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n-Pentane Hydroisomerization on Pt Containing HZSM-5, HBEA and SAPO-11

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Abstract Hydroisomerization of *n*-pentane over platinum promoted acids zeolites was studied. The effect of structure and acidity of the support was investigated at atmospheric pressure between 250 and 400 °C. Pt/HDBEA catalyst showed the best performance at 300 °C with high activity and selectivity to isopentane, due to its structure and a proper balance between acid and metallic sites. This catalyst has a high catalytic stability and regeneration under air flow after deactivation by coking, restores its activity and selectivity.

Keywords *n*-Pentane · Hydroisomerization · Supported-metal catalysts · Zeolites

1 Introduction

The worldwide in the formulation of gasoline are the reduction of evaporative emissions and more complete gasoline combustion. The general reduction in the Reid vapour pressure, aromatics, alkenes, sulphur content, will have a negative impact on the octane number of the gasoline pool, and also will reduce the total amount of gasoline produced. Taking into account the above scenario, it appears that branched paraffin components are the preferred gasoline component.

Isomerization of normal paraffin is of considerable interest and plays an important role in the petroleum industry [1]. The branching of *n*-paraffins C_4–C_7 is needed to improve the octane number of gasoline [2, 3] while that of long-chain alkanes has been used in the dewaxing processes for production of high quality diesel fuel and lube base oil [4, 5]. The isomerization process usually takes place in the presence of hydrogen, and in this case is referred as hydroisomerization. An atmosphere of hydrogen is used to minimize carbon deposits on the catalysts but hydrogen consumption is negligible. Reaction temperature of about 95–205 °C are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures. In order to achieve the low temperature necessary to obtain an acceptable yield of isomers, the catalyst systems used in the early units were based on aluminium chloride in some form. These catalyst systems, however, had the drawback of being highly corrosive and difficult to handle. In recent years, catalyst of a different type has come in use. These are solid catalysts consisting of a support having an acidic carrier and a hydrogenation–dehydrogenation function, frequently a noble metal. In this sense, zeolites, as in many other reactions, have attracted a great interest due to their useful properties, such as acidity, shape selectivity and stability, as well as the availability of many different structures.

Paraffin isomerization is a reaction typically catalyzed by very strong acid sites. More efficient than acid catalysts are metal-acid bifunctional catalysts. These catalysts are very active because they allow a dual site mechanism: *n*-paraffins are dehydrogenated to olefins on the metal, olefins are isomerized on the acid site, and *iso*-olefins produced are hydrogenated to *iso*-paraffins on the metal.

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The bifunctional catalyst is very convenient because olefins are more easily isomerized on the acid function than paraffins. Hydrogenation–dehydrogenation steps catalyzed by the metal function are very rapid, and the olefin isomerization is the slowest step [6].

The product distribution of *n*-paraffins hydroisomerization is dependent on the acid site density, acid/metal ratio, acid strength and pore structure of zeolites. Both acid and metal site density are important and their proper balance is critical in determining the activity of the catalyst [7, 8]. Several zeolites like mordenite, ZSM-5 and Beta have been tested in alkane hydroisomerization [9–12]; the latter type has a great industrial interest because its acidity and particular structure [11, 12]. Several metals have been tested as the hydrogenated–dehydrogenated function in alkane hydroisomerization. Under the metals used, Pt exhibits both high activity and selectivity [13, 14].

The purpose of the current work was to compare the activity and selectivity for *n*-pentane conversion on Pt containing HMFI, HBEA and SAPO-11 catalysts and to evaluate the role of the acidity and the pore diameter upon the selectivity and activity. The influence of reactions conditions, the catalytic stability and the effect of catalyst regeneration had been studied for the catalyst with the best performance.

2 Experimental

2.1 Preparation and Characterization of Catalysts

The bifunctional catalysts used consisted of HZSM-5, HDBEA and SAPO-11 as the acid function and Pt as the metal function. The starting ZSM-5 and BEA zeolites were commercial samples. First, the starting zeolites were ion-exchanged with a 3 M ammonium acetate solution, for 3 h, with continuous stirring at 60 °C using 20 mL of solution per gram of zeolite. Then the exchanged zeolites were calcined in flowing air at 550 °C for 4 h to obtain the hydrogen form (HZSM-5 and HBeta). HBeta was then refluxed with 1 M HCl at room temperature for 8 h, using 10 mL of solution/gram of HBeta. After the acid treatment, the sample was washed free of chloride, dried overnight at 100 °C and calcined statically under an ambient atmosphere at 550 °C, for 15 h. This product was named as HDBEA.

The synthesis procedure for SAPO-11 has been reported elsewhere [15]. The gel molar composition was Al_2O_3:P_2O_5:DPA:0.3SiO_2:50H_2O, a final crystallization temperature of 200 °C and a crystallization time of 24 h was employed.

The Pt-promoted catalysts were prepared by impregnating the calcined solids with $[Pt(NH_3)_4Cl_2]$ (from BDH, reagent grade) using the wet impregnation method with excess solution, to reach 0.5 wt% of Pt. In order to decompose the Pt complex, the catalysts were calcined under a stream of dry air (30 mL/min), the temperature was increased up to 150 °C (5 °C/min) and kept for a 2 h period. The latter was then increased up to 300 °C (5 °C/min) and kept constant for 16 h.

X-ray diffractograms (XRD) of the solids were recorded with a Philips diffractometer PW 1730 Phillips using Cu kα radiation operated at 30 kV and 20 mA, and scanning speed of 2° 2θ/min. Diffraction lines between 8 and 25° 2θ/min were taken to determine the degree of crystallinity in the usual way.

Chemical analysis for Al, P and Si of the calcined samples were performed using atomic emission spectroscopy with a source of plasma inductively coupled. Samples were previously fused with lithium metaborate and dissolved in dilute nitric acid before analyses. N_2-specific surface areas (SSA) were obtained on Micromeritics 2200 equipment at liquid nitrogen temperature. All the samples were pre-treated at 350 °C under vacuum overnight.

Surface acidity was characterized by FTIR of the pyridine/solid interaction on a Perkin Elmer 1760-X spectrometer. All the spectra in the pyridine region were recorded at room temperature, after outgassing at 250, 350 and 500 °C. The intensity of the bands at 1,550 and 1,450 cm^{-1} measured after each outgassing temperature, were taken to be proportional to the concentration of Bronsted and Lewis acid sites, respectively. For the purpose of this work three distinct acidity regions were arbitrarily defined in terms of the acid strength: total acidity (weak + moderate + strong) related to those sites retaining pyridine at 250 °C, moderate + strong acidity, ascribed to those sites retaining pyridine at 350 °C and strong acidity, associated with those sites retaining pyridine at 500 °C. Integrated extinction coefficients reported by Emeis [16] were used for the quantitative determination of the number of acid sites.

The chemisorption measurements were carried out by using a dynamic pulse technique with an argon flow and pulses of H_2. In order to calculate the metal dispersion, and adsorption stoichiometry of metal/H = 1 was assumed [16]. The equipment used was a Micromeritics TPD/TPR 2900 analyzer.

2.2 Catalytic Test

n-Pentane transformation was carried out under atmospheric pressure in a continuous fixed-bed reactor, feeding *n*-pentane by the gas flow saturation method. The feeding gas mixture consisted of H_2 (12 mL/min) with a partial pressure of *n*-pentane of 0.26 atm. To reach this pressure,

H_2 was passed through a glass vessel with *n*-pentane kept at 0 °C in an ice bath. The mass of catalyst was about 0.3 g (weight hourly space velocity WHSV = 2.5 h^{-1}). Before the reaction test, the metallic phase was reduced by a hydrogen flow (30 mL/min) at 450 °C for 2 h. The product analysis was done after 30 min on-stream by on-line chromatography using a Hewlett-Packard 5890A with silica KCl/Al2O3 capillary column and FID detector.

The total conversion (X) of *n*-pentane was calculated according to Eq. 1

$$X = \frac{\sum A_i - A_{n-\text{pentane}}}{\sum A_i} \times 100 \qquad (1)$$

where A_i is the corrected chromatographic area for a particular compound, used to express the conversion and selectivity as molar percentages.

For a reaction product, or a set of products, the selectivity (S) is defined by Eq. 2

$$S_p = \frac{A_p}{\sum A_i - A_{n-\text{pentane}}} \times 100 \qquad (2)$$

The products were grouped as follows:

- *Iso*-pentane
- Lower C_5 ($<C_5$) products: adding up the corresponding corrected areas of the C_1–C_4 products, including paraffins and olefins.
- Pentenes (C_5=): consisted of the six pentene isomers: 1-pentene, *cis*-2-pentene, *trans*-2-pentene, 2-methyl-2-butene, 2-methyl-1-butene, and 3-methyl-1-butene.
- Higher C_5 reaction products ($>C_5$): Sum of the corrected areas of C_6–C_8 products.

3 Results and Discussion

Table 1 shows some characterization data of acid supports. The SSA values lie within the range previously reported for this kind of solids [12, 15]. The acid treatment of HBeta caused 60% dealumination (Si/Al molar ratio increases from 15 to 41), retaining more than 90% crystallinity. The higher Si/Al ratio of HDBEA compared to HZSM-5 can be explain the lower amount of Bronsted acid sites reported for the former zeolite, such as is indicated in Table 1. A high proportion of strong acid site (>40%) was found for both zeolites. SAPO-11 was the support with the lowest acidity.

Table 2 shows specific surface area (SSA) and metal dispersion values of the Pt-promoted catalysts here used. It can be observed a slight decrease in SSA values, compared to supports without metal. In general, low values of metal dispersion, particularly for HZSM-5 zeolite, were obtained. These differences can be attributed to the characteristics of the supports employed.

3.1 Catalytic Test

Total conversions of *n*-pentane for HZSM-5, HDBEA and SAPO-11 without metal versus the reaction temperature are presented in Fig. 1. Between 250 and 380 °C, over HDBEA and SAPO-11, the total conversion was always below 5%. By contrary, over HZSM-5, an increase in the *n*-pentane conversion with the increase of the reaction temperature was observed. Increasing the reaction temperature from 250 to 380 °C, total conversion was between 20% and 60%, almost totally oriented towards C_1–C_4 hydrocarbons (selectivity of 80–87%), mainly propane and butane. The highest acidity of HZSM-5 (number and strength distribution) could explain its catalytic performance. An experiment without catalyst (blank) was carried out, in order to account the homogeneous reaction effect. A low conversion below 2% was obtained under these conditions.

Figure 2 shows the dependence of the *n*-pentane conversion on the reaction temperature for the Pt impregnated catalysts. In all the catalysts, the total conversion increased with the increase of the reaction temperature. A similar conversion was obtained for PtHZSM-5 and HZSM-5, however, a different behaviour was observed for PtHDBEA and PtSAPO-11 compared to the supports without metal. In these later cases, the addition of platinum increases the catalytic activity towards the *n*-pentane conversion.

As can see in Table 1, HZSM-5 zeolite presented the highest acidity, furthermore metal dispersion in Pt/HZSM-5

Table 1 Specific surface area (SSA), chemical composition, proportional crystallinity (% Cryst.) and the amount (μmol/g) of Bronsted acid sites (BAS) and Lewis acid sites (LAS) after pyridine desorption at 250, 350 and 500 °C

Sample	SSA (m^2/g)	Molar composition formula TO_2	% Cryst.	250 °C		350 °C		500 °C	
				BAS	LAS	BAS	LAS	BAS	LAS
HZSM-5	413	$H_{7.97}(Al_{7.97}Si_{88.03}O_{192})$	100	306	125	272	50	125	5
HDBEA	593	$H_{1.52}(Al_{1.52}Si_{62.5}O_{128})$	93	142	176	82	112	79	66
SAPO-11	158	$(Al_{0.5}P_{0.43}Si_{0.06})O_2$	100	53	38	45	22	4	12

Table 2 Specific surface areas, metal dispersion values and ratio nA/nPt of the Pt-promoted catalysts

Catalyst	SSA (m^2/g)	Metal dispersion (%)	nA/nPt
Pt/SAPO-11	137	16	16
Pt/HZSM-5	405	13	101
Pt/HDBEA	463	24	31

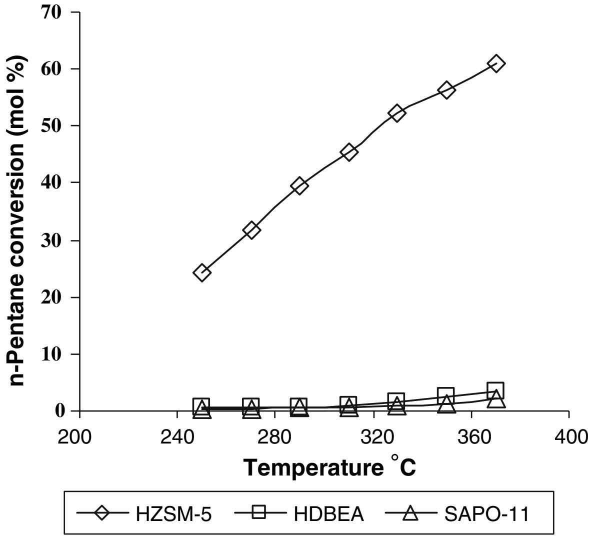

Fig. 1 *n*-Pentane conversion (X) versus the reaction temperature over HZSM-5; HDBEA and SAPO-11 zeolites. (WHSV = 2.3 h^{-1}; H_2/*n*-pentane = 2.75 mol)

was very low, such as is showed in Table 2. These characteristics originate a high number of acid sites per available platinum atom, and then the cracking reaction can be favoured. Moreover, those catalysts without a proper balance between the metallic and the acid functions are expected to follow an alternative mechanistic pathway involving bimolecular intermediates [17].

It can be seen that platinum supported on Beta and ZSM-5 zeolites were more active than that based on SAPO-11. As can be seen in Fig. 2, similar conversion was observed for Pt/HZSM-5 and Pt/HDBEA, however, selectivity is very different in both catalysts, such as is showed in Figs. 3 and 4. Pt/HDBEA catalysts showed a high selectivity towards isopentane in the whole range of temperature studied, while for Pt/HZSM-5 selectivity towards C_1–C_4 hydrocarbons increase and selectivity towards isopentane decrease with the reaction temperature.

Several authors [11, 18, 19] have reported high activity and isomerization selectivity in *n*-paraffin transformation over platinum supported beta zeolites. This behaviour had been attributed to the large pore diameter of the pore structure of the Beta zeolite. Thus, the higher selectivity towards isopentane achieved for Pt/HDBEA catalyst, can

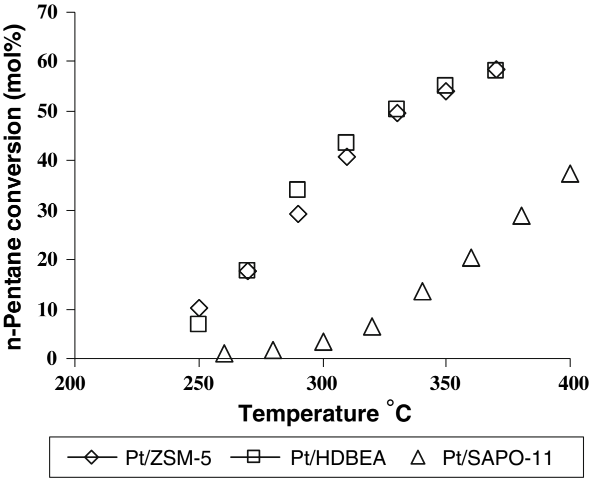

Fig. 2 *n*-Pentane conversion (X) versus the reaction temperature over the Pt impregnated catalysts Pt/HZSM-5; Pt/HDBEA and Pt/SAPO-11. (WHSV = 2.3 h^{-1}; H_2/*n*-pentane = 2.75 mol)

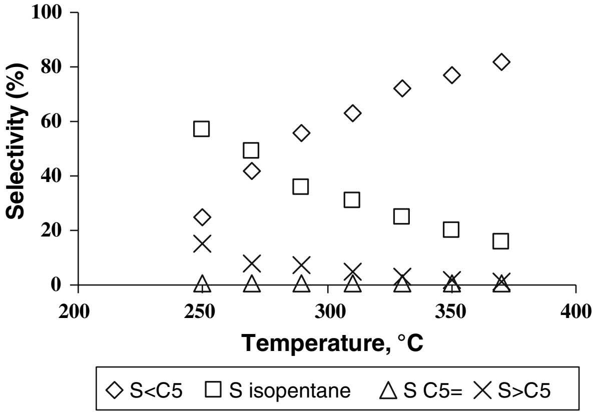

Fig. 3 Selectivity (S) versus the reaction temperature over PtHZSM-5 catalyst (WHSV = 2.3 h^{-1}; H_2/*n*-pentane = 2.75 mol)

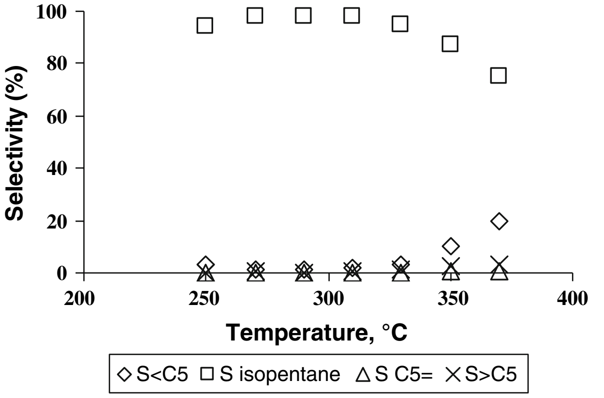

Fig. 4 Selectivity (S) versus the reaction temperature over Pt/HDBEA catalyst (WHSV = 2.3 h^{-1}; H_2/*n*-pentane = 2.75 mol)

be attributed in principle to its larger pore diameter compared to ZSM-5 and SAPO-11 zeolites. Furthermore, the obtained results suggest that Pt/HDBEA catalyst can be considered to have a proper balance between acid and metallic sites. For hydroisomerization of *n*-heptane over Pt/HMOR catalysts, Guisnet et al. [20] have reported an optimum in the number of acid sites per available platinum atom (nA/nPt) of 40. The ratio nA/nPt was calculated for Pt based catalysts and is presented in Table 2. As can be seen in this Table, the nearest value to the optimum of the ratio nA/nPt was achieved for Pt/HDBEA catalyst. The highest value of ratio nA/nPt for Pt/HZSM-5 could to explain the high selectivity towards C_1–C_4 hydrocarbons observed for this catalyst. Pt/SAPO-11 catalyst presented a low ratio nA/nPt; in this case, it is possible that the reaction exclusively catalyzed by the metallic function like hydrogenolysis would become the main reaction. In this way, the production of C_1–C_4 hydrocarbons observed for Pt/SAPO-11 could be attributed to the later reaction (see Fig. 5).

For *n*-pentane conversion at 300 °C over Pt/HDBEA catalyst, space velocities defined as weight hourly space velocity (WHSV), were varied between 1.25 and 5 h^{-1}. Figure 6 shows total conversion of *n*-pentane and Selectivity towards isopentane, versus the space velocities used in this work. The catalyst keeps its activity at least during 5 h of time on stream for each space velocity. The total conversion of *n*-pentane decreases with the increase in space velocity, however, a high Selectivity towards isopentane was observed in the whole range of space velocities studied. At the lowest WHSV of 1.25 h^{-1}, values of 54% of conversion and selectivity to isopentane 99% were obtained. This conversion value is lower than that calculated from data of equilibrium thermodynamic at 300 °C, (70%) according to data reported by Stull [21]; therefore it is possible to achieve a higher value conversion by decreasing WHSV below 1.25 h^{-1}.

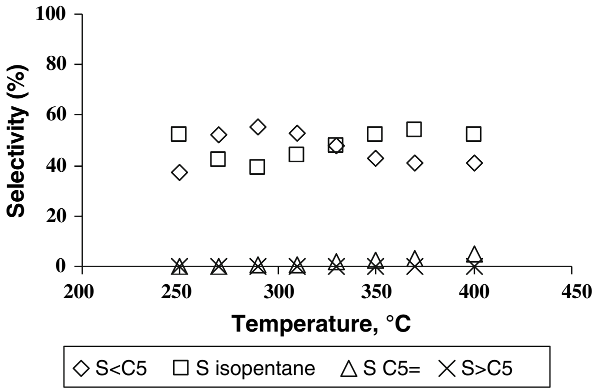

Fig. 5 Selectivity (S) versus the reaction temperature over Pt/SAPO-11catalyst (WHSV = 2.3 h^{-1}; H_2/*n*-pentane = 2.75 mol)

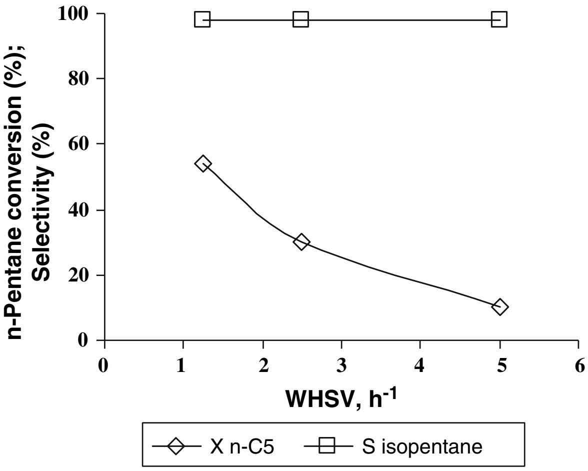

Fig. 6 *n*-Pentane conversion (X) and selectivity towards isopentane ($S_{isopentane}$) versus WHSV over Pt/HDBEA catalyst (T = 300 °C; H_2/*n*-pentane = 2.75 mol)

Using an ice-salt mixture in the recipient containing *n*-pentane, it was possible to decrease the temperature to −19 °C; in this way the H_2/*n*-pentane ratio increases to 10 mol. As observed in Fig. 7, the *n*-pentane conversion decreases by increasing the ratio H2/*n*-pentane form 2.75 to 10 mol, while selectivity towards isopentane kept a high value of 98%. The lower conversion of *n*-pentane achieved at the higher H_2/*n*-pentane ratio is consistent with the negative reaction orders in hydrogen and the positive reaction orders in n-C_5 reported by Hollo et al. [22]. It is worth noting that, for commercial processes are operated at the following reactions conditions: WHSV around 1.5 h^{-1}; H_2/*n*-pentane molar ratio, 2.75 and total pressure around 20 atm [1].

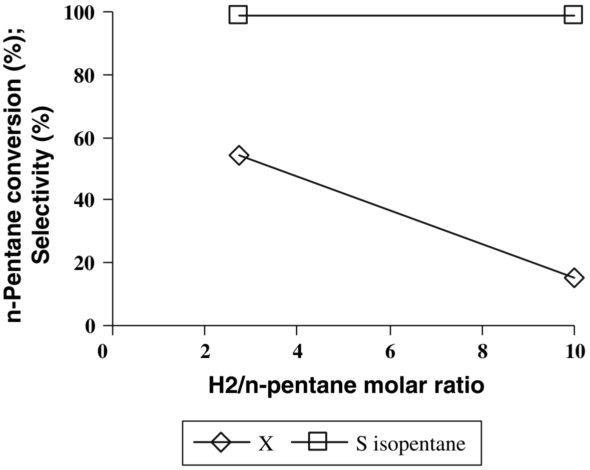

Fig. 7 *n*-Pentane (X) conversion and selectivity towards isopentane ($S_{isopentane}$) versus WHSV over Pt/HDBEA catalyst (T = 300 °C; WHSV = 2.5 h^{-1})

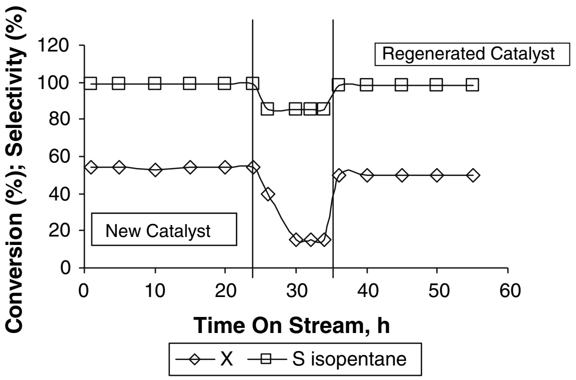

Fig. 8 *n*-Pentane conversion (X) and selectivity towards isopentane ($S_{isopentane}$) versus time on stream measured over new and regenerated Pt/HDBEA catalyst (T = 300 °C; WHSV = 1.25 h^{-1}; H_2/*n*-pentane 2.75 mol)

In order to study the catalytic stability of Pt/HDBEA catalyst, a catalytic test with 24 h of time on stream was carried out. The results of this test are shown in Fig. 7. Constant values of the *n*-pentane conversion and selectivity towards isopentane were obtained; therefore an intentional deactivation was carried out changing H_2 by N_2 as carrier gas. This change originated a deactivation of catalyst, and a decrease in the total conversion was observed. When switching back to H_2 was carried out, the activity and selectivity did not come back to previous level, of this way deactivation of the catalyst was indicated. Thereafter, the catalyst was regenerated in the same reactor under the following procedure:

First, the deactivated catalyst was heated at 5 °C/min under N_2 flow (40 mL/min) until 500 °C and kept at this temperature for 2 h period. Then, air was gradually incorporated, by decreasing N_2 flow and increasing air flow, to maintain a total flow in 40 mL/min. Finally, the catalyst was kept at 500 °C under air flow for a 6 h period. The direct regeneration in the presence of oxygen can be complicated by the fact that metal sintering can be promoted at high temperature [23].

The results using fresh and regenerated catalysts are shown in Fig. 7. A comparison between both catalysts reveals a similar catalytic performance, thus indicating that regeneration of the Pt/HDBEA catalyst does not affect its catalytic behaviour (Fig. 8).

4 Conclusions

The hydroisomerization of *n*-pentane was carried out using several platinum catalysts supported on zeolites (ZSM-5, Beta and SAPO-11). The catalysts based on Beta and ZSM-5 zeolites were more active than that based on SAPO-11. No differences in the *n*-pentane conversion were found between Pt/HZSM-5 and Pt/HDBEA catalysts. However, the selectivity to isomerization was very different. Over Pt/HDBEA catalyst, the selectivity to isomerization was higher than 95% at conversions levels between 10% and 54%. By contrary, for the catalyst based on ZSM-5 zeolite, the metal impregnation, led to catalyst whose acidity cannot be *properly balanced* by its hydrogenation–dehydrogenation activity, so that cracking is favoured. Over Pt/SAPO-11 the metallic function could be promoting the hydrogenolysis reaction.

Pt/HDBEA catalyst showed a good catalytic stability, and the selectivity and activity can be restored by calcination under air flow. An atmosphere of hydrogen is necessary for avoid the deactivation of catalyst. At atmospheric pressure, the best reaction conditions were 300 °C; WHSV 1.25 h^{-1}; H_2/*n*-pentane molar ratio, 2.75. Under these conditions 57% of total conversion with 98% of selectivity to isopentane was obtained. The conditions are compatible with some reports for commercial processes.

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