

Influence of clay binder on the liquid phase hydroisomerization of *n*-octane over palladium-containing zeolite catalysts

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Abstract

The influence of the clay binder on the properties and performance of palladium-containing zeolite catalysts in the liquid phase hydroisomerization of *n*-octane was studied. Three different framework zeolites with similar Si/Al ratio were used as catalysts: USY, mordenite and beta with or without binder. In all cases, a decrease in the catalytic activity of agglomerated samples, because of the modification of the acidity and the porosity of the zeolites by the binder, was observed. The decrease in the acidity after the agglomeration could be attributed to solid-state ion exchange between zeolite protons and clay sodium during the calcination of the catalyst. Moreover, the aluminium extraframework species (EFAL) created during the agglomeration process could cause a partial blocking of the micro-pore mouths, which would lead to an increase in the length of the effective diffusional pathway. After the agglomeration process, the monobranched isomers selectivity increased for all the samples while the multibranched isomers selectivity decreased. Due to the high pressure in the liquid phase, a significantly higher isomers selectivity was obtained as compared to vapour-phase conditions, and cracking became important only at relatively high average conversions.
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1. Introduction

Recently, alkanes and fundamentally *iso*-alkanes are being used as an alternative to other gasoline compounds like lead, aromatics, alkenes and others considered harmful to the environment or the public health. The reduction in the content of these adverse compounds will have a negative impact on the octane number of the gasoline pool. The octane number of *iso*-alkanes is higher than that corresponding of the linear ones. The former compounds may be obtained via two processes: an alkylation process, where light alkenes are alkylated with lower *iso*-alkanes or a hydroisomerization process, in which linear alkanes are converted into the corresponding branched ones [1].

The hydroisomerization of C₇ and C₈ has been widely studied [2–7], the multibranched C₈ alkanes obtained from this process are the most useful isomers because of their high octane number. However, no industrial hydroisomerization process

exists for C₇ and C₈ paraffins due to their high tendency to crack [8,9].

Under the classical bifunctional process, the rate-limiting step of hydroconversion of *n*-alkanes is assumed to be the carbenium ion rearrangement with and without β -scission on the acid sites. Both the balanced metal/acid content and the effective transport between metal and acid sites are required to obtain the desired isomerization yield in *n*-alkane conversion [10,11].

Most industrial hydroisomerization catalysts are based on zeolites, which provide the acid function. As the hydrogenating–dehydrogenating function, several metals have been tested including Pt, Pd, Rh, Ir, Ru, Re and Ni, mostly associated with mordenite or CaY. However, palladium, although rarely studied, was shown to be the most selective in the *n*-butane hydroisomerization [12,13]. Bifunctional catalysts, with both hydrogenating–dehydrogenating and isomerization function have shown high efficiency in alkane hydroisomerization. Noble metal-zeolite catalysts especially Pt or Pd loaded Y, mordenite and beta possess a high activity and selectivity for hydroisomerization of *n*-alkanes [11]. Zeolite beta presents a three-dimensional 12-MR structure and has shown to have a

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higher selectivity in isomerization and conversion than the one-dimensional 12-MR mordenite [11,14]. Y zeolite catalysts have been used because Y zeolite has the largest pore system among the crystalline aluminosilicates [15]. Both acid and metal site density are important and their proper balance is critical in determining the activity, stability and product selectivity of the catalyst [16].

On the other hand, most industrial zeolite based catalysts require the zeolite to be pelletized with a binder in order to improve the mechanical properties of the catalyst particles, thus avoiding extremely high-pressure drops in fixed-bed reactors [17]. It has been demonstrated that the binder is not active as a catalyst but could change the acid properties of a zeolite as a result of changes in the proton-exchange efficiency, trapping by the binder of coke precursors, and/or blocking of zeolite channels during the pelletization process [17,18]. Some authors have studied the influence of different binders on the catalytic performance of zeolites [19–21], even though bentonite has not been widely studied.

Bentonite is a laminar and expandable clay with wet binding properties and widely available throughout the world. The scientific interest of bentonite is due to its physical and chemical properties as well as its low price. Consequently, the industrial application of bentonite is an attractive process. The dispersability of clays in aqueous suspensions is the reason for their agglomeration properties: zeolite particles are surrounded by clay laminae and, when the water is removed, a solid phase is achieved with the zeolite particles are agglomerated by the clay. It has been shown that the acid form of clays does not have binding properties and that their sodium forms exhibit better properties [22]. Because zeolites are mainly used as acid catalysts, further transformation of the agglomerated zeolite to the acid form is required [17].

Furthermore, for experimental reasons, most of academic studies on hydroisomerization are performed in vapour phase using a hydrogen pressure below 10 bar [23], being very scarce the existing literature about the process in liquid phase.

Recently, our research group [24,25] has reported that depending on the zeolite studied, the binder (bentonite) influenced the activity for the hydroisomerization of *n*-octane in the vapour phase. The agglomeration process caused a decrease in the activity of ZSM-5 and mordenite catalysts. However, beta improved its catalytic activity when it was agglomerated.

In this work, several acid catalysts based on USY, mordenite and beta zeolites agglomerated with a clay (sodium bentonite) were prepared. As hydrogenating–dehydrogenating function, palladium was used. The aim of this work was to evaluate the influence of the binder on the catalytic activity and selectivity for the *n*-octane hydroisomerization reaction.

2. Experimental

2.1. Catalyst preparation

The parent zeolites USY (Si/Al = 13.0), mordenite (Si/Al = 10.4) and beta (Si/Al = 13.0) were supplied in the ammonium form by Zeolyst International. To obtain the protonic form, zeo-

lites were calcined at 550 °C for 15 h. Bentonite (sodium form) was supplied by Aldrich Chemical Co. USY, mordenite and beta samples on the protonic form were named to as HUSY, HMOR and HBETA.

Zeolite (35 wt%) and bentonite (65 wt%) were mixed and suspended in water at 60 °C for 2 h. The suspension was then dried at 120 °C for 12 h. After grinding and sieving, particles with an average particle size of 0.75 mm were obtained. With this size, no internal diffusion limitations in the catalytic runs were detected. Finally, the agglomerated zeolites were calcined at 550 °C for 15 h. In order to re-incorporate the acid function in the zeolite, the agglomerated catalyst was ion-exchanged with 0.6N HCl (35 ml g⁻¹) in the case of mordenite. The ion-exchange for the USY and beta zeolites was carried out three times with 1M NH₄Cl (30 ml g⁻¹). The ion-exchanged samples were subsequently calcined again at 550 °C for 15 h in order to obtain the acid form of the zeolites.

A known volume of an aqueous Pd(NO₃)₂ solution was poured over all the catalysts (with or without binder). The solvent was removed by evaporation under vacuum. The metal concentration of the impregnating solution was calculated to yield a final Pd content in the resulting catalysts of 1 wt%.

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 450 °C for 4 h.

Non-agglomerated USY, mordenite and beta samples containing both acid and metallic functions were named to as PdUSY, PdMOR and PdBETA, respectively. Agglomerated catalysts were named to as with “Bent” following the name of the non-agglomerated zeolite. For example, PdUSY/Bent corresponds to a palladium USY zeolite agglomerated with bentonite.

2.2. Catalyst characterization

Pores size distribution and BET surface area were determined by adsorption and desorption data acquired on a 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, whereas specific total pore volumes were evaluated from N₂ uptake at a relative pressure (*P/P*₀) of N₂ equal to 0.99. The Horvath–Kawazoe method was used to determine the microporous surface area and micropore volume. The Barret, Johner and Halenda (BJH) method was used to determine the distribution of the mesopores. Surface area measurements have an error of ±3%.

The concentration of the acid sites was measured by temperature programmed desorption of ammonia (TPDA) using a Micromeritics TPD/TPR 2900 analyzer. The sample was firstly heated from room temperature to the calcination temperature at 15 °C min⁻¹ under a flow of helium, holding this temperature during 30 min. After reducing the catalysts under a hydrogen flow, the system was cooled to 180 °C. Ammonia was then flowed over the sample for 15 min. Later, the sample was purged with helium for 1 h in order to eliminate physisorbed species. The temperature was ramped at 15 °C min⁻¹ from 180 to 560 °C

and TPDA data were acquired. The total acidity was obtained by integration of the area under the curve. Weak and strong acidities are defined as the concentration of weak and strong acid sites, respectively, obtained by integration of the area under the peaks at the lowest and the highest temperatures, respectively [18,26]. The average relative error in the acidity determination was lower than 3%.

The palladium dispersion was determined from chemisorption measurements. The apparatus used was the same as that described for the TPDA. The experiments were carried out using the dynamic pulse technique with an argon (99.9990%) flow of 50 ml min⁻¹ and pulses of hydrogen. In order to calculate the metal dispersion, an adsorption stoichiometry of Pd/H=1 was assumed [27]. The chemisorption experiments with hydrogen pulses were carried out at 60 °C to avoid the spill over phenomenon. Previously, the sample was pre-treated by heating at 15 °C min⁻¹ in flowing helium up to 250 °C and kept constant at this temperature for 20 min. Then, the sample was reduced in situ. After, the hydrogen was removed by flowing inert gas for 30 min, the temperature being 10 °C higher than the reduction temperature. Finally, the sample was cooled to the experiment temperature in an inert gas flow. The dispersion measurements with H₂ pulses had an error of ±5%.

Solid-state ²⁷Al NMR spectra were collected in a BRUKER Avance WB 400 spectrometer. The ²⁷Al NMR spectra were obtained at 12.5 kHz using 15° pulses and 1 s delay, a total of 5000 pulses being accumulated.

2.3. Reaction tests

The *n*-octane hydroisomerization runs were carried out in a 50 ml batch microreactor (Autoclave Engineers). Firstly, the catalyst was reduced in a fixed-bed reactor under a hydrogen flow of 190 ml min⁻¹ g⁻¹ at 450 °C for 4 h.

Then, the batch microreactor was filled with 17 ml of *n*-octane and the catalytic basket with 0.75 g (related to zeolite) of catalyst, then, it was pressurized at 80 bar with hydrogen and heated gradually at 270 °C. Once this temperature was reached, the total pressure was finally set at 90 bar. No exter-

nal diffusion control mechanism was detected when the stirring rate was over 370 rpm. Blanks runs demonstrated that *n*-octane conversion was negligible. The reaction time was elapsed up to 24 h. Samples of the vapour and liquid products were taken at regular intervals. Gas products were analyzed in a gas chromatograph (HP 5890 Series II) equipped with a flame ionization detector and a capillary column (SUPELCO Petrocol DH 50.2, 0.2 mm i.d. and 50 m length). Liquid products were analyzed in a gas chromatograph (GC-17A SHIMADZU) coupled to a mass spectrometer (QP-5000 SHIMADZU). A capillary column (SUPELCO Petrocol DH, 100-m length with a 0.25 mm internal diameter) was used in this GC.

Results from a reproduced experiment showed that conversion and isomer selectivity had an error of ±3%.

3. Results and discussion

3.1. Characterization of catalysts

Table 1 shows the surface area and palladium dispersion data for all the agglomerated and non-agglomerated samples. A slight decrease was observed in the experimental values of the surface area of the agglomerated catalysts in comparison to the theoretical ones (calculated from the contribution of the raw materials: zeolite and bentonite). These results suggest that there was not a significative blocking of zeolite channels by the binder. However, it is not possible to claim that a partial blocking of the zeolite micropore mouths by the binder would not take place [18], especially for the mordenite zeolite based catalyst. This fact cannot be supported by the measurements of surface area and pore volume achieved, which were evaluated using N₂.

It can be observed for the mordenite zeolite based catalyst that the agglomerated sample presented a higher volume of meso and macropores as compared to the corresponding non-agglomerated one. It is obvious that these meso and macropores were provided by the binder. However, the contrary effect was observed for the USY and beta samples. USY zeolite is a highly dealuminated zeolite which is obtained by hydrothermal treatment in the presence of steam followed by leaching with a

Table 1
Metal dispersion, surface area and pore volume measurements

Catalyst	Surface area ^a (m ² g _{cat} ⁻¹)	Deviation from the theoretical value (%)	D _{H2} (%)	Pore volume (μl g _{cat} ⁻¹)	
				Micropores	Mesopores and macropores
Bentonita	37	–	–	4	88
HUSY	868	–	–	–	–
HMOR	562	–	–	–	–
HBETA	636	–	–	–	–
PdUSY	781	–	32	281	179
PdMOR	552	–	31	199	105
PdBETA	612	–	35	116	840
PdUSY/Bent	291	–2.2	26	101	138
PdMOR/Bent	204	–6.5	24	75	120
PdBETA/Bent	233	–2.3	25	47	351

^a Experimental value.

mineral acid [28]. During these processes, the aluminium is expelled from the framework causing a vacancy that can grow to form mesopores [29]. Beta zeolite crystallizes with many stacking faults [30], suggesting that most of their mesoporosity is associated with intercrystallite voids [31]. When both zeolites are agglomerated, binder fills part of these mesopores, being more important the mesoporosity lost due to the filling up of the voids than the mesoporosity provided by the binder.

Table 1 also includes the surface area values of the acid form of the zeolites (HUSY, HMOR and HBETA). Slight differences in the surface area values were observed when the zeolites with and without metal were compared. These results suggest that palladium particles were located mainly on the external surface of the zeolite crystals. Otherwise, a considerable loss in the surface area value for the metal containing samples would be expected. Palladium dispersion (D_{H_2}) values were coherent with this supposition. The average diameter of the metal particles, calculated from the dispersion data and a theoretical expression [26,32], would be about 32–49 Å, too big to think that the palladium particles could be located into the zeolite main channels.

Acidity data of the different catalysts are summarized in Table 2. All the samples showed two peaks corresponding to weak and medium-strong acidity. Samples based on mordenite zeolite showed the highest acid site density; additionally, the peak in the TPDA related to strong acid sites was obtained at higher temperatures. It should be noted that for the three non-agglomerated zeolites similar acidity values were found, regardless the incorporation of palladium to the catalysts. This fact shows the scarce influence of the metal on the acidity. Moreover, as reported in previous works [24,25], the contribution of the bentonite to the acidity of the agglomerated catalysts should be considered negligible.

Table 2 also lists the acidity of agglomerated catalysts. Differences can be observed between the experimental acidity of the

agglomerated catalysts and the predicted one (calculated from the contribution of the raw materials): the experimental values of weak acidity of the agglomerated catalysts were always higher than the predicted one, the opposite effect being observed for strong acidity.

According to different authors [33,34], the decrease in the number of expected strong acid sites could be attributed to solid-state ion-exchange between zeolite protons and clay sodium during the calcination of the catalyst. Bentonite is a rich source of Na^+ cations and they are also weak acid sites [35]. Although part of them are removed and substituted by H^+ during the re-incorporation of the acid function, the Na^+ cations that remain in the sample alter the density of the acid sites because at least some of the weak sites can be attached to them.

Fig. 1 shows the ^{27}Al NMR spectra for different samples. The signal at 0 ppm was assigned to octahedral Al (EFAL) [31]. This signal was significantly higher in the agglomerated samples. The formation of these species in the agglomerated catalysts could be due to the migration of reasonable mobile cations (Al in this case) from the interlayer space of the clay structure to the zeolite [36]. These aluminium extraframework species could influence the catalytic behaviour of the catalysts. In fact, some authors [9,31,37] have suggested that for mordenite zeolite, these extraframework species could block the zeolite pores and neutralize part of the acid sites. Fernandes et al. [31] suggested that certain EFAL species could even block the acid sites of beta zeolite and probably also neutralize part of the framework charge.

3.2. *n*-Octane hydroisomerization for non-agglomerated samples

Fig. 2 shows the *n*-octane conversion versus the reaction time for the different non-agglomerated samples. It can be seen that

Table 2
Acidity data for non-agglomerated and agglomerated samples

Sample	Total acidity (mmol NH_3 g_{cat}^{-1})	Weak acidity (mmol NH_3 g_{cat}^{-1})	T_d (°C)	Strong acidity (mmol NH_3 g_{cat}^{-1})	T_d (°C)
Bentonite	0.038	0.038	274	0	–
HUSY	0.477	0.089	282	0.388	392
HMOR	0.996	0.164	312	0.832	479
HBETA	0.626	0.149	273	0.477	353
PdUSY	0.433	0.061	277	0.372	395
PdMOR	0.946	0.122	315	0.824	480
PdBETA	0.580	0.123	283	0.458	369
PdUSY/Bent	0.190 ^a 0.172 ^b	0.069 ^a 0.060 ^b +13 ^c	278	0.121 ^a 0.136 ^b –12 ^c	371
PdMOR/Bent	0.378 ^a 0.373 ^b	0.127 ^a 0.082 ^b +35 ^c	291	0.251 ^a 0.291 ^b –16 ^c	422
PdBETA/Bent	0.240 ^a 0.244 ^b	0.090 ^a 0.070 ^b +22 ^c	292	0.150 ^a 0.174 ^b –16 ^c	369

^a Experimental value.

^b Predicted value calculated from the contribution of both the non-agglomerated zeolite and the binder.

^c Deviation from the predicted value (%).

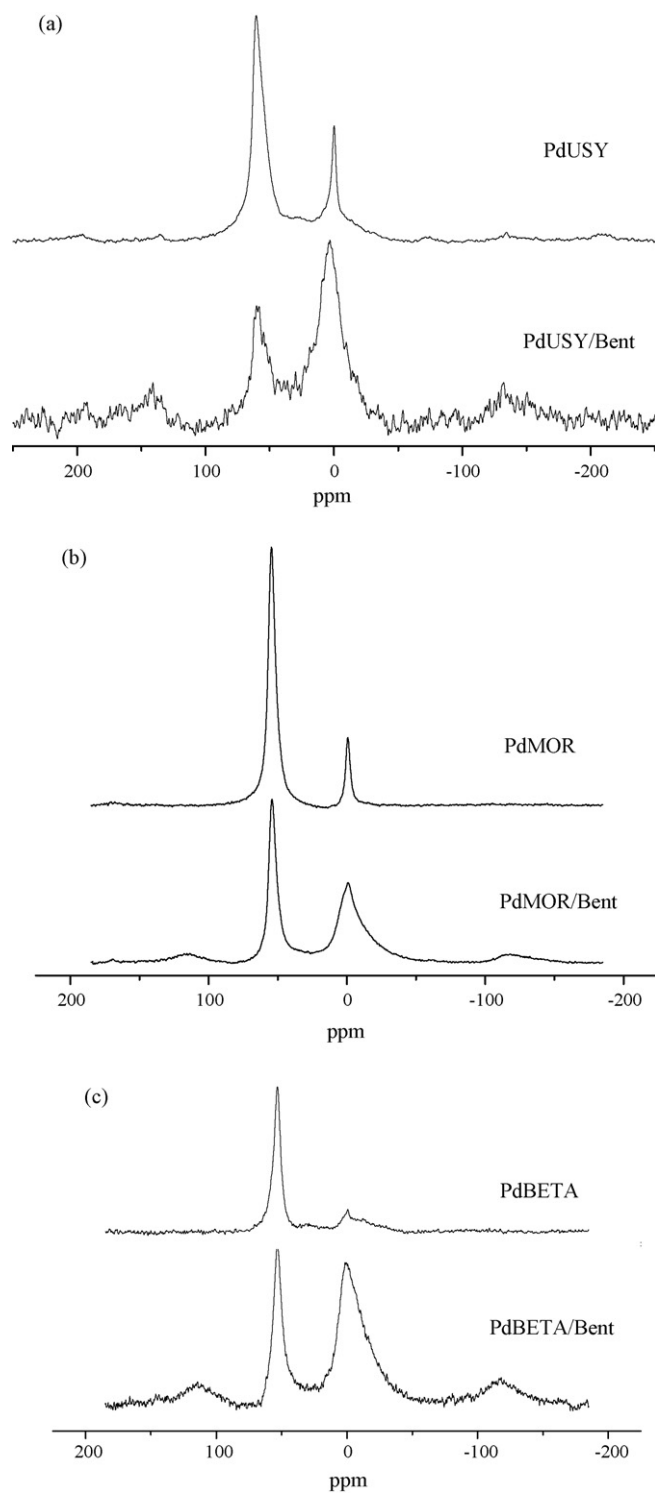


Fig. 1. ^{27}Al NMR spectra of: (a) USY samples; (b) mordenite samples; (c) beta samples.

beta zeolite was the most active. The catalytic activity for *n*-octane hydroisomerization decreased in the following order: Beta > Mordenite > USY.

According to some authors [9,38], differences in activities of several zeolite catalysts could be attributed to intrinsic differences in zeolite acidity. It can be assumed that the catalysts are well balanced (strong hydrogenating function) and the acid func-

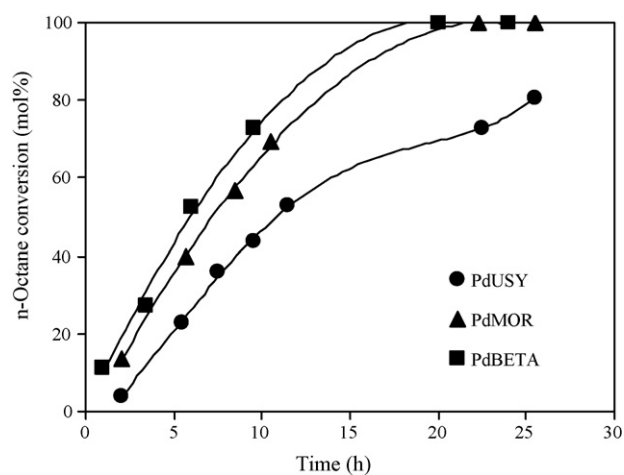


Fig. 2. Temporal *n*-octane conversion over the non-agglomerated catalysts.

tion is the limiting one [4]. Thus, a higher conversion for mordenite based catalyst should be expected due to its higher acid sites density. However, as above mentioned, a lower temporal *n*-octane conversion was obtained with mordenite as compared to that of beta zeolite (Fig. 2). This behaviour can be explained because the mordenite zeolite presents high steric hindrance that does not allow the accessibility to all of its acid sites [38,39]. According to literature data, only one-third to two-third of the acid sites of this zeolite can be accessible to alkanes [39]. The conversion obtained for USY based catalyst was the lowest, presumably due to its low acidity.

Fig. 3 shows the *n*-octane isomers selectivity versus reaction time for the non-agglomerated catalysts. It can be clearly noted how for samples PdBETA and PdUSY the *n*-octane isomers selectivity remained practically constant for all the reaction times. However, for mordenite zeolite based catalyst the selectivity declined drastically when a reaction time of 10 h was reached.

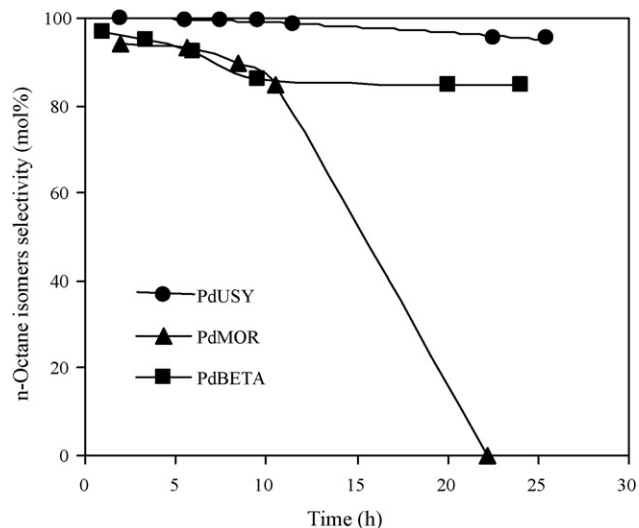


Fig. 3. *n*-Octane isomers selectivity as a function of the reaction time over the non-agglomerated catalysts.

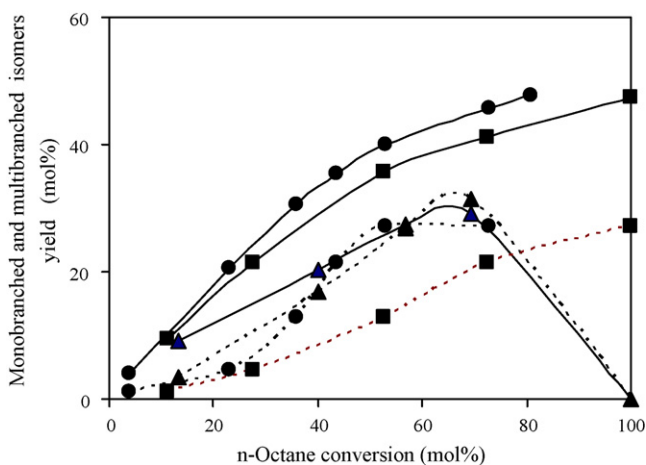


Fig. 4. Mono (continuous line) and multibranch (dotted line) isomers yield vs. *n*-octane conversion for the non-agglomerated catalysts: (●) PdUSY, (▲) PdMOR and (■) PdBETA.

It is well established that the hydroisomerization reactions proceed through successive mono-, di-, and tribranched intermediates following a consecutive scheme of reaction [40]. At low reaction times the monobranched isomers (2-methylheptane, 3-methylheptane, 4-methylheptane and 3-ethylhexane) are predominant. The conversion increased with the time, the monobranched isomers yielding the dibranched ones (2,2-dimethylhexane, 2,3-dimethylhexane, 2,4-dimethylhexane, 2,5-dimethylhexane, 3,3-dimethylhexane, 3,4-dimethylhexane and 3-ethyl-3-methylpentane). The cracking products (with carbon number lower than 8) occurred at higher reaction times and increased at high conversion values.

Fig. 4 includes the monobranched and multibranch isomers yield versus the *n*-octane conversion for non-agglomerated catalysts. The highest monobranched isomers yield was obtained with the sample PdUSY, followed by the sample PdBETA, presumably due to their moderate acidity values and to their three-dimensional structure with a large pore system. However, the highest multibranch isomers yield (31.4 mol% at a 70% of *n*-octane conversion) was obtained with the mordenite zeolite based catalyst. Since, as above mentioned, the isomerization proceeds through successive branching, high acid strength allows relatively longer residence time of the intermediate carbenium ions on the acid sites, thus providing sufficient time for the latter intermediates to be isomerized [25,40]. The fast cracking of multibranch isomers would explain the decline in the mono and multibranch yield for mordenite zeolite based catalyst.

Therefore, both the zeolite acidity (number and strength distribution) and the pore structure played an important role in the selectivity for the *n*-octane hydroisomerization.

3.3. *n*-Octane hydroisomerization for agglomerated samples

The *n*-octane conversion versus the reaction time for the agglomerated catalysts is shown in Fig. 5. As noted with the non-agglomerated catalysts, the beta zeolite based catalyst was

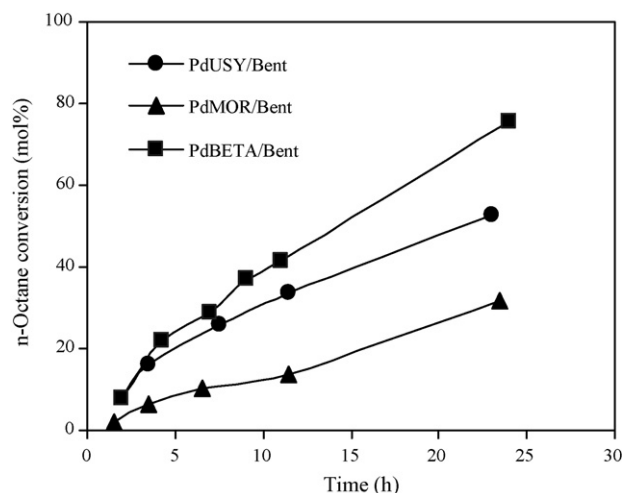


Fig. 5. Temporal *n*-octane conversion over the agglomerated catalysts.

the most active in the *n*-octane hydroisomerization. However, in contrast to the trend observed with the non-agglomerated catalysts, the conversion obtained with agglomerated USY zeolite based catalyst was higher than that obtained with the agglomerated mordenite one.

It is worth noting that, for all the zeolites, the conversion obtained at each reaction time with the agglomerated samples was lower than that corresponding to the non-agglomerated ones. In a previous work [24], the effect of the bentonite in the *n*-octane hydroisomerization in vapour phase over different zeolites (mordenite, beta and ZSM-5) using Pd as the hydrogenating–dehydrogenating function was studied. A decrease was observed in the *n*-octane conversion for the agglomerated catalysts, except for the catalyst based on beta zeolite. This zeolite improved its catalytic activity when it was agglomerated. It is thought that the presence of the aluminium extraframework species could be the responsible of the activity increase because of the synergetic effect between these species and the Brönsted acid sites. In liquid phase, however, no increase of the catalytic activity was found for this catalyst. Dorado et al. [18] also observed a decrease in the activity for the hydroisomerization of *n*-butane when the catalyst based on zeolite beta impregnated with Pd was agglomerated with bentonite.

The decrease in the catalytic activity of the agglomerated catalysts was attributed to the decrease in the number of strong acid sites (responsible of the isomerization reaction), which took place during the agglomeration process due to solid-state ions exchange between the Na⁺ cations of the clay and the H⁺ from the zeolite. Jasra et al. [36] studied the effects of bentonite on the sorption and catalytic properties of X, Y and mordenite zeolites, observing a decrease in the acidity of zeolite upon agglomeration. They also suggested that such a decrease could be due to the replacement of acidic H⁺ ions of the zeolites with exchangeable clay cations such as Na⁺, Mg²⁺, Ca²⁺ which migrate to the zeolite pores during the agglomeration process. Others authors [18,24,25] have also observed this effect.

Moreover, it was also possible that during the agglomeration process a partial blocking of the micropores mouths of the

zeolite by the binder or by the EFAL species take place, which could hinder the access to the acid sites. The experimental values of surface area of the agglomerated catalysts were close to the theoretical ones (calculated from the contribution of the binder and the non-agglomerated catalyst). However, as noted earlier, a partial blocking of the zeolite micropore mouths by the binder could take place [18], being not detected by the measurements of surface area and pore volumen achieved, which were evaluated using N_2 . The catalytic results support the partial blocking of the zeolite micropore mouths, decreasing the *n*-octane conversion when the catalysts are agglomerated.

On the other hand, some authors [9,31,37] suggested that in some mordenite samples, a channel blockage is produced by the presence of extraframework species inside the pores. Fernandes et al. [31] also suggested that certain EFAL species could block the acid sites of the beta zeolite. In Fig. 1 it can be observed the presence of EFAL species in all the agglomerated samples. The EFAL signal was significantly higher in these samples as compared to that of non-agglomerated ones. Therefore, the EFAL species, created after the agglomeration process, can also hinder the accessibility of the acid sites, especially in the mordenite zeolite based catalyst (which presents a narrower pore system). This fact explains the lower conversion obtained with the agglomerated mordenite zeolite in comparison to that obtained with the agglomerated USY zeolite based catalyst.

Fig. 6 shows *n*-octane isomers selectivity versus reaction time for the agglomerated catalysts. At practically all the reaction times, high selectivity (more than 80%) was obtained. These results agree with those reported by Denayer et al. [23], who reported that due to the high pressure in the liquid phase, the cracking products formation became important only at relatively high average conversions. As above mentioned, for each reaction time, the *n*-octane conversion obtained with the agglomerated catalysts was lower than that obtained with the non-agglomerated catalysts. Consequently, the cracking products would appear at longer reaction times.

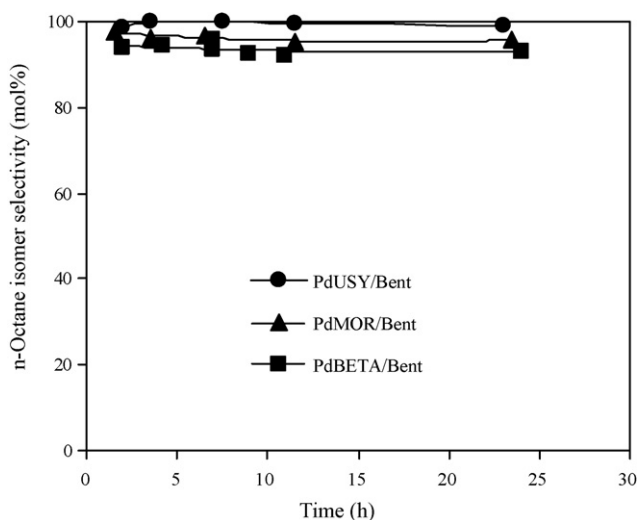


Fig. 6. *n*-Octane isomers selectivity as a function of the reaction time over the agglomerated catalysts.

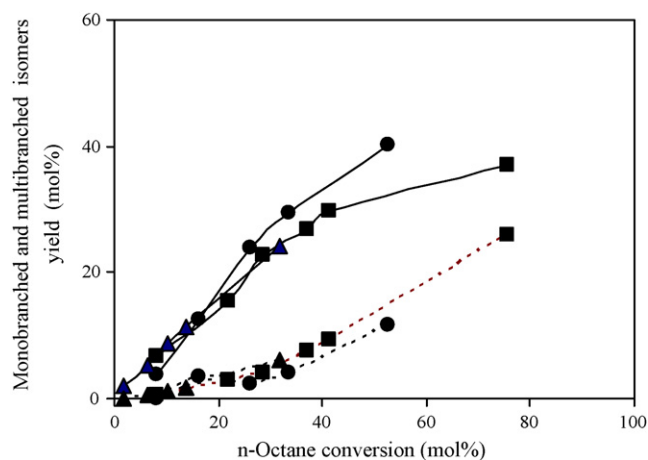


Fig. 7. Mono (continuous line) and multibranched (dotted line) isomers yield vs. *n*-octane conversion for the agglomerated catalysts: (●) PdUSY/Bent, (▲) PdMOR/Bent and (■) PdBETA/Bent.

After the agglomeration process, the monobranched isomers yield increased for all the samples while the multibranched isomers yield decreased (Fig. 7). Since the isomerization proceeded through successive branching, high acid strength should favour more branching. This fact is explained because, as above mentioned, the agglomeration process introduced Na^+ cations in the zeolite because of the solid-state ions exchange process, between H^+ from the zeolite and Na^+ from the clay, causing a decrease of the number of strong acid sites and reducing the possibility for latter intermediates to be isomerized [40].

4. Conclusions

The influence of the binder on the performance of catalysts based on USY, mordenite and beta zeolites in the liquid phase hydroisomerization of *n*-octane has been studied. The presence of the binder decreased the catalytic performance of all the catalysts because of the decrease of the number of strong acid sites as a consequence of the ion-exchange among the cations of the clay and the H^+ from the zeolite. Additionally, a possible partial blocking of the micropore mouths of the zeolites by the binder and the EFAL species created during the agglomeration process could take place, which would lead to an increase in the length of the effective diffusional pathway.

Because of the decrease in the number of strong acid sites, the monobranched isomers selectivity increased after the agglomeration process while the multibranched isomers selectivity decreased. This fact would confirm that the isomerization proceeded through successive branching and that high acid density favours more branching.

The best results were obtained with the non-agglomerated beta zeolite due fundamentally to its structural characteristics and to its moderate acidity.

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