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Hydroisomerization of a refinery naphtha stream over platinum zeolite-based catalysts

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Abstract

In this paper, the hydroisomerization of a C7–C8 stream obtained by distillation of a refinery naphtha stream using platinum zeolites (mordenite, beta and ZSM-5) agglomerated with a binder was performed. Catalysts based on beta and ZSM-5 zeolites were more active than that based on mordenite one. With this catalyst, the catalyst activity was likely controlled by the accessibility to the active sites. The aromatics compounds present in the feed were totally converted to naphthenic compounds. In this sense, their contribution to the estimated research octane number was lower than that obtained in palladium based catalysts, where the aromatics compounds were not totally converted. Nevertheless, the estimated research octane number of the product fraction obtained using platinum catalysts was higher than that reported for palladium ones. In platinum catalysts, branched products and naphthenic compounds contributed in a higher extent to the estimated research octane number of the product fraction.

Keywords: Hydroisomerization; Naphtha; Zeolites; Agglomeration; Catalysis; Petroleum

1. Introduction

Due to a heightened awareness of the environmental problems worldwide, there is a need of gasoline containing small quantities of compounds considered harmful to the environment or the public health such as aromatics and oxygenated compounds. Reductions of aromatics have a negative effect on the octane number that has to be compensated by other means [1].

Isomerization of long-chain *n*-paraffins appears to be an interesting alternative since provides branched molecules which possess higher octane number than linear ones. Isomerization is one of the several reactions occurring in the reforming of naphthas, which is undertaken to upgrade low octane naphtha to a higher octane effluent. Under the process conditions of reforming, other reactions could occur like aromatization (or dehydrocyclization), and dehydrogenation, with some cracking [2].

The reduction imposed on the aromatics content has a negative effect on the reforming units that use fundamentally heavy naphtha in the range C7–C10, providing greater quantities of aromatics. Isomerization reaction constitutes the most important alternative due not only to the production of branched paraffins with high octane number but also to the fact that ring-opening reactions of aromatics compounds from reformer feedstocks are yielded. For example, cyclohexane, a benzene precursor, can be rearranged over commercial paraffin isomerization catalysts to a mixture of branched paraffins.

The industrial processes of *n*-paraffins hydroisomerization need the presence of bifunctional catalysts, which present two kinds of active or functional sites: (i) an acid function provided by zeolites, and (ii) a hydrogenating–dehydrogenating function provided by a noble metal [3–6].

The performance of this kind of catalysts has been confirmed almost exclusively by using either powders or tablet-shaped catalysts formed by simple compressing and hardening of zeolite powders. However, the high-pressure drops caused by powder catalysts in industrial reactors require that catalysts are shaped for industrialization, improving the crush strength to prevent the catalyst from breaking down into powder-like materials in commercial use. In this sense, materials like clays, oxides, etc., have been used as binders. Information regarding the influence of

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the binder on the acidity and catalytic performance of zeolites is very important for the development of industrial catalysts. Some authors have studied the influence of different binders on the catalytic performance of zeolites [7–10]. In previous works [3,4], the advantages of the bentonite as a binder were reported.

Concerning the hydroisomerization reactions, hydrocarbon binary and ternary mixtures have been tested [5,6,11]. Jiménez et al. [6] studied the hydroisomerization of a hydrocarbon feed containing *n*-hexane, *n*-heptane and cyclohexane over zeolite catalysts. Tests involving binary mixtures of these three hydrocarbons revealed that *n*-heptane was the main source of cracking products. Gopal et al. [5] reported the hydroisomerization of C5–C7 alkanes and simultaneous saturation of benzene over Pt/H-ZSM-12 and Pt/Beta. Although Pt/Beta was much more active and had better sulfur resistance, the capability of Pt/H-ZSM-12 to provide a significantly higher yield of isomers made it an attractive catalyst. In a previous work, the use of palladium containing zeolites for the hydroisomerization of a C7–C8 complex feedstock was studied [12].

The aim of this work was to study the hydroisomerization of a C7–C8 stream, obtained by distillation of a refinery naphtha stream, by using catalysts based on the following zeolites: mordenite, beta and ZSM-5, all of them agglomerated with a binder (bentonite) and impregnated with platinum. The influence of the zeolite structure was investigated and the results were compared to those previously reported for palladium catalysts [12].

2. Experimental

2.1. Catalyst preparation

Commercial ammonium zeolites, mordenite (Si/Al = 10.4), beta (Si/Al = 13.0) and ZSM-5 (Si/Al = 15.6) were supplied by Zeolyst International. The samples were calcined at 550 °C for 15 h in order to obtain the protonic form of the zeolite. The obtained samples were named to as HMOR, HBETA and HZSM-5, respectively.

Bentonite was supplied by Aldrich Chemical Co. For the agglomeration process, the protonic form of the zeolite (35 wt.%) and bentonite (65 wt.%) were mixed together and suspended in water at 60 °C for 2 h. The suspension was then dried at 120 °C overnight. After grinding and sieving, particles with an average particle size of 0.75 mm were obtained. Finally, the agglomerated zeolite was calcined at 550 °C for 15 h.

After the agglomeration process, agglomerated beta zeolite samples were ion-exchanged three times with 1 M NH_4Cl (30 ml g^{-1}). The samples with mordenite and ZSM-5 zeolites were ion-exchanged with 0.6N HCl (35 ml g^{-1}). Then, all the samples were calcined again at 550 °C for 15 h.

All the catalysts were impregnated with an aqueous H_2PtCl_6 solution. The metal concentration of the impregnating solution was calculated to yield a final Pt content of 1 wt.% in the resulting catalysts. After the impregnation process, 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} at 410 °C for 4 h.

The final catalysts were firstly identified with the symbol of the metal (Pt), following by the name of the zeolite (MOR, BETA and ZSM-5). The term “Bent” originates from the name of the binder (bentonite).

2.2. Catalysts characterization

Surface area was determined by using N_2 as the sorbate at 77 K in a static apparatus (Micromeritics ASAP 2010 adsorptive and desorptive apparatus). The samples were evacuated 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%.

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

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 pretreated 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%.

The 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). In order to calculate the metal dispersion, an adsorption stoichiometry of Pt/H = 1 was assumed [13]. The apparatus used was the same as that described for the TPDA. Dispersion measurements with H_2 pulses were carried out at 60 °C to avoid the spill over phenomenon [14]. Previously, the sample was pretreated 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%.

2.3. Distillation procedure

A naphtha stream supplied by the company REPSOL-YPF (from Spain) was the feed to a pilot plant distillation unit (a scheme was depicted in [12]). Table 1 shows the naphtha stream composition. In order to define a specific stream to develop the

Table 1
Molar composition of the naphtha stream supplied by REPSOL-YPF

Carbon atoms	Molar composition (%)					Total
	n-Paraffins	*iso*-Paraffins	Olefins	Naphtenes	Aromatics	
5	0.04	0.01	0.00	0.12	0.00	0.17
6	4.82	3.81	0.00	4.83	0.90	14.36
7	6.71	6.97	0.88	10.50	6.91	31.97
8	5.47	9.81	0.25	9.63	9.17	34.33
9	2.32	4.98	0.94	3.81	2.22	14.27
10	0.57	1.83	0.11	1.32	0.49	4.32
11	0.07	0.40	0.00	0.00	0.03	0.50
12	0.01	0.00	0.01	0.00	0.06	0.08

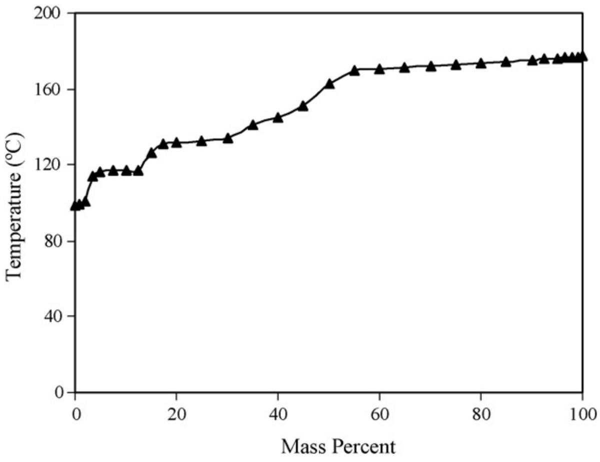

Fig. 1. ASTM curve obtained by HYSYS.

hydroisomerization process, a distillation process was carried out. It was obtained three main fractions: C5–C6 and C7–C8 fractions and a third one consisting of hydrocarbons with a carbon atoms number equal or higher than 9. In order to estimate the boiling temperature of each fraction, a HYSYS application (by AspenTech) was developed. Thus, the distillation temperatures of each of the three fractions were: 59–98, 98–127 and >127 °C, respectively. The corresponding ASTM curve calculated using HYSYS is shown in Fig. 1.

The batch distillation procedure was as follows: the naphtha stream was placed in the reboiler. The temperature was increased to reach the boiling point of the liquid feed. At first, all the vapour phase was condensed and returned to the column. Once the steady state was achieved, a liquid phase was obtained as the distillate (reflux ratio of 0.4). The composition of the C7–C8 stream, obtained by distillation of the refinery naphtha stream, is given in Table 2.

Table 2
Molar composition of the C7–C8 distillated stream (feed)

Carbon atoms	Molar composition (%)					Total
	n-Paraffins	*iso*-Paraffins	Olefins	Naphtenes	Aromatics	
6	2.75	0.87	0.00	3.88	0.73	8.23
7	17.86	11.31	0.13	19.40	4.99	53.69
8	8.25	20.27	0.00	9.56	0.00	38.08

2.4. Catalytic experiments

The C7–C8 fraction hydroisomerization reactions were carried out in vapour phase 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 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, 290–390 °C; total pressure, 10 bar; WHSV = 10 $g_{C7C8}\,h^{-1}\,g_{zeolite}^{-1}$; H_2/hidrocarbon 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 an automatic valve for continuous analysis. The reactor exit 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

The characterization data of the raw materials and catalysts used in this work are summarized in Table 3. First, it is important

Table 3
Characterization data of the raw materials and the three catalysts

Catalyst	Surface area ($m^2\,g_{cat}^{-1}$)	D_{H_2} (%)	Acidity values (mmol $NH_3\,g_{cat}^{-1}$)		
			Total	Weak, T (°C)[a]	Strong, T (°C)[a]
Bentonite	37	–	0.038	0.038 (274)	–
HMOR	560	–	0.996	0.164 (312)	0.832 (479)
HBETA	636	–	0.626	0.129 (273)	0.497 (353)
HZSM-5	412	–	0.573	0.085 (275)	0.488 (390)
PtMORBent	206 (10.6%)[b]	80.9	0.401	0.132 (305), 0.082[c]	0.269 (432), 0.291[c]
PtBETABent	237 (5.0%)[b]	72.9	0.264	0.093 (300), 0.070[c]	0.171 (388), 0.174[c]
PtZSM-5Bent	154 (5.1%)[b]	57.1	0.201	0.057 (284), 0.054[c]	0.144 (418), 0.171[c]

[a] Desorption ammonia temperature (°C).
[b] Deviation from the theoretical surface area value (%).
[c] Predicted acidity value calculated from the contribution of the non agglomerated zeolite and the binder.

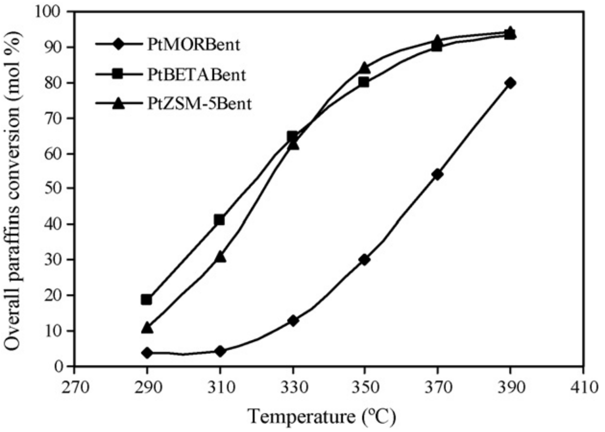

Fig. 2. Overall paraffins conversion (mol%) vs. the reaction temperature for the three catalysts: PtMORBent, PtBETABent and PtZSM-5Bent.

to note the low acidity of the bentonite clay, it even did not show any strong acidity. Therefore, the contribution of the bentonite to the acidity of the agglomerated catalysts must be considered negligible. The only effect observed after the incorporation of the bentonite was the differences between the experimental acidity values and the theoretical ones. The latter was calculated from the contribution of the raw materials (non agglomerated zeolite and bentonite). It was found higher values of the weak acid density of the catalysts than that predicted from the contribution of the raw materials, the opposite effect being observed for the strong acidity. It was demonstrated that the sodium cations of the bentonite clay incorporated to the catalysts through a solid-state ion exchange with the zeolite protons were the responsible of the higher values of the weak acid site density compared with the theoretical ones [15–18]. In a more extensive work [4], the influence of the binder on the acid properties of platinum zeolite catalysts was studied.

It can be observed higher dispersion values for the catalysts based on mordenite and beta zeolites [4]. The high acid site density and the high surface area of the catalysts based on mordenite and beta zeolites enabled a better platinum dispersion. In all the cases, the platinum particles were located outside the main channels of the zeolite, because their big size (15 Å for PtMORBent, 16 Å for PtBETABent and 21 Å for PtZSM-5Bent) [19,20].

3.2. Hydroisomerization of the C7–C8 stream

3.2.1. Paraffins conversion

Fig. 2 shows the overall paraffins conversion, defined as the conversion of linear hydrocarbons (i.e., conversion of *n*-heptane and *n*-octane), versus the reaction temperature for the different catalysts used in this work. Thermal conversion of the C7–C8 distillated stream, lesser than 1 mol%, can be neglected at the experimental conditions used.

It can be seen that catalysts based on beta and ZSM-5 zeolites were more active than that based on mordenite zeolite. Since paraffins conversion in the hydroisomerization reaction is related to the acid site density [21], the catalyst PtMORBent should be the most active (Table 3), being observed the opposite effect.

Both, the zeolite acidity (number and strength distribution) and the pore structure play an important role in the overall paraffins conversion. Mordenite has one-dimensional pore structure with side-pockets whereas beta or ZSM-5 consists of three-dimensional channels. It has been reported [22,23] that only one-third to two-third of the acid sites from mordenite are accessible to alkanes. Carvill et al. [24] have argued that in one-dimensional zeolites, the catalyst activity was controlled by the accessibility to the active sites, because the effect of “single file diffusion”. Actually, the overall paraffins conversion was lower for PtMORBent than that for both PtBETABent and PtZSM-5Bent in spite of the higher acid site density of the former (Table 3). Similar results were obtained by Gopal et al. [5] for the hydroisomerization of C5–C7 alkanes over Pt/H-Beta. The three-dimensional structure of beta zeolite allowed easy access to a greater number of active sites compared to that of one-dimensional zeolites.

According to the acidity values (Table 3) and structure of beta zeolite, the overall paraffins conversion of PtBETABent should be higher than those obtained in PtZSM-5Bent. However, similar overall paraffins conversion values were observed in both catalysts (Fig. 2). Similar results were reported by Lugstein et al. [25], suggesting that even though the pore dimensions in beta zeolite are greater and all acid sites are accessible, its activity can be smaller in comparison with that of a catalyst based on ZSM-5 zeolite. The catalytic activity of zeolites might differ significantly, even when the intrinsic acid strength of the zeolite proton is the same. This fact is attributed to the heat of adsorption of alkanes, which is correlated with the micropore diameter. Therefore, an optimum ratio between the size of hydrocarbons and the size of the zeolite pores should exist. This way, it could be possible that for catalysts based on beta and ZSM-5 zeolites, both having three-dimensional framework, the difference in pore size could cause the apparent activation energy to be smaller in ZSM-5 zeolite than in beta one.

3.2.2. Branched products

The molar product distribution, at 50 mol% of overall paraffins conversion, is given in Table 4. Whereas the overall paraffins conversion was changed by varying the reaction temperature, the product distribution was only a function of the level of conversion, regardless the reaction temperature. Same results were observed by other authors [26]. Over all catalysts, the same kind of products were obtained, which included C1–C6 hydrocarbons (considered as cracking products obtained from the β-scissions of C7 and C8 hydrocarbons), products with 7–8 carbon atoms (monobranched, dibranched and tribranched isomers and the corresponding linear paraffins), naphthenic and aromatics compounds. C9 or higher products were not observed.

Since the purpose of the hydroisomerization process is to achieve an increase in the octane number of the gasoline, it is interesting to note the formation of multibranched isomers from the C7–C8 distillated stream used as the feed. Fig. 3 shows the molar percentage of *iso*-paraffins (6, 7, and 8 carbon atoms number) versus the overall paraffins conversion obtained for the three catalysts. The total amount of *iso*-paraffins contained in the feed was 32.45 mol%. At low overall paraffins

Table 4
Composition (mol%), at approximately 50 mol% of overall paraffins conversion, for the products obtained in the hydroisomerization of the C7–C8 distillated stream

Catalyst	Feed	PtMORBent, 370[a]	PtBETABent, 310[a]	PtZSM-5Bent, 330[a]
C1 + C2	0.00	0.00	0.00	0.00
C3	0.00	6.11	1.67	9.46
iso-C4	0.00	10.71	4.24	7.45
n-C4	0.00	3.96	1.47	3.19
iso-C5	0.00	4.67	1.55	5.13
n-C5	0.00	0.73	0.27	1.34
2,3-DMC4	0.04	0.13	0.00	0.00
2-MC5	0.36	0.37	0.27	0.62
3-MC5	0.47	0.30	0.28	0.42
n-C6	2.75	1.35	1.10	1.45
2,2-DMC5	0.11	0.25	0.45	0.10
2,4-DMC5	0.29	0.74	0.56	0.34
2,2,3-TMC4	0.03	0.22	0.00	0.03
3,3-DMC5	0.11	0.24	0.28	0.07
2-MC6	3.97	4.01	4.58	4.42
2,3-DMC5	1.25	1.04	0.67	1.02
3-MC6	5.55	4.61	4.61	4.75
n-C7	17.86	8.61	11.41	4.85
2,2-DMC6	1.40	1.67	1.23	1.76
2,5-DMC6	1.66	2.17	1.07	1.82
2,4-DMC6	1.25	1.44	2.69	1.55
3,3-DMC6	0.00	0.37	1.18	0.00
2,3,4-TMC5	0.14	0.66	0.84	0.11
2-M-3-EC5	0.97	0.96	1.05	0.82
2,3-DMC6	0.68	0.61	0.59	0.80
2-MC7	6.42	2.87	4.68	1.99
4-MC7	1.69	1.19	2.81	0.95
3,4-MC6	0.47	0.36	0.55	0.52
3-MC7	4.33	4.08	5.83	2.52
3-EC6	1.26	3.28	4.93	4.72
n-C8	8.25	3.84	4.44	1.54
Naphthenes				
MCP (methylcyclopentane)	1.39	1.53	1.16	1.07
CH (cyclohexane)	2.49	1.20	1.40	2.26
DMCP (dimethylcyclopentanes)[b]	6.53	8.88	8.64	6.52
MCH (methylcyclohexane)	12.87	8.93	12.52	16.27
TMCP (trimethylciclopentanes)[c]	3.33	1.12	3.24	3.33
DMCH (dimethylciclohexanes)[d]	6.24	6.56	6.74	6.45

[a] Reaction temperature (°C).

[b] DMCP: 1,1-dimethylcyclopentane; 1,2-*trans*-dimethylcyclopentane; 1,3-*trans*-dimethylcyclopentane; 1,2-*cis*-dimethylcyclopentane; 1,3-*cis*-dimethylcyclopentane.

[c] TMCP: 1-*trans*-2-*cis*-4-trimethylcyclopentane; *cis*-*trans*-*cis*-1-2-3-trimethylcyclopentane.

[d] DMCH: *cis*-1,3-dimethylcyclohexane; *trans*-1,4-dimethylcyclohexane; *trans*-3-ethylcyclopentane; *cis*-3-ethylcyclopentane; *trans*-2-ethylcyclopentane; 1-ethyl-1-methylcyclopentane; *trans*-1,2-dimethylcyclohexane.

conversion values, the *iso*-paraffins content increased from the initial value. With increasing overall paraffins conversion the content of *iso*-paraffins decreased, because these compounds cracked over the acid sites. PtBETABent was the most selective catalyst for isomerization, obtaining higher *iso*-paraffins content than that obtained with the other two catalysts. The three-dimensional structure of beta facilitates a rapid diffusion of branched products, avoiding the interaction with other sites that could cause their cracking [6]. However, in mordenite (with a one-dimensional pores system) and in ZSM-5 (with a small pore size), paraffinic intermediates may have longer life time on strong acid sites and more possibilities to undergo successive rearrangement and cracking reactions, mainly due to steric constraints at the acid sites [27].

3.2.3. *Aromatic and naphthenic compounds*

Among the aromatics compounds, it was found benzene and toluene on the feed, as can be seen in Table 2 (aromatics compounds of 6 and 7 carbon atoms number). Benzene and aromatics compounds are known to have a substantial impact on health. Environmental concerns have promoted legislation to limit the amount of total aromatics, and particularly benzene, in gasoline [1,5]. The limits imposed in the benzene and aromatic compounds are 1 and 35 vol.%, respectively. All the catalysts used in this work reached both a total aromatic and benzene elimination (100 mol% of conversion).

The molar composition of the naphthenic compounds in the feed and in the catalysts used in this work is shown in Table 4. Methylcyclopentane (MCP) and cyclohexane (CH)

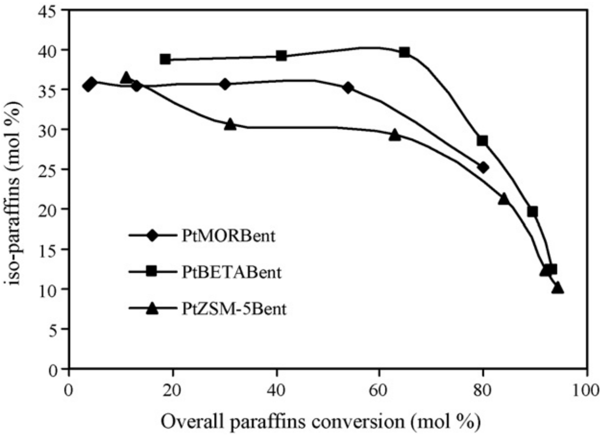

Fig. 3. *iso*-Paraffins (mol%) vs. the overall paraffins conversion for the three catalysts: PtMORBent, PtBETABent and PtZSM-5Bent.

are the typical products obtained during the hydrogenation of benzene over bifunctional catalysts [1,5,28]. Benzene hydrogenation occurs as a monofunctional reaction on metals via three subsequent hydrogenation steps, leading to the formation of CH, which in presence of acid sites produces MCP by isomerization [28]. Fig. 4 shows the MCP/CH ratio versus the reaction temperature for the three catalysts used in this work. In accordance with the thermodynamic equilibrium, MCP is produced in higher quantities during the hydroisomerization [5]. In fact, the MCP/CH ratio increased with the reaction temperature. The highest MCP/CH ratio was obtained with the sample PtBETABent, yielding a MCP/CH ratio of 4.0 at 390 °C. The catalysts PtMORBent and PtZSM-5Bent reached a value of approximately 1.5 at the same temperature. One can conclude that the isomerization of CH was more favoured over the catalyst based on beta zeolite. This fact is a consequence of its three-dimensional framework which does not cause steric hindrances.

PtZSM-5Bent obtained the lowest amount of MCP in the whole range of temperatures, suggesting a high capacity to yield ring-opening reactions: (i) endocyclic rupture resulting in *n*-hexane, 2-methylpentane and 3-methylpentane, or (ii) exocyclic C–C rupture resulting in cyclopentane formation plus methane [29]. Neither cyclopentane nor methane were observed as products (Table 4), concluding that the ring-opening reaction of MCP would yield *n*-hexane, and the monobranched isomers (2-methylpentane and 3-methylpentane). Actually, the amount of these hydrocarbons was higher over PtZSM-5Bent than that found for the other two catalysts, at the same level of overall paraffins conversion.

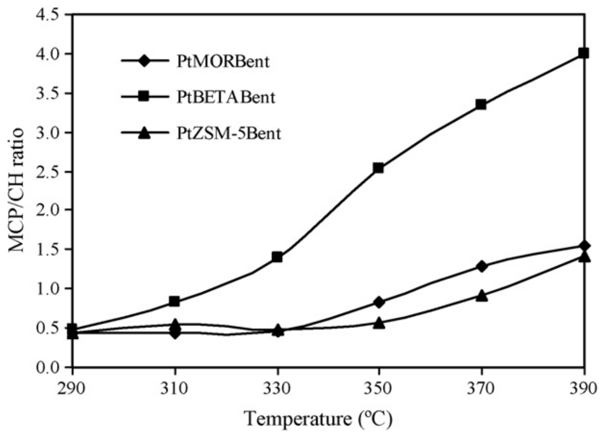

Fig. 4. MCP/CH ratio vs. the reaction temperature for the three catalysts: PtMORBent, PtBETABent and PtZSM-5Bent.

On the other hand, methylcyclohexane (MCH) was obtained by toluene hydrogenation [30,31]. The rearrangement of MCH in terms of isomerization reactions leads to dimethyl (1,1-, 1,2-*cis* and -*trans* and 1,3-*cis* and -*trans*) and ethyl-cyclopentanes (DMCP and EtCP, respectively). Isomerization of MCH to DMCP and EtCP is supposed to take place on the acid sites of the zeolite while the hydrogenation of toluene is performed by a metal function [32]. The MCH composition in the product was lower than that in the feed (Table 4) when PtMORBent and PtBETABent were used as catalysts whereas the opposite effect was observed in PtZSM-5Bent, even showing higher MCH composition than that found in the feed. It is clear that over the latter, the MCH was the result of the toluene hydrogenation. However, over the former catalysts, the MCH yielded DMCP by isomerization, observing higher DMCP concentration than that observed in the feed, even at higher temperatures. The isomerization of MCH yielding DMCP was not favoured in the catalyst PtZSM-5Bent for the whole range of temperature because the DMCP concentration in the product was nearly the same as that observed in the feed. It was clear that ring-opening reaction was not favoured over all the catalysts used in this work. This suggests that the formation of *iso*-paraffins with 7 carbon atoms number may be only due to the isomerization of *n*-heptane.

Other naphthenic compounds, like dimethylcyclohexanes (DMCH) and trimethylcyclopentanes (TMCP), were detected as final products. However, their concentration was very similar as that observed in the feed, at a level of overall paraffins conversion of 50 mol% (Table 4). Ring-opening reactions were not present at this level of conversion. However, at 390 °C, the conversion of these naphthenic compounds reached a value of 50 mol%, because the contribution of the ring-opening reactions to the disappearance of these compounds, obtaining branched octane isomers [33].

As commented above, at 50 mol% of overall paraffins conversion, the contribution of the ring-opening reactions to the disappearance of TMCP and DMCH was nearly negligible, so the presence of branched octane isomers were only due to the isomerization of *n*-octane. An increase in the overall paraffins conversion not only contributes to the cracking of the branched isomers (Fig. 3) but also to the ring-opening reactions of the naphthenic compounds followed of the cracking of the branched isomers obtained.

3.2.4. *Cracked products*

Concerning the cracking products, the absence of methane and ethane revealed that hydrogenolysis did not contribute to the cracking reaction. C3, C4 and C5 hydrocarbons were mostly detected. C3 and C4 products could result from the classical *n*-heptane cracking mechanism. This was not the case for C5 and C6 because complementary C2 and C1 fragments were

Table 5
Relationship among the cracking products obtained at approximately 50 mol% of overall paraffins conversion

Catalyst	PtMORBent, 370[a]	PtBETABent, 310[a]	PtZSM-5Bent, 330[a]
C4/(C3 + C5)	1.3	1.6	0.7
iso-C4/*n*-C4	2.7	2.9	2.3
iso-C5/*n*-C5	6.4	5.8	3.8
C3/C5	1.1	0.9	1.5
C3/C4	0.4	0.3	0.9

[a] Reaction temperature (°C).

not observed. Cracking products with three, four and five carbon atoms could be also obtained from the *n*-octane cracking. Table 5 shows the relation among the different cracking products at 50 mol% of overall paraffins conversion. The cracking pathway towards C4 fragments was favoured (high values of C4/(C3 + C5) ratio) over PtMORBent and PtBETABent. In contrast, on PtZSM-5Bent more cracking to C3 + C5 was found. The higher *iso*-C4/*n*-C4 and *iso*-C5/*n*-C5 ratios were obtained for PtMORBent and PtBETABent, which could only result from cracking of di- and tribranched isomers. The low ratios obtained for PtZSM-5Bent was a consequence of the cracking from dibranched isomers [25]. In order to confirm the main cracking pathway present in each catalyst, C3/C5 and C3/C4 ratios were compared. The fact that the concentrations of C3 and C5 hydrocarbons were almost equal would indicate that they were the result of primary cracking of either linear or branched C8 carbenium ions [21]. This way, the *n*-octane cracking was favoured with catalysts PtMORBent and PtBETABent. The contribution of the classical *n*-heptane cracking was estimated as the molar yield of C3 and an equimolar yield of C4 [34], as can be observed with sample PtZSM-5Bent.

Among the cracking products from C6 hydrocarbons, it could be possible to highlight: 2C3 (depropylation), C2 + C4 (deethylation) and C1 + C5 (demethylation) [29]. The high amount of propane and the lack of methane and ethane in the product would confirm the cracking of C6 hydrocarbons towards propane when PtZSM-5Bent was used.

3.3. Research octane number

In order to compare the performance of the different catalysts used in this work, the research octane number of the C5+ fraction in the product was estimated. Fig. 5 shows this estimation versus the overall paraffins conversion. The RON of the mixture was evaluated as the product of the volume fraction of the individual C5 and higher hydrocarbons and their corresponding RON, then summing up the contributions of all the compounds [5]. This way, the estimated research octane number of the C7–C8 distillated stream (feed) was 43.7.

In practice, octane numbers do not blend linearly. To accommodate this, complex blending calculations employing blending octane numbers as opposed to the values for pure hydrocarbons are routinely employed. In general, the blending octane numbers are greater than the corresponding pure octane numbers, e.g., MCP has a higher estimated research octane number than CH, but the blending octane numbers of both MCP and CH are similar. Therefore the formation of both products from benzene should be acceptable. This method for estimating the RON value of mixtures is likely to be different from the real RON value, the latter being generally higher [5].

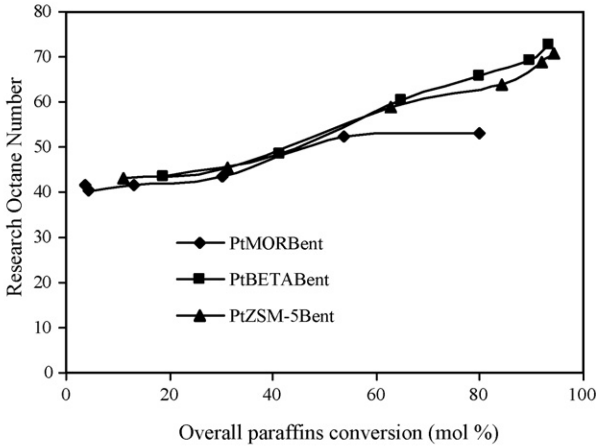

Fig. 5. Estimated research octane number (RON) as a function of the overall paraffins conversion for the three catalysts: PtMORBent, PtBETABent and PtZSM-5Bent.

PtBETABent yielded a higher amount of multibranched isomers which led to a high RON values than those corresponding to linear alkanes. By using the catalyst PtZSM-5Bent, a high RON value was obtained too, mainly because a higher contribution of naphthenic compounds.

3.4. Comparison with bifunctional catalysts containing palladium

In a previous work, it was carried out different experimental runs with catalysts based on the same zeolites (mordenite, beta and ZSM-5) but using palladium as the hydrogenating/dehydrogenating function [12]. In Table 6, the overall paraffins conversion values at 370 °C for the catalysts impregnated with palladium and platinum are given. It is remarkable the higher overall paraffins conversion values found for platinum catalysts, compared with those found for palladium ones. It is well known the great hydrogenating–dehydrogenating capacity of the platinum in hydroisomerization processes [4]. As expected, platinum catalysts obtained a higher overall paraffins conversion values than those obtained with palladium catalysts (Table 6). The higher dispersion values of platinum particles allowed a high amount of metal sites available to produce alkenes, which are involved in the carbenium ion formation.

Environmental concerns have promoted legislation to limit the amount of total aromatics, particularly benzene, in gasoline [1,5]. Reduction of aromatics will have a negative impact on gasoline octane. The higher hydrogenating–dehydrogenating capacity of platinum was the responsible to the higher aromatics conversion values obtained for platinum catalysts compared to those obtained for palladium ones. These results were in agreement with those reported in the literature [35]. The contribution of aromatics products on the estimated research octane

Table 6
Overall paraffins and aromatics conversion, *iso*-paraffins and naphthenes content and estimate maximum RON for the catalysts used in this work, compared with palladium catalysts

Catalysts	D_{H_2} (%)	Overall paraffins conversion (mol%)[a]	Aromatics conversion (mol%)[b]	*iso*-Paraffins (mol%)[c]	Naphthenes (mol%)[d]	Estimate maximum RON
PtMORBent	81	30.2	100	35.3	28.2	53.1
PtBETABent	73	79.8	100	39.5	34.7	72.7
PtZSM-5Bent	57	84.1	100	29.4	35.9	70.8
PdMORBent	24[e]	24.0	89.8	28.2	28.5	47.2
PdBETABent	25[e]	24.2	70.4	24.3	26.9	53.4
PdZSM-5Bent	16[e]	9.9	97.5	23.8	24.9	45.6

[a] Reaction temperature, 370 °C.
[b] Aromatic conversion at 370 °C.
[c] Overall paraffins conversion of 50 mol%.
[d] Overall paraffins conversion of 50 mol%.
[e] Reported in a previous work [12].

number would be higher on palladium catalysts where the aromatics products were present but always under the imposed limits.

Platinum catalysts also obtained higher amount of *iso*-paraffins than that obtained for the palladium ones, being these compounds ones of the responsible to the high estimate maximum RON value (Table 6) showed by the platinum catalysts. However, it could be noted that in samples PtBETABent and PtZSM-5Bent, the contribution of naphthenic compounds was higher than in PtMORBent, leading to an increase of the estimate maximum RON. Since the aim of the hydroisomerization reaction is to achieve a product with a high estimated research octane number, platinum catalysts based on zeolites agglomerated with bentonite result to be attractive catalysts for this process.

4. Conclusions

The hydroisomerization of a C7–C8 stream obtained by distillation of a real naphtha stream was carried out using platinum zeolites (mordenite, beta and ZSM-5) agglomerated with a binder.

The overall paraffins conversion, defined as the conversion of linear hydrocarbons, increased with reaction temperatures. Differences between the conversion values obtained with all the zeolite-based catalysts were observed which were related to the differences in the acidity and, in the case of zeolite mordenite, to the particular accessibility to the active sites.

The catalyst based on beta zeolite was the most selective for hydroisomerization, obtaining higher *iso*-paraffins content than that obtained by the other two zeolite-based catalysts.

The aromatics compounds present in the feed were totally converted to naphthenic compounds. In this sense, their contribution to the estimated research octane number was lower than that obtained in palladium based catalysts, where the aromatics compounds were not totally converted. Nevertheless, the estimated research octane number of the product fraction obtained using platinum catalysts was higher than that reported for palladium ones. In platinum catalysts, branched products and naphthenic compounds contributed in a higher extent to the estimated research octane number of the product fraction.

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