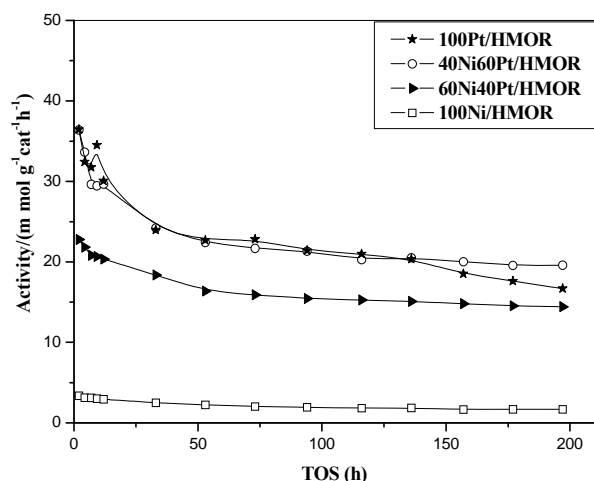


Figure 4. The activity of catalysts with 180 $\mu\text{mol/gat}$ during 3-h reaction.

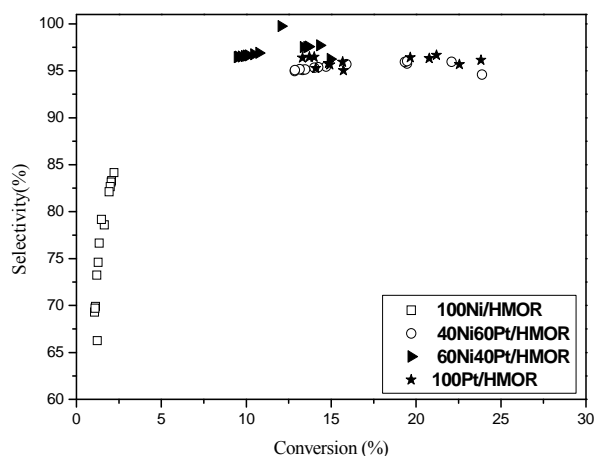


Figure 5. Selectivity for mono-branched products as a function of global conversion.

When comparing the values obtained for the mono- and bimetallic catalysts it is clear that the selectivity was always above 65%, except for the catalyst only containing nickel (100Ni/HMOR) which proved to be less selective isomerization thus confirming its weak dehydrogenating power capacity and low adsorption of molecules of n-hexane. However, it appears that increasing the platinum content bimetallic catalysts for the conversion of the reactant increases and the selectivity to isomerization. Studies by Jordão [32] showed that the isomerization selectivity is low ($\sim 60\%$) and this fact gives great ability of nickel to promote the formation of cracking products stemmed from the hydrogenolysis reactions of this metal.

Figures 6 and 7 illustrate the relationship between the mono- and di-branched isomers as a function of conversion for mono and bimetallic catalysts.

Figure 6 shows that the catalysts exhibited a high

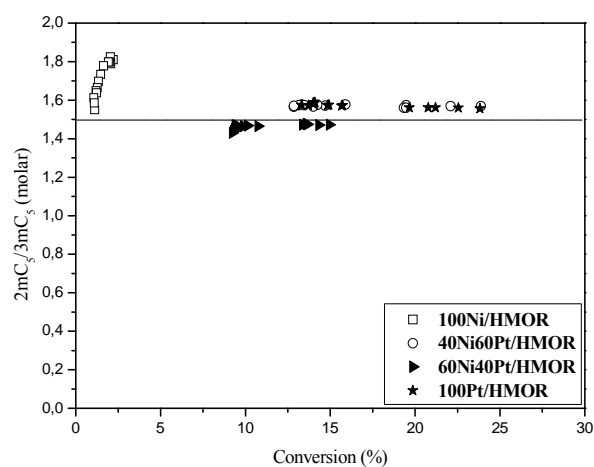


Figure 6. Ratio between the mono-branched isomers of n-hexane as a function of the conversion for mono and bimetallic catalysts.

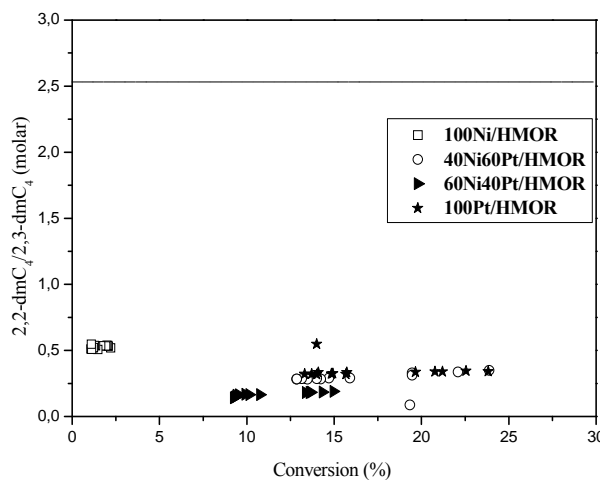


Figure 7. Ratio between the di-branched isomers of n-hexane as a function of the conversion for mono and bimetallic catalysts.

value of the ratio of mono-branched isomers (2-mC₅/3-mC₅) and this ratio was almost constant for all catalysts, the balance being above (1.5) only 60Ni40Pt/HMOR catalyst showed less than the equilibrium value which can be attributed to segregation of particles of this catalyst PtO₂ observed by XRD analysis.

These results indicate that there is a higher selectivity to the formation of 2-mC₅ the formation of 3-mC₅, which makes them the most promising catalysts for isomerization, since the 2-methyl-pentane has a higher octane number (RON = 75) than 3-mC₅ (RON = 73).

It is noted in **Figure 7** that the molar ratio of branched bi-products (2,2-dmC₄/2,3-dmC₄) for all the catalysts was considerably below the equilibrium value (2, 5). This behavior can be explained by the higher stability of the tertiary carbocation, compared to the secondary, promoting the formation of the product 2,3-dmC₄. The formation of 2,3-dmC₄ requires two successive branches through protonation of cyclopropane in the acidic sites. This branch corresponds to the limiting step of the bifunctional mechanism of 2,3-dmC₄ succeed in that methyl pentane, simultaneously with the formation of 2,2-dmC₄. Thus, this is advantageous because the isomer which has a higher octane number (RON = 100) is 2,3-dimethyl-butane, while 2,2-dimethyl-butane presented RON equal to 92, which is somewhat lower when compared to 2,3-dimethyl-butane.

4. Conclusions

The profiles obtained from TPR suggest that, for bimetallic catalysts, the presence of platinum facilitates the reduction of Ni²⁺ cations.

The mono and bimetallic catalysts were more selective for the formation of isomers with high octane index (2-mC₅ dmC₄ and 2.3) which are products of interest in the petroleum industry.

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.

5. Acknowledgements

The authors would like to make special acknowledgements to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) and Petrobras for their financial support to this research.

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