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Hydroisomerization of *n*-hexane over Pt–Ni/HBEA using catalysts prepared by different methods

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Bimetallic catalysts Pt–Ni/HBEA prepared by different methods, were studied in the reaction of *n*-hexane hydroisomerization and compared with Pt and Ni/HBEA. The results showed that the highest conversion and selectivity were obtained for the bimetallic catalysts, prepared by ion exchange with simultaneous addition of Pt and Ni, which reveals a synergistic effect between the two metals.

KEY WORDS: bimetallic catalysts; BEA zeolite; hydroisomerization; *n*-hexane.

1. Introduction

The current specification for gasolines and diesel fuels imposes strong restrictions on their contents in aromatic compounds [1]. As a result, the need to maintain adequate octane numbers involves the hydroisomerization of low octane linear paraffins such as *n*-hexane or *n*-heptane into high octane isomers, with higher branching of the carbon chain.

Zeolites containing platinum are the most common *n*-alkane hydroconversion catalysts [2]. Nevertheless, the poor dispersion sometimes achieved leads to the presence of large metal particles, promoting the occurrence of hydrogenolysis reactions. Simultaneously, the lack of proximity between metal and acid sites favours the cracking reactions at the acid sites.

According to several studies, bimetallic catalysts display higher activity, selectivity and stability than monometallic systems in several reactions. Córdoba *et al.* [3] observed a higher activity of Ru–Pd/SiO_2 in *o*-xylene hydrogenation (when compared whit Pd/SiO_2 catalysts). The same effect was observed by Masalska [4] on Ru–Ni/ZSM-5 catalysts. Barrio *et al.* [5] studied the aromatics hydrogenation on Pd–Ni/silica–alumina catalysts and noticed a greater resistance to deactivation due to coke formation.

It is known that Pt alloys with other metals increase the metal dispersion due to the formation of bimetallic clusters [6]. A few works have been published concerning the influence of bimetallic catalysts containing Ni–Pt in some reactions. Malyala *et al.* [7] tested the hydrogenation of acetophenone in Ni and bimetallic Ni–Pt/Y zeolite and concluded that Ni–Pt zeolites were found to be more active and stable when compared to monometallic Ni catalysts. Jao *et al.* [8] showed that the addition of a moderate amount of Ni to Pt catalyst facilitates the formation of branched isomers in light naphtha isomerization reactions. Jordão *et al.* [9] reported that bimetallic Pt–Ni/HUSY catalysts containing 20% Pt and 80% Ni, relating to the total amount of metal, showed better activity and selectivity for di-branched products than monometallic Pt catalysts in *n*-hexane hydroisomerization. Higher Ni contents showed poor activity due to pore blockage by larger bimetallic particles and incomplete metal reduction. According to these authors, the behaviour of the bimetallic catalysts can be explained taking into account the following factors: first, the presence of platinum enhances the reduction of the nickel cations, increasing the dispersion of the two metals, and second, as the nickel particles are not very much active in the isomerization reaction, the increase in di-branched products suggests that nickel particles are serving as support for the Pt atoms.

The common bifunctional catalyst preparation method is a multi-step process consisting mainly of the following: (i) deposition of metal precursor compound over the support surface either by impregnation, ion exchange or mechanical mixing (ii) drying and calcination of the catalysts and (iii) transformation of the precursor compound into the active metallic phase by reduction. It is well established that the metal dispersion and thus the metal/acid ratio depends markedly on the way the metal is introduced [10].

The present work focuses the importance of the preparation method of the bimetallic catalysts

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Pt–Ni/HBEA and its influence in the catalysts behaviour during the hydroisomerization of *n*-hexane. The results were compared to those obtained with the same zeolites containing only Pt or Ni.

2. Experimental

HBEA zeolite with Si/Al = 12.5 was supplied by PQ Corporation. The metals Pt and Ni were introduced by ion exchange using solutions of $Pt(NH_3)_4Cl_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ at ambient temperature and then calcined at 300 °C for 3 h for Pt catalysts and at 500 °C during 3 h for Ni catalysts. The monometallic samples were named Pt/HBEA and Ni/HBEA. The bimetallic catalysts containing Ni and Pt were prepared by ion exchange and the metals added upon different ways: (i) ion exchange with Pt and Ni simultaneously at ambient temperature – Pt–Ni/HBEA-A or (ii) at 80 °C – Pt–Ni/HBEA-B and finally by (iii) sequential ion exchange of Ni at $T = 80$ °C, followed by the introduction of Pt at ambient temperature, with intermediate calcination – Pt–Ni/HBEA-C. The metal content is approximately 20% of Pt and 80% of Ni, regarding the total amount of metal. After metal loadings all bimetallic catalysts were calcined under air flow at 500 °C for 3 h.

The chemical composition of the samples was determined by atomic absorption spectroscopy (AA).

The samples were characterized by both Temperature Programmed Reduction (H_2-TPR) and catalytic reaction of toluene hydrogenation.

Temperature programmed reduction (H_2-TPR) experiments were carried out using 130 mg of zeolite sample that was placed in a quartz reactor and pre-treated at 200 °C for 1 h under air flow (1 ml min^{-1}) and then cooled to room temperature. The gas was then switched to a 5% H_2/Ar mixture flowing at the same rate. During the TPR experiments temperature was increased at a rate of 7 °C min^{-1} and the consumed H_2 was monitored by a TCD detector.

Toluene hydrogenation was performed in a continuous flow reactor under a total pressure of 1 bar in the presence of hydrogen. The samples were previously reduced *in situ* under a flow of H_2 (6 l h^{-1} g^{-1}) at 500 °C for 3 h. The reaction was carried out at 110 °C, the feed consisted of a mixture of H_2 and toluene (toluene diluted in *n*-hexane with 1:5 ratio) with a molar ratio of 45 and a space velocity of 100 h^{-1}. The analysis of the reaction products was carried out in a gas chromatograph (Dani GC 1000) equipped with a FID detector, using a capillary column PONA and a multi-loop sample valve.

The *n*-hexane transformation was performed at 250 °C with a molar ratio $H_2/n\text{-}C_6 = 9$ and changing the space velocity from 6.6 to 53.4 h^{-1}. The reaction products were analysed by gas chromatography (HP 6890) with a FID detector and a capillary column CP-SQUALANE. The results are reported as conversion (molar percent of reactant converted) and product selectivity's (moles of product divided by moles of *n*-hexane reacted, in percentage).

3. Results and discussion

The chemical composition of the catalysts is presented in table 1. In samples prepared by simultaneous ion exchange of both metal precursors, Pt–Ni/HBEA-A and Pt–Ni/HBEA-B, the ratio 20% Pt:80% Ni was achieved. For the sample prepared by sequential ion exchange, Pt–Ni/HBA-C, the ratio obtained was 9% Pt:91% Ni. For comparison purposes monometallic samples Pt/HBEA and Ni/HBEA were used, with different metal contents.

The H_2-TPR profiles are shown in figure 1. For Pt05BEA sample two peaks are detected, the first one at low temperature, located at 100–200 °C and a second one around 400 °C. Ni1/HBEA shows only one broad

Table 1
Chemical composition of the samples

Sample	Wt.%	
	Pt	Ni
Pt092/HBEA	0.92	–
Pt05/HBEA	0.5	–
Pt–Ni/HBEA-A	0.05	0.23
Pt–Ni/HBEA-B	0.07	0.34
Pt–Ni/HBEA-C	0.07	0.82
Ni026/HBEA	–	0.26
Ni1/HBEA	–	1.0

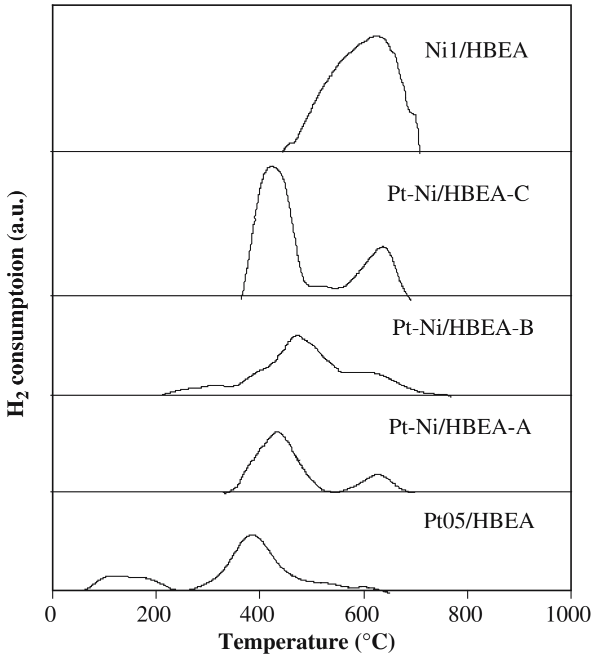

Figure 1. TPR profiles for mono and bimetallic catalysts.

peak located at 580 °C. For all bimetallic Pt–Ni/HBEA catalysts, reduction peaks are detected in a large range between 200 and 700 °C, with the main peak centred around 400–470 °C. This peak is always located at intermediate temperatures, between that required for the reduction of monometallic Pt/HBEA and Ni/HBEA catalysts. This shift in the temperature of the TPR profiles has been observed earlier for Ni–Pt/SiO_2 [11] and, more recently, for Pt–Ni/MOR catalysts [8]. According to Malyala *et al.* [7] these observations can be interpreted either as the reduction of Ni catalysed by Pt or the interaction of the two metals leading to an alloy formation. Jentys *et al.* [12] suggest that the presence of reduced Pt triggers the reduction of Ni, probably by dissociation and spilled over of hydrogen. The bimetallic catalysts present also a second peak at temperature closer than that of Ni reduction on Ni/HBEA sample, which indicates that part of Ni introduced, did not interact with Pt. This behaviour is particularly evident in Pt–Ni/HBEA-C sample, with a higher content in Ni.

In order to characterize the metal sites dispersed in the bifunctional catalysts, toluene hydrogenation was chosen as a model reaction. To obtain an accurate value of the initial activity, a multiple loop valve was used to allow the product analysis at short time-on-stream. Under the chosen operating conditions the reaction was totally selective into methylcyclohexane, neither isomerization or ring opening products were observed. Table 2 shows the initial activities for mono and bimetallic catalysts, obtained for the first data point at 30 s time on stream. The presented values are reported as activity per mole of metal introduced in the catalyst. For all catalysts, there is a very fast initial decrease in activity, followed by a quasi plateau after about 2 min time on stream. Some examples of the deactivation curves are shown in figure 2 for the bimetallic catalysts.

The initial activity for Ni026/HBEA catalysts is much lower than the observed for Pt/HBEA catalysts, due to the poor hydrogenating capacity of Ni when compared to Pt. The bimetallic catalysts Pt–Ni/HBEA-A and Pt–Ni/HBEA-B present a significant increase in hydrogenating activity when comparing with Ni026/HBEA. This aspect is particularly relevant considering that the three samples have comparable contents in Ni, and a small addition of Pt provokes a substantial increase in hydrogenating activity. The bimetallic catalyst Pt–Ni/HBEA-C presents a distinct behaviour that can be related both with the preferential occupation of the exchange sites by the two metals, and with a low metal dispersion. According to the studies of Dedecek *et al.* [13], concerning the distribution of Co ions in Beta zeolite, three cationic sites were detected, namely α, β, and γ-sites. The preferential occupation of the cations goes to the β-sites and the other two positions are only taken at higher metal loadings. In Pt–Ni/HBEA-C the sequential ion exchange of Ni is followed by the introduction of Pt, with intermediate calcination. According to this preparation method the Ni cations occupy preferentially the β-sites. After calcination, the Pt cations from the second ion exchange will probably occupy the α and γ-sites that are still free for exchange. Consequently the two metal cations will be placed in different positions inside the zeolite structure, leading to a poor interaction between the two metals and consequent low hydrogenating activity. In Pt–Ni/HBEA-A and Pt–Ni/HBEA-B catalysts the simultaneous ion exchange of the two metal precursors led to a homogeneous distribution of the two cations in the three exchange sites, which causes a better interaction between the two metals, increasing the hydrogenating activity.

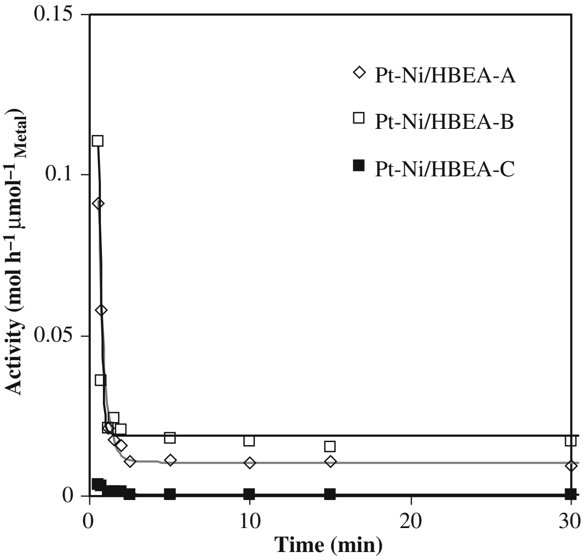

Figure 2. Deactivation curves for toluene hydrogenation at 110 °C.

Table 2

Initial activities for toluene hydrogenation at 110 °C

Sample	Init. Act. (mol h^{-1} $\mu mol^{-1}{}_{Metal}$)
Pt092/HBEA	0.27
Pt05/HBEA	0.19
Pt–Ni/HBEA-A	0.09
Pt–Ni/HBEA-B	0.11
Pt–Ni/HBEA-C	0.005
Ni026/HBEA	0.002
Ni1/HBEA	n.d.

In the hydroisomerization of *n*-hexane the total conversion as a function of the space velocity is shown in figure 3. The highest conversions are achieved for the bimetallic catalysts prepared by simultaneous ion exchange, Pt–Ni/HBEA-A and B. The samples Ni026/HBEA, Ni1/HBEA and Pt–Ni/HBEA-C (not shown) presented conversions below 10%.

The main reaction products for all samples are the isomerization products, monobranched methylpentanes (2-MP and 3-MP) and di-branched dimethylbutanes

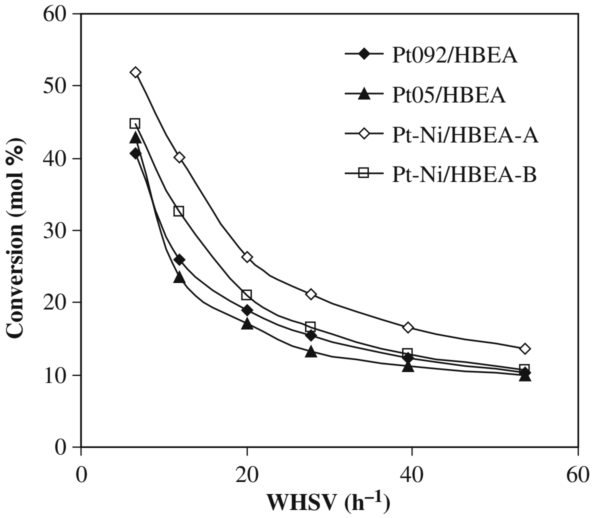

Figure 3. Evolution of conversion as a function of space velocity for *n*-hexane hydroisomerization performed at 250 °C.

(2,3-DMB and 2,2-DMB), cracking products and small amounts of methylcyclopentane and benzene.

The selectivities to the reaction products obtained during *n*-hexane hydroisomerization at 250 °C are presented on table 3. The ratio Isomerization/Cracking (*I*/*C*) presents high values for all catalysts, except for Pt–Ni/HBEA-C and Ni/HBEA samples. These catalysts present high selectivity in light products, originated from cracking (mainly C_2–C_4 products) and hydrogenolysis (C_1 + C_5) reactions. Hydrogenolysis reaction occurred mainly in the case of Pt–Ni/HBEA-C for which a significant quantity of C_1 was detected, confirming that this sample has larger metal particles and a poor dispersion. These results agree with the low hydrogenating activity presented by these catalysts. In fact, according to Chupin *et al.* [14] there is a linear correlation between the hydrogenating activity and the number of accessible metal atoms. Thus, the low *I*/*C* ratio presented by these catalysts evidenced the presence of a reduced number of accessible metal atoms that can be explained by both the difficulty in the reduction of Ni particles and the poor metal dispersion.

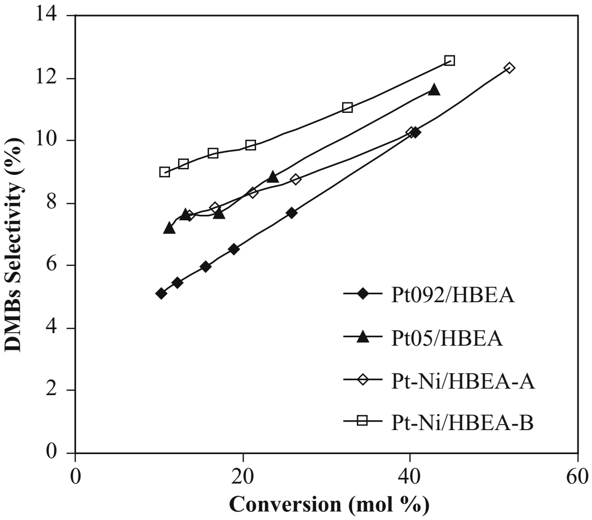

Figure 4. Evolution of selectivity in dimethylbutanes (DMBs) as a function of *n*-hexane conversion.

Figure 4 shows the evolution of dimethylbutanes (DMBs) selectivity with the conversion. The highest selectivity into di-branched products is observed for the catalyst prepared by simultaneous ion exchange of Pt and Ni precursors at 80 °C, Pt–Ni/HBEA-B. The higher temperature used during the ion exchange of this sample led to an increase of DMBs selectivity. This behaviour is due to a more effective diffusion of metal precursors promoted by the higher temperature, leading to a better distribution of metals and protonic sites inside the porous structure. The sample Pt–Ni/HBEA-A shows a DMBs selectivity comparable to Pt05/HBEA. Taking into account the low content in Pt and considering that the presence of cracking products in these samples is quite comparable to Pt/HBEA catalyst, it is clear that the high DMBs selectivity presented by these samples is due to the interaction of Ni and Pt metal particles.

4. Conclusions

From the analysis of the results obtained during the characterization of the metal function in monometallic

Table 3

Selectivities to the reaction products obtained during hydroisomerization of *n*-hexane at $T = 250$ °C at similar conversions (25–30%), except Ni/HBEA and Pt–Ni/HBEA-C at 4–5% conversion

Sample	Selectivity (%)							*I*/*C* ratio
	C_1 + C_5	C_2–C_4	2,3-DMB	2,2-DMB	2-MP	3-MP	Others	
Pt092/HBEA	0.1	0.5	5.3	2.4	56.9	33.7	1.1	196.6
Pt05/HBEA	0.1	0.6	5.6	3.0	55.0	33.6	2.1	162
Pt–Ni/HBEA-A	0.2	0.5	7.3	1.5	58.6	30.4	1.5	195.6
Pt–Ni/HBEA-B	0.1	0.6	8.9	2.1	55.5	31.4	1.4	163.2
Pt–Ni/HBEA-C	28.4	6.9	1.9	0.3	31.9	20.9	9.7	7.9
Ni026/HBEA	4.6	10.9	6.1	1.7	45.8	23.2	7.7	7
Ni1/HBEA	3.0	7.5	7.0	2.2	49.5	25.5	5.3	11.2

and bimetallic Pt–Ni/HBEA zeolites it can be concluded that the presence of the two metals changes the hydrogenating properties of the materials. The samples prepared by simultaneous ion exchange of both metals, Pt–Ni/HBEA-A and B present a significant increase in hydrogenating activity compared to Ni026/HBEA sample, with similar Ni content. The sample prepared by sequential introduction of the metals, Pt–Ni/HBEA-C, present hydrogenating activities closer to Ni026/HBEA catalyst. This occurs, probably, due to the location of the two metals in different exchange sites of the zeolite structure, leading to a poor interaction between them and also due to low metal dispersion. The H_2-TPR experiments evidenced that the presence of small amounts of Pt facilitates the reducibility of Ni species. Moreover, it is possible to verify that there are some Ni species that, due to their localization in the zeolite porous structure, are far from Pt influence.

The changes detected in metal characteristics influenced the behaviour of the bifunctional catalysts for the hydroisomerization of *n*-hexane. The highest conversion and DMBs selectivity is obtained for the catalysts prepared by ion exchange with simultaneous addition of Pt and Ni, revealing a synergistic effect between the two metals.

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