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Influence of the Addition of a Second Metal on the Catalytic Performance of Pt-Beta Agglomerated Catalyst in the Hydroisomerization of *n*-Octane

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Abstract In this work, the hydroisomerization of *n*-octane on mono and bimetallic beta agglomerated zeolite based catalysts was investigated. As the metal function, platinum and combinations with nickel and tin were studied. Test reactions were carried out at 10 bar and 290–410 °C. The bimetallic catalyst with the lowest amount of Ni yielded the greatest multibranched selectivity.

Keywords Zeolite · Binder · Bimetallic

1 Introduction

The current environmental requirements are giving rise to a general reduction in both Reid vapour pressure and aromatics, alkenes, sulphur and Methyl *tert*-butyl ether (MTBE) contents, which will have a negative impact on the octane number of the gasoline pool [1]. Isomerization of long-chain *n*-alkanes appears to be an interesting alternative since provides branched molecules which possess higher octane number than linear ones.

Isomerization of alkanes is carried out over bifunctional catalysts consisting of an acid function, provided by solid acids; i.e., zeolites, and a metallic function (noble metals). Isomerization takes place in the acid sites of the bifunctional catalyst whereas the metal provides hydrogenation-dehydrogenation capability. Both acid and metal site density are important and their proper balance is critical in determining the activity of the catalyst [2].

As the hydrogenating-dehydrogenating function, several metals have been tested including Pt, Pd, Rh, Ir, Ru, Re and Ni [3]. In an extensive study, Guisnet [4] reported the benefits that platinum produces in zeolites. With high values of the metal/acid balance, the platinum acid zeolites are very stable, because the metal avoids deactivation by coke.

Additionally, it has been proved that catalytic performance of a metal catalyst may be improved by the addition of a second metal. Geetha Bhavani et al. [5] reported the formation of bimetallic Ni–Pt particles on zeolites beta and mordenite. The best metal–acid balance between bimetallic particles and acid sites of the support allowed an enhanced activity, isomerization selectivity and sustainability of the catalysts for ethylbenzene hydroisomerization. Jordão et al. [6] observed how the catalytic activity and stability of the Ni/HUSY catalyst were much lower than the monometallic Pt/USY. The presence of small platinum amounts in the bimetallic catalysts improved both properties and produced more active catalysts in *n*-hexane hydroisomerization. Passos et al. [7] reported the characterization and catalytic activity of bimetallic Pt–In/Al_2O_3 and Pt–Sn/Al_2O_3 in some processes like *n*-heptane conversion. The addition of In or Sn improved the stability of the catalyst. The addition of Sn promoted a higher selectivity for isomerization products.

In an early work [2], our research group reported the influence of bimetallic particles Pt–Pd in the hydroisomerization of *n*-octane. Bimetallic particles favoured the formation of branched products. Platinum in these catalysts did not promote the methane and ethane formation, due to interactions with palladium in a bimetallic particle. Recently, Fúnez et al. [8] studied the hydroisomerization in liquid phase of a C7–C8 stream obtained by distillation of

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real naphtha using Pt–Ni Beta zeolite catalysts. An increase in the percentage of multibranched isomers was detected when Ni content increased in the catalysts.

The aim of this work was to study the influence of nickel and tin addition on the characteristics of platinum beta agglomerated catalysts and how the combination of these metals, in the same catalyst, modified the catalytic performance in the hydroisomerization of *n*-octane.

2 Experimental

2.1 Catalyst Preparation

The bifunctional catalysts used in this work consisted of H-Beta as the acid function and sodium bentonite as the binder. Beta zeolite (Si/Al = 12.5) was supplied in the ammonium form by Zeolyst International. Calcination at 550 °C for 15 h yielded the acid form of the zeolite. Sodium bentonite was supplied by Aldrich Chemical Co.

H-Beta was bound with sodium bentonite (35/65 w/w) by preparing a homogeneous aqueous suspension of both materials, under continuous agitation, and heating at 60 °C for 2 h. Then, the suspension was dried at 120 °C overnight. After grinding and sieving, particles with 0.75 mm average particle size were obtained. Finally, the agglomerated zeolite was calcined at 550 °C for 15 h.

The acid form of the zeolite was obtained by exchanging three times the Na^+ with 1 M NH_4Cl (30 mL g^{-1}) under agitation at 80 °C for 12 h and calcined again at 550 °C for 15 h.

Monometallic catalysts (Pt, Sn and Ni) were prepared by the incipient wetness technique, using the corresponding aqueous metal precursor solution (H_2PtCl_6, $SnCl_2$ and $Ni(NO_3)_2$, respectively). The sample was placed in a glass vessel and kept under vacuum at room temperature for 2 h in order to remove water and other compounds adsorbed on the zeolite. A known volume of an aqueous metal precursor solution was then poured over the zeolite. Next, the solvent was removed by evaporation under vacuum. The metal content added to the catalyst was controlled by measuring the metal concentration in the impregnating solution. In this way, catalysts with 1 wt.% of metal were synthesized (samples 1Ni, 1Sn and 1Pt). In the case of bimetallic catalysts, a simultaneous impregnation with both precursors was employed with a total metal content of 1 wt.%. In this sense, two sets of catalysts, bimetallic Ni–Pt and Sn–Pt, were synthesized.

After metal incorporation, the catalysts were calcined at 400 °C for 4 h, and reduced in situ under a hydrogen flow of 190 mL min^{-1} g^{-1}.

Bimetallic samples have been identified as follows: firstly, the metal content (0.25, 0.50, 0.75 and 1 wt.%) was indicated; secondly, the metal (Ni, Sn or Pt) was considered. For example, sample 0.75Ni0.25Pt consisted in a catalyst containing 0.75 wt.% Ni and 0.25 wt.% Pt.

2.2 Catalyst Characterization

In order to quantify the total amount of metal incorporated in the catalyst, atomic absorption (AA) measurements were performance using a SpectrAA 220FS spectrophotometer. The error of these measurements was of ±1%.

BET surface area was determined by nitrogen adsorption and desorption data acquired on a Micromeritics ASAP 2010 apparatus. The sample was pretreated overnight at 350 °C under vacuum of 5×10^{-3} Torr at 350 °C for 15 h. Specific total surface areas were calculated using the BET equation. Surface area measurements had an error of ±3%.

The total acid site density and the acid strength distribution of the catalysts were measured by temperature programmed desorption of ammonia (TPDA), using a Micromeritics TPD/TPR 2900 analyzer. The samples were housed in a quartz tubular reactor and pre-treated in flowing helium ($\geq$99.9990% purity) while heating at 15 °C min^{-1} up to the calcination temperature of the sample. After reducing the catalysts under a hydrogen flow, the samples were cooled to 180 °C and saturated for 15 min in an ammonia stream ($\geq$99.9990% purity). The catalyst was then allowed to equilibrate in a helium flow at 180 °C for 1 h. Next, ammonia was desorbed by heating at a rate of 15 °C min^{-1}. Temperature and detector signals were simultaneously recorded. The total acidity was obtained by integration of the area under the curve. This curve was fitted using two peaks, which were classified as weak and strong acidity depending on the desorption temperature. The use of these peaks was not based on any peak assignment to a specific Brönsted or Lewis acid sites but it was a convenient way to categorize the acid strength distribution obtained by this method. The average relative error in the acidity determination was lower than 3%.

Chemisorption measurements were carried out by using a dynamic pulse technique with an argon flow of 50 mL min^{-1} and pulses of H_2 ($\geq$99.9995% purity). The apparatus used was the same as that described for the TPDA. Previously, the sample was pre-treated by heating at 15 °C min^{-1} in argon flow up to 250 °C and kept constant at this temperature for 20 min. Then, the sample was reduced in situ. Next, the hydrogen was removed by flowing argon for 30 min, the temperature being 10 °C higher than the reduction temperature. Finally, the sample was cooled to the experiment temperature in an argon gas flow. The dispersion measurements with H_2 pulses had an error of ±5%.

Temperature programmed reduction (TPR) measurements were carried out with the same apparatus described above (Micromeritics TPD/TPR 2900 analyzer). After loading, the sample was outgassed by heating at 20 °C min^{-1} in an argon flow up to the calcination temperature of the sample and kept constant at this temperature for 30 min. Next, it was cooled to room temperature and stabilized under an argon/hydrogen flow ($\geq$99.9990% purity, 85/15 volumetric ratio). The temperature and detector signals were then continuously recorded while heating at 20 °C min^{-1} up to 560 °C. The liquids formed during the reduction process were retained by a cooling trap placed between the sample and the detector. TPR profiles were reproducible, standard deviations for the temperature of the peak maxima being ±2%.

2.3 Catalytic Experiments

Hydroisomerization of *n*-octane reactions were carried out in an Autoclave Engineers (BTRS-Jr) micro reactor that consisted of a tubular stainless steel reactor with vertical placing and downward flow. The liquid feed (*n*-octane) was performed by a HPLC pump. A backpressure regulator valve allowed high-pressure experiments. Experimental conditions were as follows: weight of catalyst, 1.5 g; temperature, 290–410 °C; total pressure, 10 bar; WHSV = $10\, g_{n-C_8}\, h^{-1}\, g_{zeolite}^{-1}$; and $H_2/n\text{-}C_8$ molar ratio, 14. All data were collected at 1 h on stream. Reaction products were analyzed with a HP 5890 Series II gas chromatograph equipped with a flame ionization detector and automatic valve for continuous analysis. The reactor effluent stream was sent for analysis through a heated line (about 180 °C) to the automatic valve. The gas chromatograph was equipped with a capillary column SUPELCO Petrocol DH50.2, 0.2 mm i.d. and 50 m length. Results from a reproduced experiment showed that conversion and isomer selectivity had an error of ±4%.

3 Results and Discussion

3.1 Catalysts Characterization

Acidity data of all Ni–Pt and Sn–Pt bimetallic catalysts and the corresponding monometallic ones are given in Table 1. TPD profiles characterizing NH_3 adsorbed on the different catalysts are shown in Fig. 1. In all cases, desorption curves were deconvoluted and fitted into two peaks, corresponding to the desorption of ammonia on weak and strong acid sites, respectively. The first peak of desorption occurs in the temperature range of 300–350 °C for all catalysts tested. The second peak of desorption occurs at 450–500 °C for Ni–Pt catalysts and at 375–425 °C for Sn–Pt catalysts. The amount of ammonia desorbed and the desorption temperature were considered as a measure of total acidity and acid strength of catalysts, respectively [9]. Peak position did not vary substantially with the different metal concentration combinations. Therefore, it is possible to claim that the strength of the acid sites in the different bimetallic catalysts did not change noticeably [7, 8, 10].

Table 1 Acidity data for Ni–Pt and Sn–Pt bimetallic catalysts

Sample	Total acidity (mmol $NH_3\ g_{cat}^{-1}$)	Weak acidity (mmol $NH_3\ g_{cat}^{-1}$)	Strong acidity (mmol $NH_3\ g_{cat}^{-1}$)
1Ni	0.222	0.123	0.099
0.75Ni0.25Pt	0.197	0.144	0.053
0.50Ni0.50Pt	0.243	0.119	0.124
0.25Ni0.75Pt	0.264	0.109	0.156
1Pt	0.264	0.093	0.171
0.25Sn0.75Pt	0.299	0.150	0.150
0.50Sn0.50Pt	0.274	0.144	0.130
0.75Sn0.25Pt	0.215	0.092	0.123
1Sn	0.170	0.086	0.084

As far the ammonia desorption is concern (Table 1), total acid site density values corresponding to Ni–Pt bimetallic catalysts were in between of those observed from monometallic ones with the same metal loading [2]. However, sample 0.75Ni0.25Pt showed a decrease in the strong acidity value as well as in the total acidity, exhibiting a different behaviour to the others. Similar results were obtained by Fúnez et al. [8]. It can be noticed how the total acidity of the catalysts decreased with increasing Ni loading [5, 8, 10]. The decrease in acidity of the Ni–Pt bimetallic catalysts with higher nickel loadings can be accounted for in terms of occupation of some acid sites by added nickel species [5, 10–12]. This process may occur in parallel with Ni combining with Pt particles and the probable growth of Ni–Pt particles [5]. The catalysts with 0.75 wt.% Ni and 0.25 wt.% Pt yield a higher growth of the bimetallic particles occupying the greatest part of acid sites. This growth was confirmed by surface area and metal dispersion measurements. The area BET value decreased in a 10% and the metal dispersion value was nearly negligible.

Sn–Pt bimetallic catalysts showed a different behaviour (Table 1). It was observed an increase in the total acidity as increasing the platinum content, even being higher than that observed for the monometallic sample 1Pt. Moreover, the higher contribution was due to the weak acidity as can be subtracted from the values in Table 1. Neri et al. [13] reported the formation of Lewis acid sites because of the interaction between Sn and Pt. This kind of acidity is linked to Sn sites [13]. Furthermore, it is possible to claim that part of Sn is present as oxidized tin species, as later TPR evidenced.

Temperature-programmed reductions were carried out in order to determine the relative differences in the

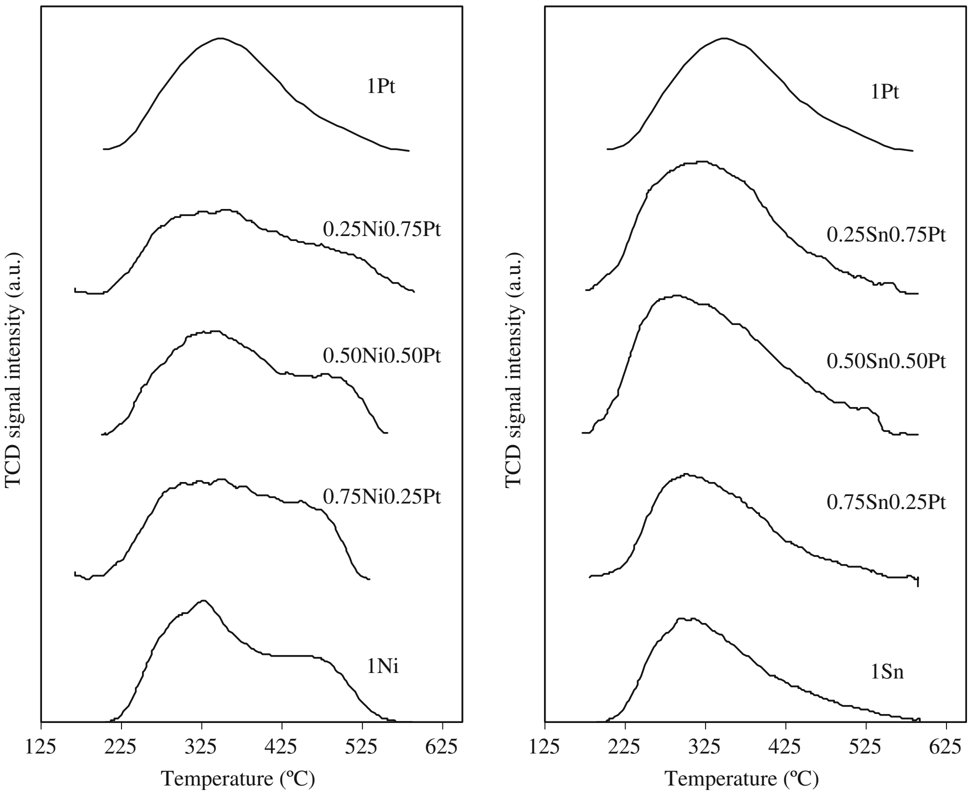

Fig. 1 Temperature programmed desorption of ammonia (TPD) profiles

reducibility of catalysts impregnated with both metals at different loadings. TPR profiles of Ni–Pt and Sn–Pt bimetallic catalysts are shown in Fig. 2. The catalyst 1Pt showed a reduction peak at 390 °C (not shown) [2] attributed to the reduction of Pt^{2+} to Pt^0 [2, 8].

Two reduction peaks at 500 °C and 700 °C, respectively, were detected for the sample 1Ni. Both reduction peaks were obtained at higher temperatures than those observed by Fúnez et al. [8], using beta zeolite without binder. This fact allowed us to confirm that the metal in agglomerated catalysts interacted strongly with the support.

The peak at 500 °C could be related to the reduction of NiO to Ni^0 [14]. The second peak at 700 °C was due to the reduction of stabilized Ni^{2+} species located into zeolite sites, where the access for H_2 molecules should be difficult [15]. Moreover, these ions located in small cavities could strongly interact with the zeolite structure in order to form less reducible species.

It can be clearly appreciated two reduction peaks for all Ni–Pt bimetallic catalysts. The first peak corresponded to the reduction of Pt and Ni species. A little amount of platinum in Ni–Pt bimetallic catalysts did not contribute to the reduction of Ni species. Similar results were obtained by Geetha Bhavani et al. [5]. These authors reported that the added Pt was postulated to favour the reduction of Ni cation in the region 0–0.3 wt.% Ni. NiO is observed at higher Ni loading. This fact was in line with the TPD data: 0.75Ni0.25Pt catalyst showed an acidity value lower than that observed for other Ni–Pt bimetallic catalysts. Larger bimetallic particles and incomplete reduction of nickel species could explain the behaviour of catalyst 0.75Ni0.25Pt. When the loading of platinum was increased not only the hydrogen consumption but also the reduction temperatures were decreased, even sample 0.25Ni0.75Pt did not show the peak corresponding to the nickel reduction at high temperature. The decrease in Ni reduction temperature with increasing Pt concentration may indicate a catalytic reduction of Ni. Presumably, mobile platinum oxide and/or nickel oxide particles collide into each other by thermal migration and the nickel oxide particles are catalytically reduced by prereduced Pt particles. This postulate suggests the formation of Ni–Pt bimetallic interactions [10].

Regarding Sn–Pt bimetallic catalysts, in Fig. 2 the TPR profiles of Sn monometallic catalyst and Sn–Pt bimetallic catalysts are depicted. The TPR profile for the catalyst with 1 wt.% tin showed one broad reduction peak starting at 300 °C with the maximum around 600 °C, probably indicating the presence of at least two different forms of tin [7]. When a little amount of platinum was added (0.25 wt.%), the TPR profile showed two peaks: the first one could be due to a co-reduction of Pt and Sn. This peak appeared in the zone of the Pt reduction in the monometallic catalyst. However, the reduction peak of Pt in this catalyst shifted to

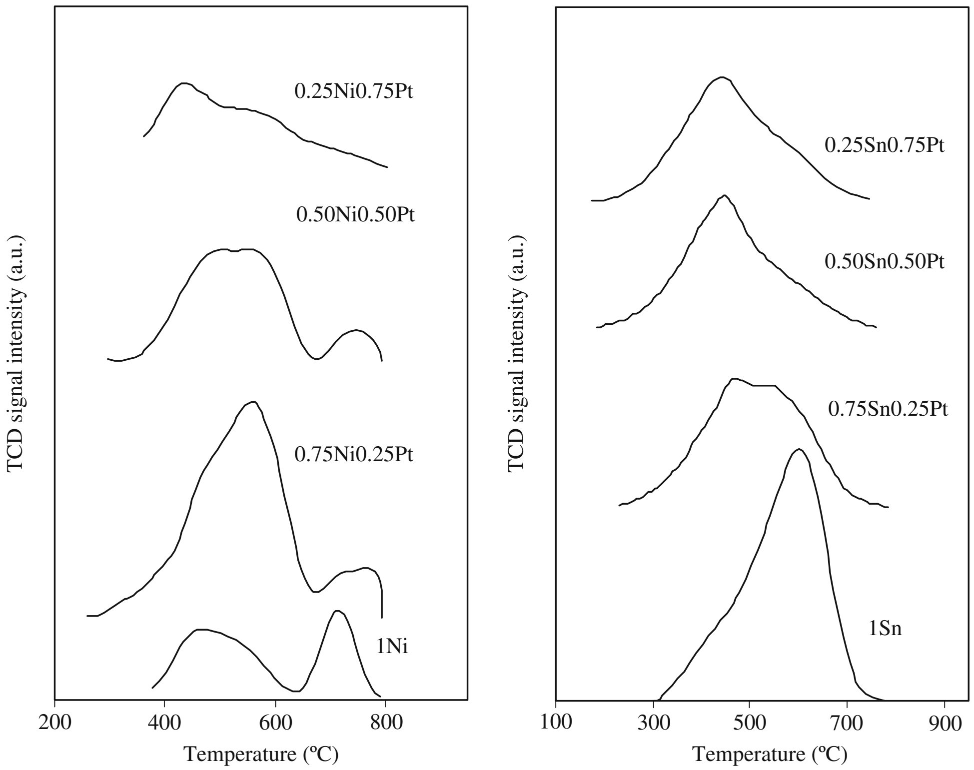

Fig. 2 Temperature programmed reduction (TPR) profiles

higher temperature, indicating that the reduction of platinum was depressed by the addition of tin [16]. The second one appeared at temperatures nearby the Sn species that were hardly reducible and could be due to Sn species that did not interact with Pt [17]. However, a little decrease in the reduction temperature was observed compared with the Sn monometallic catalyst, even this peak disappeared when high loadings of platinum were loaded. According to these results, it is reasonable to say that the presence of platinum induced the reduction of Sn species by hydrogen spillover from the reduced Pt, and thus promoting the reduction of tin oxide [16].

3.2 Hydroisomerization of *n*-Octane

Figures 3 and 4 show the *n*-octane conversion versus the reaction temperature for Ni–Pt and Sn–Pt bimetallic catalysts, respectively. A typical dependence of *n*-octane conversion over bifunctional catalysts with the reaction temperature was observed: paraffin conversion increased as increasing reaction temperature [18].

For Ni–Pt bimetallic catalysts (Fig. 3), *n*-octane conversion increased as increasing the platinum content, except for the catalyst 0.75Ni0.25Pt that showed the lowest conversion in all the range of temperature. This behaviour can be explained according to the acid site density of the catalyst (Table 1), which affected to the paraffins conversion [19, 20]; specifically, strong acid sites were the responsible of the isomerization reaction [21]. As above mentioned, the acidity values decreased as the nickel content was increased. This was in line with the *n*-octane conversion values obtained. Catalyst 0.75Ni0.25Pt showed the lowest total and strong acidity value (Table 1), confirming the lowest *n*-octane conversion value obtained.

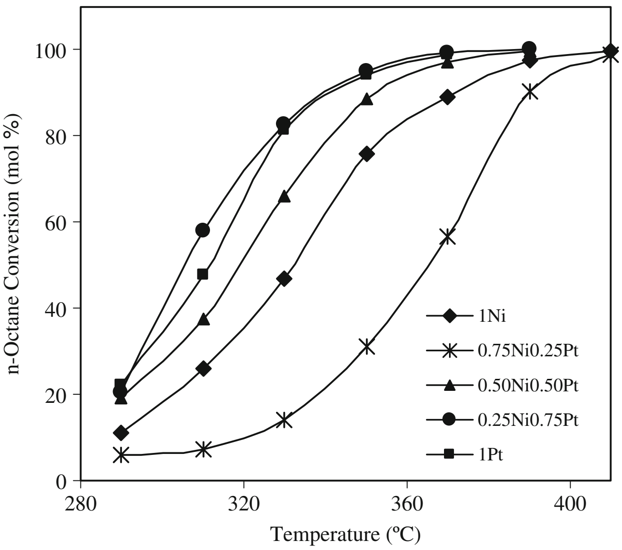

Fig. 3 *n*-Octane conversion versus reaction temperature for Ni–Pt bimetallic catalysts

Regarding Sn–Pt bimetallic catalysts (Fig. 4), an increase in *n*-octane conversion in all the range of temperatures was observed as increasing the amount of

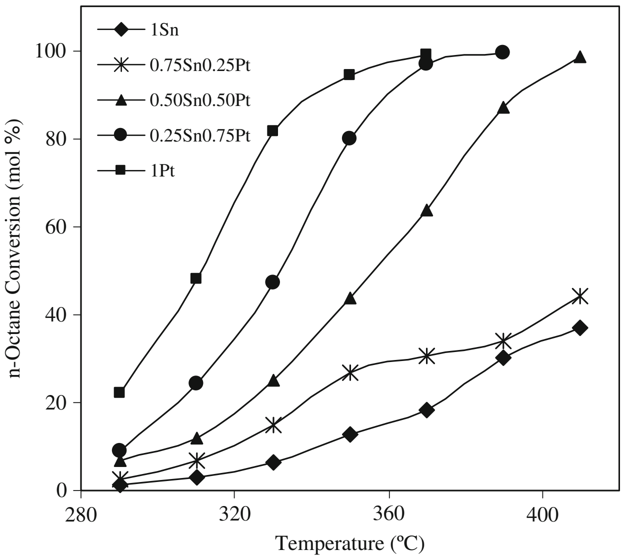

Fig. 4 *n*-Octane conversion versus reaction temperature for Sn–Pt bimetallic catalysts

platinum. As above mentioned, the higher contribution of the Sn presence was due to the weak acidity. However, hydroisomerization of paraffins is promoted by strong acid sites. As was expected, the conversion of *n*-octane decreased with the Sn content.

Table 2 reported the selectivity of different products obtained at approximately 50 mol% of *n*-octane conversion for all catalysts used. Product analysis showed that 2-methylheptane (2-MC7), 3-methylheptane (3-MC7), 4-methylheptane (4-MC7) and 3-ethylhexane (3-EC6), as monobranched isomers; and 2,2-dimethylhexane (2,2-DMC6), 2,3-dimethylhexane (2,3-DMC6), 2,4-dimethylhexane (2,4-DMC6), 2,5-dimethylhexane (2,5-DMC6), 3,3-dimethylhexane (3,3-DMC6), 3,4-dimethylhexane (3,4-DMC6) and 2-methyl-3-ethylpentane (2M-3EC5), as dibranched isomers, were major products due to the skeletal rearrangement in *n*-octane.

As cracking products, hydrocarbons from C1 to C7 were obtained, being the hydrocarbons with 3, 4 and 5 carbon

Table 2 Selectivity of different products obtained at approximately 50 mol% of *n*-octane conversion for all the catalysts used

Sample	1Ni	0.75Ni0.25Pt	0.50Ni0.50Pt	0.25Ni0.75Pt	1Pt	0.25Sn0.75Pt	0.50Sn0.50Pt	0.75Sn0.25Pt	1Sn
X (mol%)[a]	46.7	56.6	55.9	57.8	48.0	47.2	43.9	44.0	36.9
T (°C)[b]	330	370	320	310	310	330	350	410	410
C1 + C2	1.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C3	10.8	4.6	3.1	1.0	1.4	2.2	6.1	7.2	10.4
i-C4	30.4	15.0	11.3	3.0	2.7	7.8	21.9	20.8	31.1
C4	14.7	7.3	5.2	1.5	1.5	3.3	9.7	10.8	17.1
i-C5	12.4	6.9	4.6	1.4	1.6	3.2	8.7	9.1	18.1
C5	5.5	1.0	0.4	0.4	0.9	0.4	1.8	2.8	8.2
i-C6	2.1	0.2	0.0	0.0	0.4	0.0	0.0	0.0	4.3
C6	1.4	0.2	0.0	0.1	0.4	0.0	0.0	0.0	1.1
i-C7	0.4	0.2	0.0	0.0	0.0	0.0	0.0	0.0	3.5
C7	0.8	0.5	0.0	0.1	0.3	0.0	0.0	0.0	0.6
2,2-DMC6	0.1	0.1	3.5	3.6	2.9	1.9	1.2	0.6	0.4
2,5-DMC6	0.9	2.6	4.9	5.1	4.0	5.0	3.7	3.1	0.6
2,4-DMC6	1.5	3.7	6.7	6.9	5.6	6.1	4.2	3.0	0.8
3,3-DMC6	0.0	0.0	1.9	2.1	2.0	1.0	0.5	0.5	0.0
2,3-DMC6	0.2	0.0	3.2	3.3	3.1	3.2	2.4	1.4	0.0
2M-3EC5	0.3	0.1	0.3	0.4	0.4	0.4	0.3	0.0	0.0
2-MC7	4.2	19.0	19.5	26.1	25.6	24.0	14.9	15.9	1.4
4-MC7	3.4	8.0	8.6	11.1	11.4	9.8	5.6	4.6	1.1
3,4-DMC6	1.2	0.2	1.5	1.4	1.3	1.5	1.0	0.8	0.0
3-MC7	8.4	21.9	22.4	28.7	30.7	26.9	16.2	18.2	1.4
3-EC6	0.2	0.5	3.5	4.0	3.5	3.3	1.8	1.2	0.0
S_{mono} (mol%)[c]	16.2	49.4	54.0	69.8	71.2	64.0	38.5	40.0	3.9
S_{multi} (mol%)[d]	4.3	6.7	22.0	22.7	19.3	19.1	13.3	9.4	1.7

[a] *n*-Octane conversion (mol%)

[b] Reaction temperature (°C)

[c] Monobranched selectivity (mol%)

[d] Multibranched selectivity (mol%)

atom number, the most dominant. The predominated presence in all the catalysts of *iso*-butane as cracked product was a consequence of the prevalence of type A β-scission route (tertiary carbenium ion to tertiary), responsible for generating two *iso*-butane molecules [22]. Monometallic catalysts loading with Ni or Sn yielded a higher selectivity to cracking products than the platinum monometallic catalyst.

The presence of hydrogenolysis products, C1 and C2, were only patent in Ni monometallic catalyst and even in the bimetallic catalyst with higher content of nickel (0.75Ni0.25Pt). It is well documented by many authors in a wide variety of studies that hydrogenolysis of alkanes on Ni-containing catalysts occurs mainly at terminal carbon–carbon bonds [23–28], evidencing the presence of light alkanes.

Figures 5–8 show for all catalysts used the monobranched and multibranched selectivity, respectively, as a function of the *n*-octane conversion. A maximum in the selectivity of monobranched isomers at low conversions can be observed (Figs. 5 and 7). As the conversion was increased (increasing the temperature), the selectivity towards these products decreased, yielding the multibranched ones, whose selectivity reached a maximum (Figs. 6 and 8). The production of cracked products decreased the selectivity of multibranched ones, mainly at high conversion values.

Concerning Ni–Pt bimetallic catalysts, the selectivity to monobranched isomers increased with the increase in platinum content [8]. Multibranched selectivity values reached a maximum at high *n*-octane conversion values, being higher the multibranched selectivity yielded by the catalyst 0.25Ni0.75Pt than that obtained with the Pt monometallic catalyst. This behaviour has been studied by several authors. Jao et al. [10] observed that the addition of a moderate amount of Ni (from 0.2 to 0.5 wt.%) to Pt/HMOR enhanced the rate of branched isomer formation. Yoshioka et al. [15] observed for monometallic catalysts containing Ni an increase in the formation of di-ramified isomers. The selectivity values for the catalyst 0.75Ni0.25Pt were in line with the rest of catalysts. However, if we take into account how the total selectivity changed with the reaction temperature (Fig. 9), a different trend was observed.

As explained earlier, catalyst 0.75Ni0.25Pt showed an acidity value lower than that observed for other Ni–Pt bimetallic catalysts. Larger bimetallic particles and incomplete reduction of nickel species could explain the behaviour of catalyst 0.75Ni0.25Pt. Although this catalyst required higher temperatures for achieving high selectivity values (Fig. 9), at high temperatures yielded the highest isomer selectivity values. The decrease in acidity of the Ni–Pt bimetallic catalysts with higher nickel loadings can be accounted for in terms of occupation of some acid sites by added nickel species [5, 10–12]. It was proposed that the addition of Ni reduces the acid sites that promote hydrocracking reactions, forming sites which were selective for the isomerization of *n*-octane.

Mono and multibranched isomer selectivity for Sn–Pt bimetallic catalysts followed a similar trend with the *n*-octane conversion. In this case, the selectivity for Pt monometallic catalyst was always higher than that observed for the bimetallic catalysts. However, the effect of temperature on the selectivity (Fig. 10) showed that the selectivity for Pt monometallic catalyst decreased faster in comparison with the fall in the selectivity of bimetallic

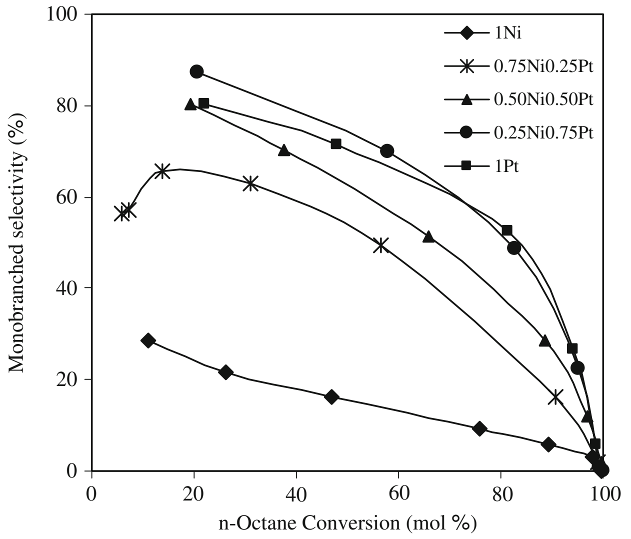

Fig. 5 Monobranched selectivity versus *n*-octane conversion for Ni–Pt bimetallic catalysts

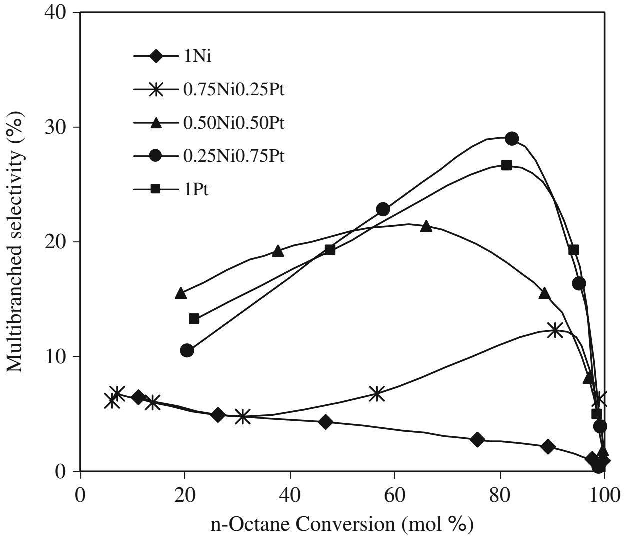

Fig. 6 Multibranched selectivity versus *n*-octane conversion for Ni–Pt bimetallic catalysts

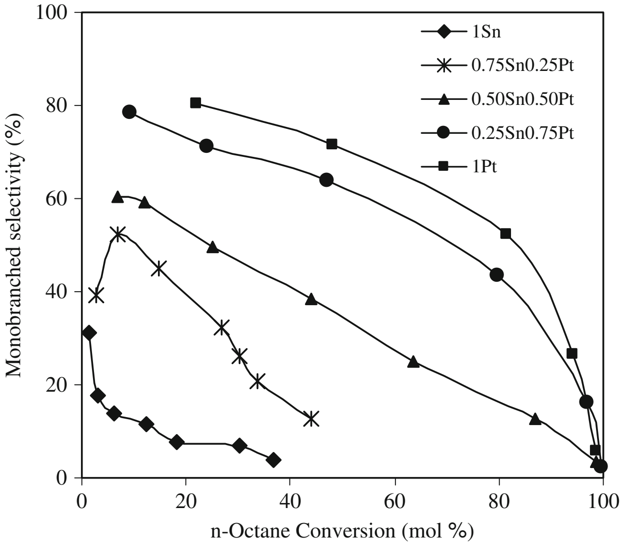

Fig. 7 Monobranched selectivity versus *n*-octane conversion for Sn–Pt bimetallic catalysts

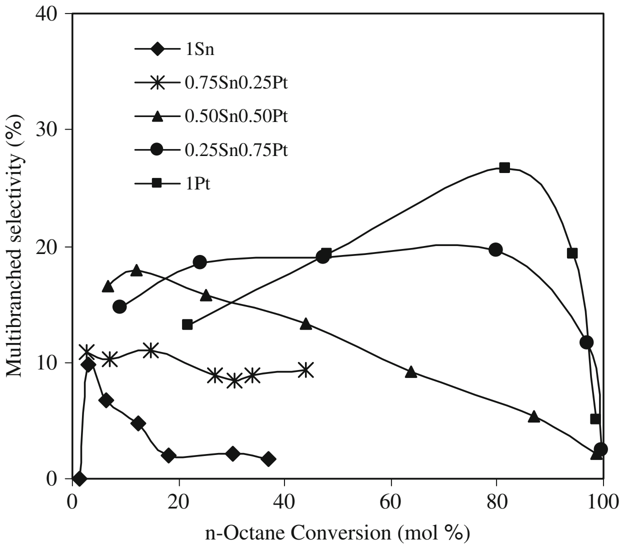

Fig. 8 Multibranched selectivity versus *n*-octane conversion for Sn–Pt bimetallic catalysts

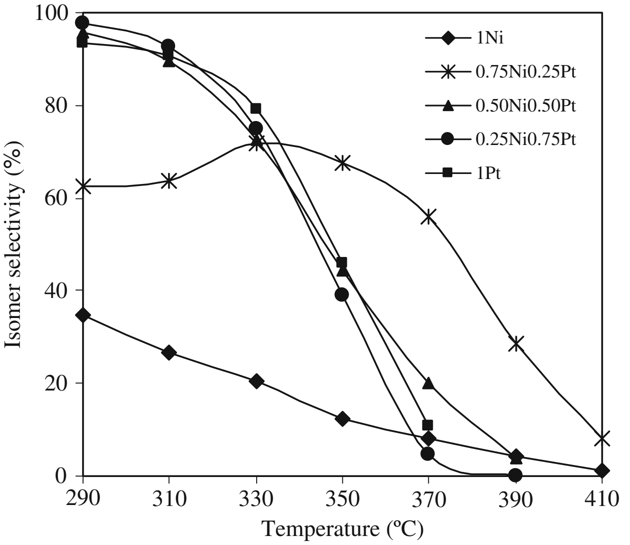

Fig. 9 Isomer selectivity versus reaction temperature for Ni–Pt bimetallic catalysts

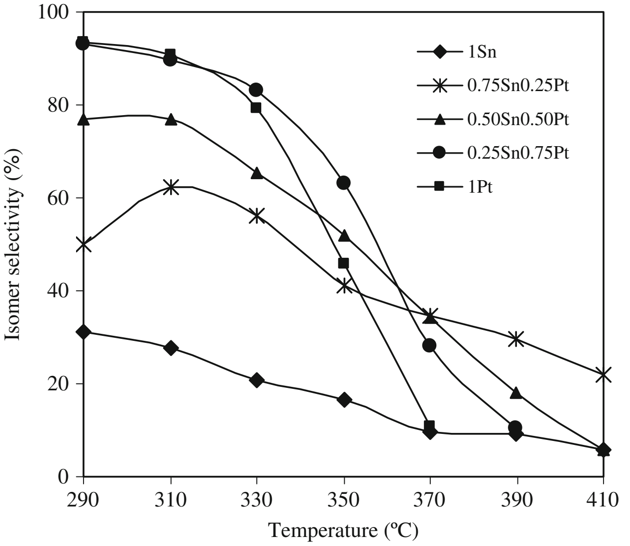

Fig. 10 Isomer selectivity versus reaction temperature for Sn–Pt bimetallic catalysts

catalysts. The role of Sn on the catalyst stability has been documented [7]. It is possible to observed (Fig. 10) how at high temperatures the bimetallic catalyst with the highest Sn content (sample 0.75Sn0.25Pt), yielded the highest selectivity values. This fact confirmed that Sn promoted a higher selectivity to isomerization products.

4 Conclusions

The addition of Ni or Sn to monometallic platinum beta agglomerated catalysts affected the reaction of *n*-octane hydroisomerization. Temperature programmed desorption of ammonia indicated that the strength of the acid sites in the different bimetallic catalysts did not change considerably. It was observed that the total acidity of the catalysts decreased with increasing Ni loading. The decrease in acidity of the Ni–Pt bimetallic catalysts with higher nickel loadings can be accounted for in terms of occupation of some acid sites by added nickel species.

Temperature-programmed reductions revealed that a little amount of platinum in Ni–Pt bimetallic catalysts did not contribute to the reduction of Ni species. Regarding Sn–Pt bimetallic catalysts, when a little amount of platinum was added, a co-reduction of Pt and Sn was produced. When the loading of platinum was increased, the reduction of Sn species by hydrogen spillover was induced from the reduced Pt, thus promoting the reduction of tin oxide.

For Ni–Pt bimetallic catalysts, *n*-octane conversion increased with increasing the platinum content, except for the catalyst 0.75Ni0.25Pt. This behaviour can be explained according to the acid site density of the catalyst. Regarding Sn–Pt bimetallic catalysts, an increase in *n*-octane conversion in all the range of temperature was observed as increasing the amount of platinum.

Concerning Ni–Pt bimetallic catalysts, the selectivity to monobranched isomers increased with increasing the platinum content. Multibranched selectivity values reached a maximum at high *n*-octane conversion values. It was proposed that the addition of Ni reduces the number of acid sites that promote hydrocracking reactions, forming sites which were selective for the isomerization of *n*-octane.

At high temperatures, the bimetallic catalyst with the highest Sn content yielded the highest selectivity values confirming the promotional effect of Sn over the selectivity to isomerization products.

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