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PLATINUM LOADED DEALUMINATED H-MOR AND H-BEA ZEOLITES FOR N-HEXANE HYDROCONVERSION

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ABSTRACT

n-Hexane was isomerized in a micro-catalytic pulse reactor over a series of platinum loaded dealuminated H-MOR and H-BEA catalysts with various Si/Al ratios. Steaming and HCl processes were applied in the dealumination of the two zeolites. TPD data showed that H-MOR zeolite and its dealuminated samples possess higher acid sites number and strength than the corresponding H-BEA zeolite versions, whereas the dispersion of 0.35wt%Pt was higher on the latter samples. The results showed that the steam treatment inhibits the hydroisomerization activity on both zeolites due to the formation of extra-framework aluminum species in the pores of the zeolites as shown from SEM studies. However, acid leaching promotes the catalytic activity by widing the pore opening. Generally, H-BEA containing catalysts either untreated or dealuminated showed higher hydroisomerization activities than the other H-MOR containing catalysts.

KEY WORDS

Hydroconversion, n-hexane, H-MOR zeolite, H-BEA zeolite, dealumination, platinum

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1. INTRODUCTION

Environmental protection agency regulations for phasing out lead additives and oxygen-containing components like MTBE and ETBE as well as aromatics from gasoline had a significant impact on the refinery industry [1]. As a result, there has been a sharp rise in the requirements for octane enhancement processes. This rise is achieved by isomerizing n-pentane and n-hexane, which are the main components of light naphtha, to the corresponding iso-pentane and mono and dibranched hexanes which have higher octane number [2-5].

The Pt/(Cl)Al$_2$O$_3$ catalyst traditionally used for isomerization [6] is now being replaced by Pt/H-zeolite catalysts, and in particular Pt/H-MOR [7] by virtue of its higher resistance to heterocompounds in the feed, greater thermal stability and non-corrosiveness. Some authors have reported that zeolite beta and mazzite would be potential acid catalysts for hydroisomerization of n-alkanes [8, 9].

More recently, Roldand et al. [10, 11] studied the hydroisomerization of light paraffins over platinum supported on H-BEA, USY, H-MOR, FER and ZSM-5 zeolites with different Si/Al ratios. They concluded that the Pt/H-BEA catalyst with Si/Al ratio of 25 provided the best results to convert C$_6$ and C$_7$ with high conversion and selectivity to their isomers.

The classical bifunctional reaction mechanism of hydrocarbon isomerisation includes dehydrogenation of alkanes on the metal sites, followed by a rearrangement of the intermediates on the acid sites and subsequent hydrogenation on the metal sites [12, 13].

The acid properties and resultant catalytic activity of zeolitic materials are known to be related to the degree of substitution of aluminum for silicon in the framework. The modification of catalytic properties through dealumination of zeolitic lattices by various treatments has therefore been a matter of considerable interest.

Chao et al. [14] studied the hydroconversion of n-heptane over platinum-loaded H-forms MOR and BEA zeolites. They observed that the isomerisation and cracking products are formed either simultaneously or consecutively as a function of reaction pressure and pore structure as well as the density of acid sites in the zeolites. The intraframework void spaces of zeolite BEA are less hindered than those of zeolite MOR. In this case, Pt/H-BEA was found to be close to an ideal bifunctional catalyst for n-heptane transformation and iso-heptane formation, and the effect of pressure is less pronounced [15]. The isomerisation selectivity on Pt/H-MOR was significantly improved by increasing reaction pressure, Pt concentration and Si/Al ratio of H-MOR.

A number of researchers [16-18] have observed that the degree of lattice dealumination of faujasite zeolites following steam treatment is dependent on the temperature at which the treatment is carried out; higher temperature lead to a higher degree of dealumination. Dealumination of H-BEA by steaming results in a much lower density of acid sites compared to the samples dealuminated by acid or ammonium hexafluorosilicate treatment [19]. Since the steamed sample contains all the extra-framework aluminum species (EF-Al) generated during dealumination, its lower acidity may be ascribed to blocking of acid sites by highly polymerized EF-Al species, and probably also to the neutralization of a part of the framework charge by cationic-type EF-Al species.

2. EXPERIMENTAL

2.1. Preparation of the Catalysts

The parent zeolites (Na-MOR and Na-BEA) were calcined in air at $500^{o}C$ for 3h to remove any templating agents remaining after the zeolite synthesis. These Na-forms were transformed to the corresponding NH_4-forms via exchanging a molar solution of NH_4NO_3 under reflux system at $70^{o}C$ several times for 8h each using fresh solutions. The NH_4-forms produced were then separated, washed several times with distilled water to remove NO_3^{-} ions, dried at $110^{o}C$ overnight then calcined in air at $500^{o}C$ for 3h to convert them to the corresponding acid forms (H-MOR and H-BEA). H-MOR and H-BEA zeolites were hydrothermally treated according to a procedure given by Haag and Lago [20]. This steaming was carried out in a tube furnace maintained at $530^{o}C$ for 3h using nitrogen gas as a steam carrier. H-zeolites were partially dealuminated using 2N hydrochloric acid (10 ml HCl for each gram zeolite) at $150^{o}C$ under reflux for 4h, washed with distilled water several times till neutral, dried at $110^{o}C$ overnight then calcined at $500^{o}C$ in air for 3h.

The current as-synthesized and dealuminated zeolites were impregnated with an aqueous solution containing the requisite quantity of chloroplatinic acid to obtain 0.35wt%Pt in the finished catalysts. A small amount of citric acid was added to the Pt precursor solution to improve the penetration of the Pt into the zeolite pores in order to achieve optimum dispersion of the metal [21–23]. The prepared catalysts were dried at $110^{o}C$ overnight, calcined at $500^{o}C$ in air for 3h and reduced in a flow of dry hydrogen of $20cm^{3}min^{-1}$ for 8h at $500^{o}C$ before carrying out the hydroconversion runs.

2.2. Reactor system

A micro-catalytic tube jacketed with an electrically thermostated copper block heater was installed at the injection port of a gas-chromatograph (Sigma-3 Perkin Elmer). The reactor contained always 0.20 g of a catalyst whereupon the H_2 carrier gas flow of $20cm^3$/min passed to serve also as a reactant. The feed injected was always 0.5 μl of AR n-hexane. Reaction temperature from $500^{o}C$ downward ($25^{o}C$ intervals) were used. Eluted reaction products passed directly to a GC column, 3.0 m long and internal diameter of 5 mm, packed with 10wt% OV-101 on Chromosorb W of 60-80mesh. The column temperature was isothermally maintained at $60^{o}C$.

2.3. Temperature programmed desorption (TPD)

The procedure adopted by the authors [24, 25] to follow the desorption of presorbed NH_3 on the catalysts was used. NH_3 adsorption was first carried out in a silica tube furnace after evacuation at 1.33×10^{-3}Pa whilst heating at 500°C and subsequent cooling to 50°C (under vacuum). NH_3 was passed on the catalyst at a flow rate of $50cm^3min^{-1}$. The catalyst was measured in a DSC-30 (Differential Scanning Calorimetry) unit (Mettler TA-3000) with a gold sensor using Al crucibles. NH_3 desorption was then carried out in N_2 purge gas at a flow rate of $50cm^3min^{-1}$. The heating rate was $10Kmin^{-1}$ and full-scale range of the heat flow was 25mW.
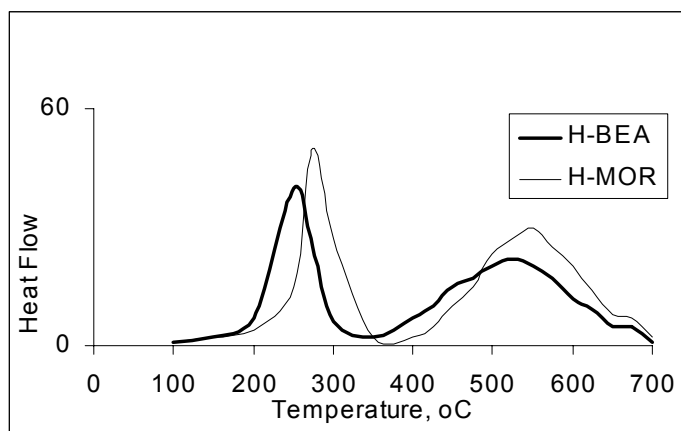

Fig.1. Temperature programmed desorption of chemisorbed NH_3 on the acid sites of the zeolites followed by its desorption using the programmed heat increasing in a differential scanning.

Fig. 1 shows that two endothermic peaks appeared in each desorption thermogram; a low temperature peak appearing between ~ 50 and 350°C, representing ΔH of NH_3 desorption from the weaker acid sites and a higher temperature peak appearing between 350 up to 700°C, representing the enthalpy of ammonia desorption from the strong acid sites which are responsible for the catalytic activities of the reactions taking place on the catalysts under study.

Table 1. Characterization of unloaded zeolite samples

Zeolite	Dealumination method	Si/Al ratio	Acidity		Crystallinity
			ΔH_d, Jg^{-1}	Peak temp.,^{o}C	
H-MOR	As synthesized	6.44	125	550	100
St-H-MOR	Steaming	6.59	109	531	100
DA-MOR(HCl)	2.0 N HCl	8.59	113	538	~100
H-BEA	As synthesized	3.04	105	525	100
St-H-BEA	Steaming	3.21	90	510	~100
DA-H-BEA(HCl)	2.0 N HCl	41.25	85	498	50

2.4. Metal dispersion (fraction of metal exposed) in the catalysts

Dispersion of Pt in the current Pt containing catalysts whether supported on H-MOR and H-BEA zeolites was determined by H_2 chemisorption using a pulse technique similar to that of Freel [26]. The calcined catalysts were heated in the chemisorption furnace at 500°C for 3h in a H_2 flow of 50cm^{3}min^{-1} then in a N_2 flow of 30cm^{3}min^{-1} for 2h (degassing). The furnace was shut off and the catalyst was cooled to room temperature. H_2 was then pulsed into the N_2 carrier till saturation (appearance of H_2 peaks equivalent to un-chemisorbed pulses). The H_2 uptake was calculated as hydrogen atoms adsorbed per total metal atoms on the basis of 1:1 stoichiometry [27].

Table 2. Characterization of 0.35wt%pt loaded zeolite catalysts

Catalyst	ΔH_d, Jg^{-1}	Acidity Peak temp., ^{o}C	Dispersion, %
Pt/H-MOR	105	522	66
Pt/St-H-MOR	90	506	68
Pt/DA-MOR(HCl)	96	510	72
Pt/H-BEA	85	500	71
Pt/St-H-BEA	70	485	71
Pt/DA-BEA(HCl)	64	474	75

2.5. Scanning electron microscopy (SEM)

The SEM samples were mounted on Al slabs and sputter-coated with a thin gold layer of ~ 150Å thicknesses using an Edward sputter-coater. The samples were then examined in an SEM model JXA Electron probe micro analyzer (JEOL) at 30kV.

3. RESULTS AND DISCUSSION

Catalytic activities of the current catalysts for n-hexane hydroconversion

The hydroconversion of n-hexane using the catalysts under study includes, in general, hydroisomerization, hydrocracking and dehydrocyclization reactions. Hydroisomerization of n-hexane gives four branched iso-hexanes, whereas its hydrocracking yields light C_1-C_5 hydrocarbons. Hydroisomerization takes place at relatively lower temperatures, attaining a maximum as temperature increases then these C_6 isomers decline with a further increase of temperature as a result of their hydrocracking. At higher temperatures, n-hexane cyclizes and dehydrogenates to benzene.

3.1. Hydroisomerization of n-hexane:

A series of catalysts containing 0.35%Pt supported on H-MOR zeolite, steamed (hydrothermally treated) H-MOR or HCl leached H-MOR, and another series also containing 0.35%Pt supported on respective H-BEA zeolite forms have been tested

for the hydroisomerization of n-hexane. The H-BEA containing catalysts are significantly more active and selective than the three respective H-MOR supported versions (Figs. 2a-2c and 3a-3c). For instance, iso-hexanes reach a maximum of 58.5% at 300°C with 87.0% selectivity using the Pt/H-BEA catalyst, compared to a maximum of 47.1% at 275°C with 75.5% selectivity using the Pt/H-MOR catalyst. The higher hydroisomerization activity of the Pt/H-BEA catalyst can be attributed to the following: (i) A higher Pt dispersion of 71.0% compared to 66.0% estimated for the Pt/H-MOR catalyst (Table 2). (ii) A somewhat lower acid sites number and strength of the Pt/H-BEA catalyst (ΔH_{des} 85.0Jg^{-1} and 500°C ammonia desorption peak temperature, respectively) compared to those estimated for the Pt/H-MOR catalyst (105.0Jg^{-1} and 522°C, respectively)(Table 2).
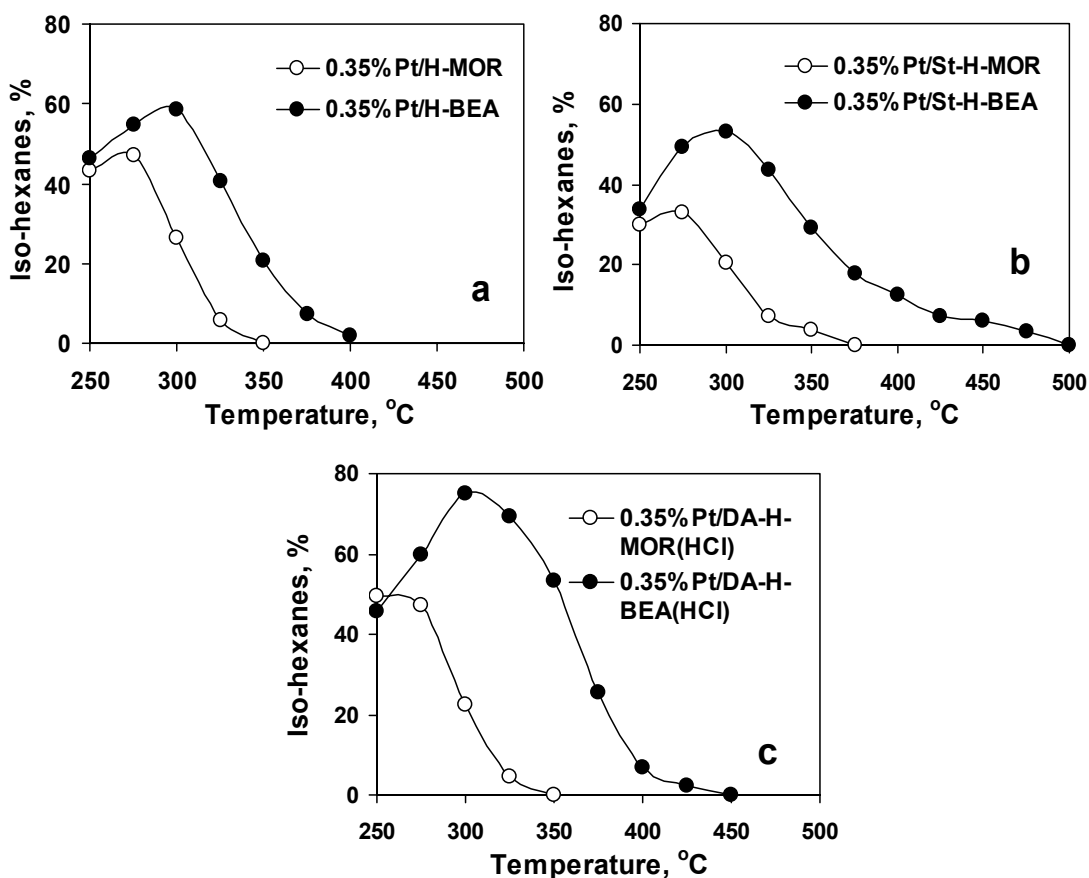

Fig.2. Hydroisomerization of n-hexane as a function of reaction temperature using 0.35wt%Pt supported on (a) H-MOR and H-BEA, (b) St-H-MOR and St-H-BEA (c) DA-H-MOR(HCl) and DA-H-BEA(HCl) catalysts.

The higher acidity of Pt/H-MOR has enhanced its hydrocracking activity on the expense of hydroisomerization. Although hydroisomerization is known [28] to require catalysts with higher hydrogenation-dehydrogenation activity and higher acid function, these data may give evidence that the acid sites strength in the Pt/H-MOR catalyst exceeds the balancing limit allowable for hydroisomerization level. (iii) Moreover, some physical aspects appear to have also contribution to the difference in n-hexane hydroisomerization activities of the Pt/H-MOR and Pt/H-BEA catalysts.

Diffusion of n-hexane and its isomers along the pores of the Pt/H-MOR catalyst is more restricted than in the pores of the Pt/H-BEA catalyst. H-BEA zeolite acquires a tridirectional channels system consisted of linear channels (0.76×0.64 nm) of 12 membered ring (12-MR) and tortuous channels (0.55×0.55 nm) with channels intersections, whereas H-MOR zeolite acquires 12-MR unidirectional channels (0.65×0.70 nm) with side-pockets of 8-MR (0.57×0.26 nm) at the wall of the main channels [29-32]. The latter channels are too narrow to permit any molecular species to diffuse along them. It has been assumed that most of the Brönsted acid sites included in H-MOR are located in side-pockets. Van de Runstraat et al. [33] assume that 2/3 of the acid sites in H-MOR are inaccessible by n-hexane because of their accumulation in the side-pockets.
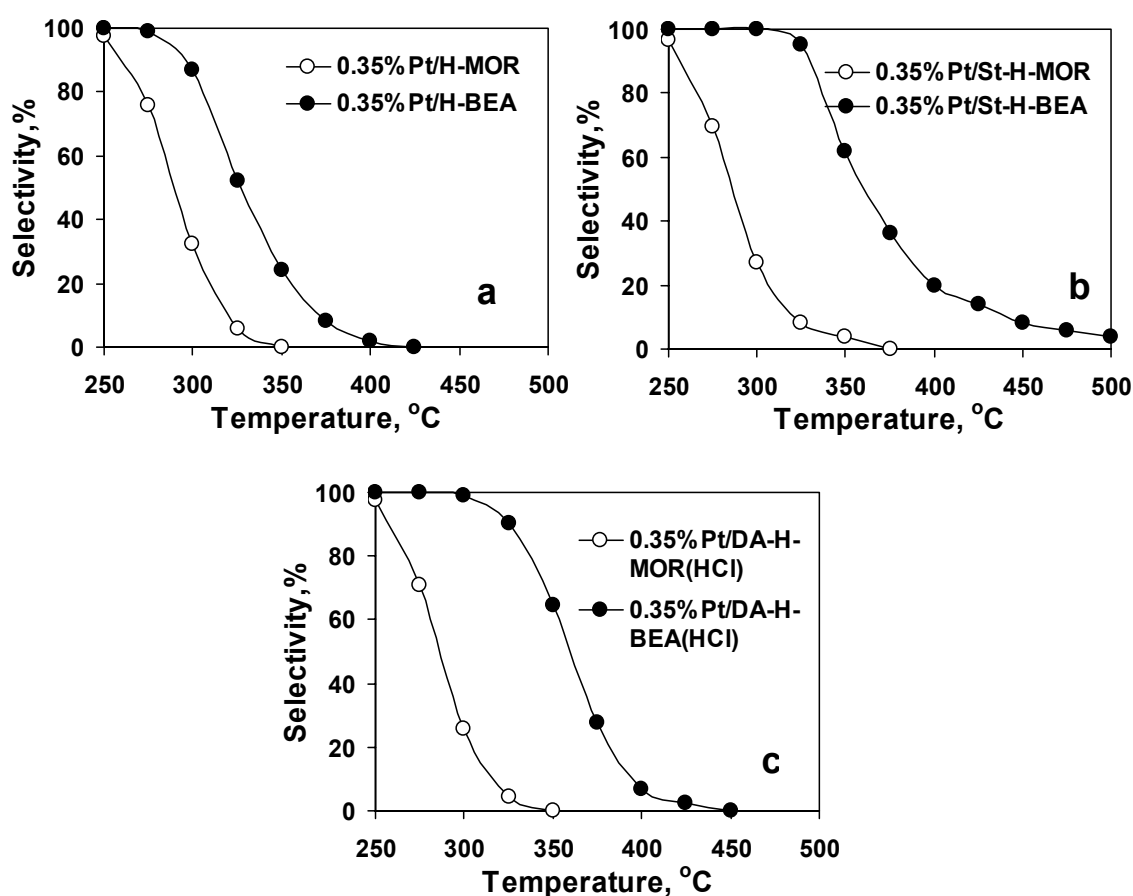

Fig.3. Selectivity of iso-hexanes as a function of reaction temperature using 0.35wt%Pt supported on (a) H-MOR and H-BEA, (b) St-H-MOR and St-H-BEA (c) DA-H-MOR(HCl) and DA-H-BEA(HCl) catalysts.

Comparing Figs. 2a and 2b show that the steaming of H-MOR and H-BEA has significantly decreased the n-hexane hydroisomerization activity. For instance, the maximum isomers yield on the Pt/H-MOR and Pt/H-BEA catalysts amounted to 47.1 and 58.5%, respectively compared to 33.0 and 53.1% using Pt/St-H-MOR and Pt/St-

H-BEA catalysts, respectively. This may be attributed to: (i) a significant decrease of the number and strength of the acid sites after steaming (Tables 1 and 2), (ii) however, it seems that the most effective reason for this inhibition is diffusion restriction along the zeolitic pores caused by the deposition of some extra-framework hydroxylated aluminum species (debris) as shown from SEM studies (Figs. 4a-4f). Fig. 4a shows the SEM picture obtained at 2000 times magnification for the cross sectional surface of a H-MOR pellet. It shows particles of irregularity size; particles as small as fractions of a µm up to aggregates. The view shows also deep depression on the surface. On the other hand, Fig. 4b shows that the surface of the crystallites become somewhat more polished or cleaned via steaming, which may indicate that any debris formed through hydrothermal dealumination has been precipitated in the cavities either outside the channels, in between the crystallites, or partially in the channels.

The topology of the sample surface in the microscopic view of St-H-BEA zeolite seems to have been decreased, indicating a more compact texture than before steaming (Figs. 4d and 4e), as revealed via comparing the superficial porosity. The compaction of the zeolitic texture occurring after steaming may be attributed to the formation and deposition of extra-framework aluminum (EF-Al) species intermingling between the crystallites in the form of matrix. It is also clear that a more amorphous appearance is observed in comparison to that of the untreated zeolite where agglomerates appear more porous.
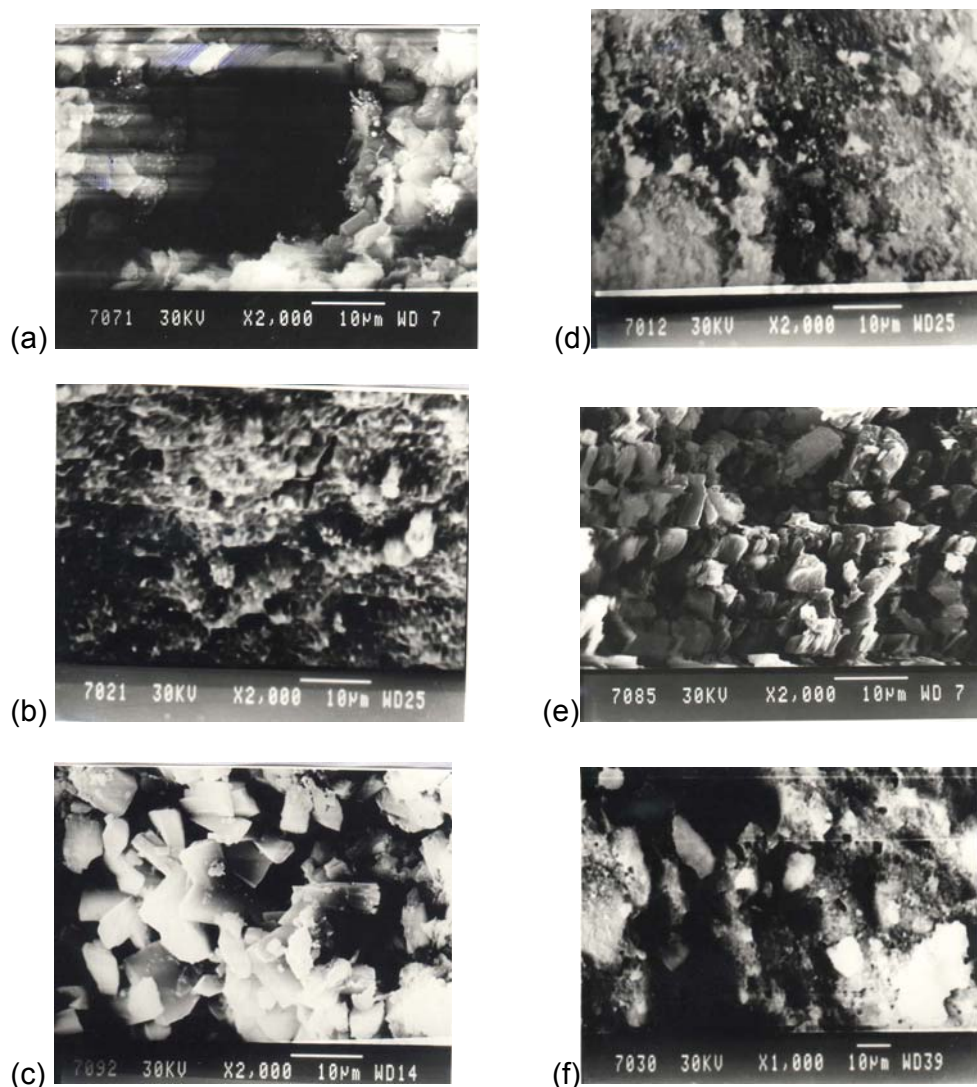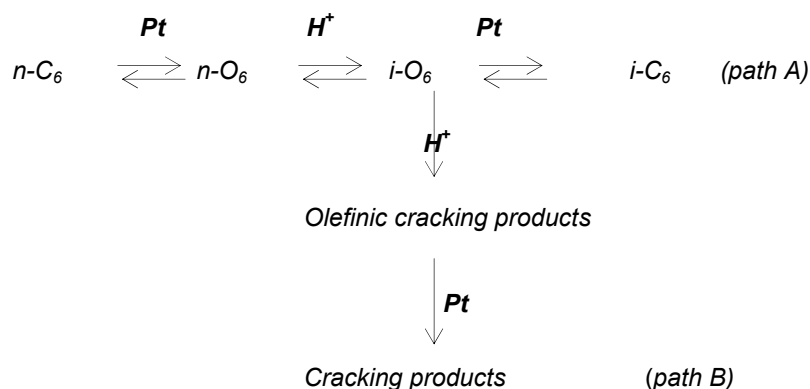
Fig.4. SEM pictures of dealuminated H-MOR and H-BEA zeolites
at ×2000 ; (a) H-MOR, (b) St-H-MOR, (c) DA-H-MOR(HCl), (d) H-BEA,
(e) St-H-BEA and (f) DA-H-BEA(HCl).

However, Corma et al. [34] have stated that during steam dealumination, the EF-Al species produced can block the channels such that the accessibility of n-hexane molecules to the acid sites is reduced due to diffusion restriction [19, 34]. However, it has been reported that EF-Al may be positively effective [35, 36], negatively effective [37, 38] or dependent on the level of extracting this EF-Al species [39]. Extraction of the latter can be accomplished by acid leaching.

We have here examined the effect of leaching the zeolites H-MOR and H-BEA with HCl solution before incorporating Pt. This treatment proves to achieve the highest level of isomerization of n-hexane associated with highest selectivities. Using the Pt/DA-H-MOR(HCl) and Pt/DA-H-BEA(HCl) catalysts, maximum iso-hexanes comprise 49.5 and 75.1% at 250 and 300°C, respectively. The mean reasons for this superiority (Figs.2a-2c and 3a-3c) can be attributed to the following: (i) Acquiring the

highest dispersion of Pt in the acid leached supporting zeolites (72.0 and 75.0% for Pt/DA-H-MOR(HCl) and Pt/DA-H-BEA(HCl), respectively). (ii) Achieving an extra-cleaning of the zeolitic channels via removing the traces of aluminum hydroxide debris remaining after the zeolite synthesis. Fig. 4c shows that the crystallites of H-MOR seem to have been significantly cleaned via acid treatment and the well developed faces and edges of the crystals have become more clear. (iii) Formation of mesopores upon acid leaching which facilitate the accessibility of n-hexane to the acid sites. Fig. 4f shows that the HCl treatment applied to H-BEA zeolite gives larger pores and more clear crystals than in the untreated SEM picture in Fig. 2d. This can be attributed to the dissolution of a large part of the amorphous debris originally precipitated during the synthesis of the zeolite.

Tromp et al. [40] assumed that leaching a zeolite with acid generates mesopores, giving chance for the acid sites to be more accessible and facilitates desorption of the reaction products. Faster desorption and diffusion of the bulkier iso-hexanes are important parameters for a successful isomerization catalyst.

$$n\text{-}C_6 \underset{\substack{\longleftarrow \\ \longrightarrow}}{\overset{Pt}{}} n\text{-}O_6 \underset{\substack{\longleftarrow \\ \longrightarrow}}{\overset{H^+}{}} i\text{-}O_6 \underset{\substack{\longleftarrow \\ \longrightarrow}}{\overset{Pt}{}} i\text{-}C_6 \quad (path\ A)$$

$$\downarrow H^+$$

Olefinic cracking products

$$\downarrow Pt$$

Cracking products   *(path B)*

Scheme1. Schematic representation of bifunctional mechanism.

Here, O represents an intermediate olefin and H^+ an acid sites.

HCl dealumination of the H-BEA and H-MOR zeolites is particularly more pronounced when applied to H-BEA than to H-MOR. The Si/Al ratio for these zeolites amounts to 41.3 and 8.59, respectively, compared to 3.04 and 6.44 using the respective forms (Table 1). The effectiveness of HCl dealumination applied to H-BEA can be attributed to the three directional arrangements of the channels in this zeolite, compared to the unidirectional arrangement in H-MOR. In H-BEA, aluminum is more accessible by HCl acid than in H-MOR. So, in zeolites with higher Si/Al ratios, e.g., DA-H-BEA(HCl) (Table 1), each intermediate olefin formed at Pt dehydrogenating site well come into contact to very few acid sites between two Pt sites (Scheme 1, path A), which may favorably lead to the formation of isomerized products [41], whereas, in zeolites with lower Si/Al ratios, e.g., DA-H-MOR(HCl), each intermediate olefin comes into contact with a large number of acid sites between two Pt sites (path B), which can lead to the formation of cracking products.

3.2. Hydrocracking of n-hexane:

The hydrocracking reaction of n-hexane is strongly enhanced by reaction temperature. Evidently, the hydrocracking activities of the three versions of H-MOR supported catalysts are more active than the corresponding H-BEA supported catalysts (Figs. 5a-5c). At 350°C, hydrocracking reaches 90.0-100.0% using the H-MOR supported catalysts, whereas at 400°C using the H-BEA catalysts, hydrocracking of n-hexane amounts to 84.3, 64.5 and 59.3% using the Pt/H-BEA, Pt/St-H-BEA and Pt/DA-H-BEA(HCl) catalysts, respectively. The hydrocracking activities for the H-BEA supported catalysts can be arranged in the order:

Pt/H-BEA > Pt/St-H-BEA > Pt/DA-H-BEA(HCl)

This order is compatible with acid sites number and strength of these catalysts (Table 2). Evidently, the acid sites decrease in number and strength in the HCl dealuminated H-BEA zeolite is in favour of decreasing the hydrocracking activity (Figs. 5a-5c) and enhancing the hydroisomerization activity. Moreover, hydrogen consumption will be lower using the H-BEA supported catalysts (economical advantage), since hydrocraked fragments require hydrogen saturation. Since hydrocracked products in the isomerization process are usually considered as a loss of the feed to undesired gases, it can be said that the H-BEA containing catalysts give more promising hydroisomerization catalysts.
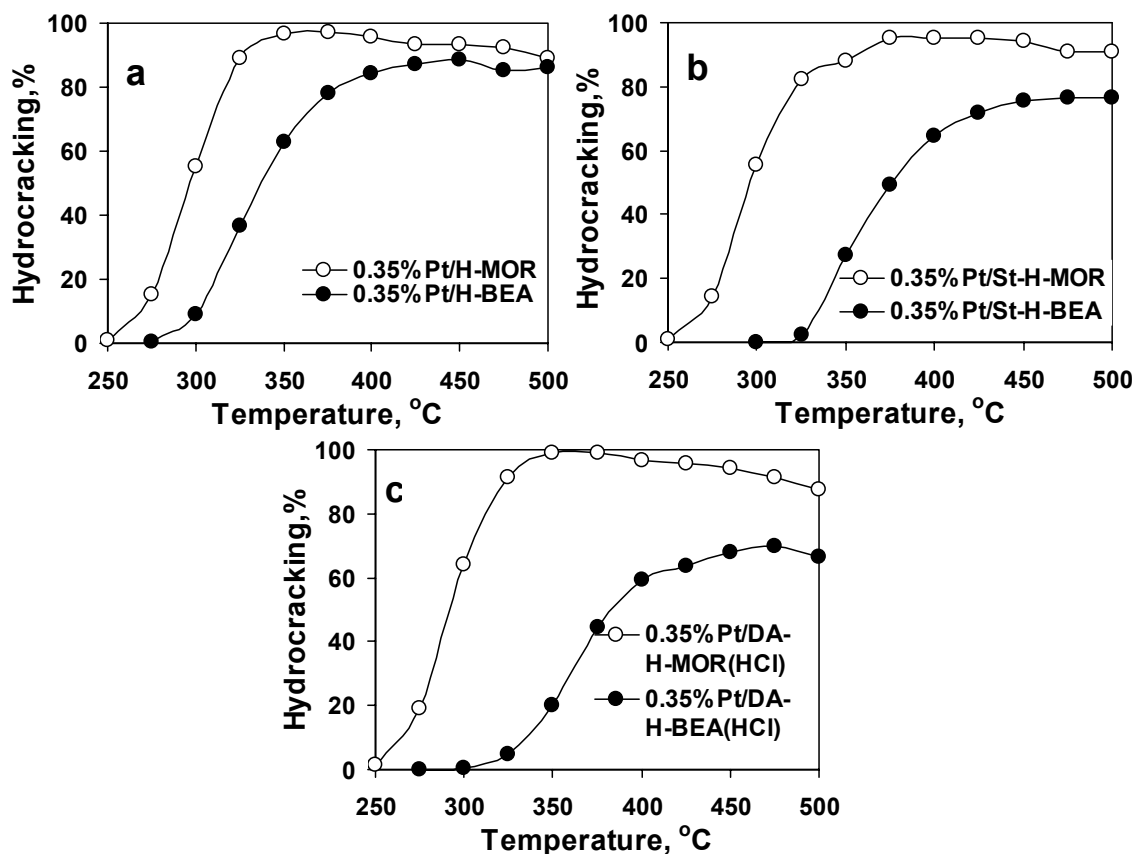
Fig. 5. Hydrocraking of n-hexane as a function of reaction temperature using 0.35wt%Pt supported on (a) H-MOR and H-BEA, (b) St-H-MOR and St-H-BEA (c) DA-H-MOR(HCl) and DA-H-BEA(HCl) catalysts.

3.3. Dehydrocyclization of n-hexane:

Benzene is the sole aromatic compound formed during n-hexane hydroconversion, suggesting that no other mechanisms except dehydrocyclization occur.

Dehydrocyclization of n-hexane to benzene on the current catalysts is compared in Figs. 6a-6c. All catalysts whether supported on H-MOR or H-BEA zeolites are of comparable activities during the temperature range investigated, except for the Pt/DA-H-BEA(HCl) catalyst, where benzene production is almost 3-fold those obtained using the other catalysts (Fig. 6c).

The larger surface area and pore volume of the H-BEA zeolite ($700m^{-2}g^{-1}$ and $0.234ccg^{-1}$, respectively) than those of the H-MOR zeolite ($500m^{-2}g^{-1}$ and $0.209ccg^{-1}$, respectively) should have assisted in obtaining higher Pt dispersion in H-BEA than in H-MOR (Table 2). This higher dispersion has increased the dehydrocyclization activity of the Pt/DA-H-BEA(HCl) catalyst, since this reaction is a metal catalyzed one. The HCl dealuminated catalyst should acquire the widest channels among other treated and untreated versions. In addition to acquiring mesopores, as indicated above, the pores, whether, micro- or meso-, are clean because of leaching preferably any EF-Al species. Moreover, H-BEA zeolite is more hydrophilic than H-MOR, hence assists the formation of higher yield of benzene.
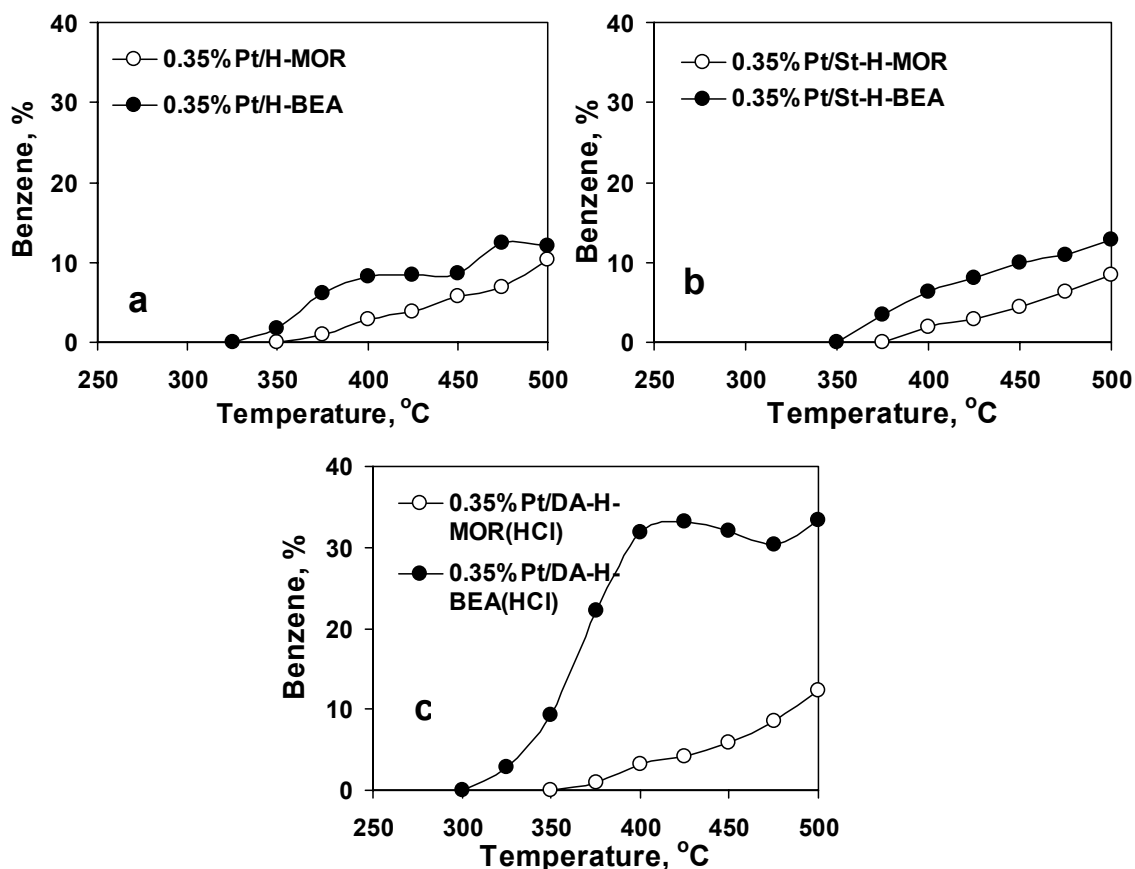

Fig.6. Benzene production as a function of reaction temperature using 0.35wt%Pt supported on (a) H-MOR and H-BEA, (b) St-H-MOR and St-H-BEA (c) DA-H-MOR(HCl) and DA-H-BEA(HCl) catalysts.

CONCLUSIONS

Modifications of H-MOR and H-BEA zeolites have been carried out via dealumination using hydrothermal treatment (steaming) as well as HCl leaching. All dealumination procedures give lower acid sites number and strength than the untreated zeolites. Generally, H-MOR and its dealuminated versions possess higher acid sites number and strength than the corresponding H-BEA and its dealuminated versions.

Dispersion of 0.35wt%Pt in H-BEA zeolite and its treated samples are higher than in the H-MOR and its treated samples, due to the larger surface area and pore volume of H-BEA zeolite. In both zeolites, the Pt dispersion increases with increasing the Si/Al ratio.

Incorporation of 0.35wt%Pt in steamed H-MOR and H-BEA zeolites gives lower hydroisomerization activity than the corresponding un-steamed zeolite containing catalysts due to the blockage of the zeolite channels by the condensed EF-Al species produced. However, the HCl treatment of H-MOR and H-BEA zeolites containing catalysts promotes skeletal isomerization activity due to the widening of the zeolite channels via acid leaching. Generally, the H-BEA containing catalysts either untreated or dealuminated showed higher hydroisomerization activities and selectivities than the corresponding H-MOR containing catalysts at all reaction temperatures under investigation.

All dealuminated H-MOR containing catalysts exhibit higher hydrocracking activities than the corresponding dealuminated H-BEA containing catalysts due the higher acid sites number and strength of the former catalysts.

Finally, the dehydrocyclization activities are always higher on all dealuminated H-BEA containing catalysts compared to the corresponding dealuminated H-MOR loaded catalysts which can be attributed to the larger pore volume, higher metal dispersion and lower acidity of the former catalysts.

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