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### Catalytic performance of nanostructured Pt/ZSM-5 catalysts synthesized by extended Charnell's method in hydroisomerization of n-pentane

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#### ABSTRACT

Na-ZSM-5 zeolite, synthesized by extended Charnell's method was used to prepare Pt/ZSM-5 catalyst for n-pentane hydroisomerization. The influence of ion exchange, alkaline treatment and method of platinum incorporation on the Na-ZSM-5 zeolite was investigated. It was found that the presence of Trien affected the physicochemical properties of the synthesized catalyst. The synthesized catalysts showed high performance so that the sample prepared in rotating mode at 24 h and Pt loaded via impregnation showed conversion and selectivity about 75 and 97 %, respectively. Also, a maximum yield for this catalyst was achieved at 250 °C.

Keywords: ZSM-5, Extended Charnell's method, Trien, Nanocatalyst, Hydroisomerization

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#### 1. Introduction

Nowadays isomerization of light linear alkanes to iso-alkanes is the best way to produce environment-friendly gasoline with favored combustion properties and higher octane number [1,2]. The current industrial catalyst which has been mostly used in recent years is Pt/Mordenite catalyst. However, the two-dimensional structure of Mordenite makes it vulnerable in the case of coke formation as one of the main problems of isomerization reactions [3,4]. Hereupon a great effort has been conducted to use the ZSM-5 zeolite as a catalyst in the isomerization of normal Paraffin. ZSM-5 has widespread use in catalytic processes due to unique properties such as intrinsic acidity, uniform pore size, high thermal stability, and the unique capability to stabilize metal species [5,6]. The special pore size of ZSM-5 prevents coke formation in its channels. Moreover, due to the very low rate of carbonaceous deposits, it has a long catalytic life. Also, the three-dimensional structure of the ZSM-5 zeolite active sites makes them easy to access [7,8].

Catalytic activity and acidic properties of ZSM-5 zeolite mainly depend on the Si/Al ratio and an actual number of Al atoms [3]. It was reported that in order to achieve high catalyst activity in the isomerization of n-pentane, Si/Al molar ratio must be low between 10-50 [9]. However, it is difficult to synthesize the ZSM-5 samples with low Si/Al ratios (<25), high purity and without the presence of other phases [10]. With increasing the Al content in zeolite structure, nucleation increases and zeolite with small particles is produced and consequently, control of zeolite properties becomes more difficult. The reason is that the nucleation rate increases with increasing the Al<sup>3+</sup> concentration in the reactant solution and it results in small crystals. To overcome this problem Charnell developed a method to synthesize large crystals of Al-rich ZSM-5 by adding chelating agents. Therefore, the crystals grow to be large [11]. However, in Charnell's method, triethanolamine plays both a structure-directing role and a chelating role. Yokomori and Idaka improved Charnell's method and called this synthesis method the "extended" Charnell's method or the "chelate addition" method. In their method the chelating reagent and the templating reagent are different. The addition of Trien (Triethylenetetramine) is important in this synthesis. Trien acts as a chelation reagent of Al<sup>3+</sup> and also suppresses the formation of nuclei containing Al<sup>3+</sup> leading to bigger crystals and better control of properties [12]. Consequently, a zeolite with well-defined structure could be synthesized at low Si/Al ratio.

Notwithstanding chelating agents play an important role in the synthesis of zeolites; few works report the development of chelation agent-based methods in the synthesis of ZSM-5 zeolite. The synthesis parameters, such as temperature, time and mode of stirring have been reported to influence the physicochemical and catalytic properties of zeolite catalysts [5]. Karimi et al investigated some effective parameters on ZSM-5 synthesized with chelate addition method [13]. But to the best of our knowledge, there are no investigations reported in the open literature on the catalytic properties and performance of ZSM-5 zeolites prepared by Charnell and extended Charnell methods and possibly that how zeolites with high Al content may be affected by acid and alkaline treatments for catalytic applications.

In the present study, structural changes occurring in ZSM-5 synthesized by extended Charnell's method at different levels of converting the Na-ZSM-5 zeolite to Pt/ZSM-5 catalyst like ion exchange by acid treatment, alkaline treatment, and Pt incorporation were investigated. The synthesized samples were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and BET specific surface area techniques. Also, activity and product selectivity of the synthesized Pt/ZSM-5 catalysts were evaluated in n-pentane hydroisomerization.

#### 2. Experimental

#### 2.1. Catalyst synthesis and characterization

#### 2.1.1. Preparation of nano-crystalline Na-ZSM-5 and H-ZSM-5 zeolites

Nanostructure Na-ZSM-5 zeolite was synthesized following the procedure reported earlier [13]. Briefly, solution A was prepared by adding Tetrapropylammonium hydroxide and deionized water to Tetraethyl orthosilicate. Solution B was prepared from aluminum isopropoxide and deionized water. Triethylenetetramine (Trien) and a mixture of NaOH and deionized water were added to solution A. Then solution B was added to the mixture A under continuous stirring. After completing the addition, the mixture was stirred for 2 h to obtain a homogeneous mixture. The mixture was transferred to a stainless-steel autoclave including Teflon holder and sealed autoclave. Crystallization was carried out at 175 °C for a given time. To evaluate the effect of autoclave rotation during crystallization, the crystallization was studied in both stationary and rotating mode. When the synthesis was completed, the

autoclave was quenched and the products were filtered, washed with distilled water and dried at 100 °C.

The Na-type ZSM-5 (Na-ZSM-5) samples were obtained by calcination of the assynthesized samples at 550 °C to remove the template. The calcined Na-ZSM-5 samples were converted to proton form by ion exchange with 1 mol/L NH<sub>4</sub>Cl solution at room temperature for 48 h. The solids were then separated by centrifugation and washed with deionized water to remove chloride ions, dried at 110 °C and calcined at 540 °C for 4 h to obtain H-ZSM-5. The notation used along the manuscript was ZS for the zeolites synthesized in stationary mode and ZR for the zeolites synthesized in a rotating mode. Also, IX suffix was used for samples converted to H-form by ion exchange.

#### 2.1.2. Alkaline treatment

2.00 g of calcined Na-ZSM-5 was added to 100 ml of 0.1 mol/L NaOH aqueous solution at 70 °C stirred for 8 h. The zeolite suspension was then cooled down immediately using an ice-water bath, filtered, washed with deionized water to remove remaining NaOH until neutral pH and dried at 120 °C for 12 h [14]. The prepared samples were denoted by AT-ZS. The alkaline-treated sample was converted into the H-form by the conventional cation-exchange procedure described in Section 2.1.1. The obtained sample in this step was labeled as AT-ZS-72-IX.

#### 2.1.3. Synthesis of Pt/ZSM-5 nanocatalyst

Platinum incorporation was carried out by using two different techniques: impregnation and ion-exchange methods. The nominal platinum concentration was 1 % g/g Pt. In the impregnation method, 1.00 g of the H-ZSM-5 sample was impregnated with a minimum amount of H<sub>2</sub>PtCl<sub>6</sub> solution required to wet the solid and stirred for 16 h at ambient temperature. Then, the solvent was removed by evaporation at 100 °C for 12 h. Ion exchange was performed by adding 1.00 g of the H-ZSM-5 sample in 0.0025 mol/L solution of H<sub>2</sub>PtCl<sub>6</sub>. The mixture was kept under agitation at ambient temperature for 16 h, followed by filtration, washing with deionized water and drying at 100 °C. Finally, the samples prepared under different conditions were carefully calcined at a heating rate of 0.5 °C/min to 450 °C in flowing air and maintaining this temperature for 2 h. The Pt/ZSM-5 catalysts synthesized by impregnation and ion exchange methods were labeled as PtM and PtX respectively.

#### 2.1.4. Characterization

X-ray powder diffraction was performed using the Siemens-D5000 diffractometer with Cu-K $\alpha$  radiation (30 kV, 40 mA) with a 2 $\theta$  range of 5-50°. Scherrer equation can be used to calculate the size of crystals and is as follows:

(1)

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where D is the crystallite size (nm),  $\lambda$  is the radiation wavelength (0.15406 nm),  $\theta$  is the diffraction peak angle and  $\beta$  is the corrected half-width at half-maximum intensity (FWHM) [9]. The average crystal size was determined from the average of crystal size between  $2\theta=23-25^{\circ}$  and  $2\theta=7-8^{\circ}$ . The Fourier transform infrared spectra were recorded on Unicam 4000 FT-IR spectrometer using KBr pellets. The surface morphology of samples was characterized by Quanta tax-QX2 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analysis (EDX) attachment which could provide the catalyst surface elemental composition information. The surface area of the samples was determined using Quantachrome3000 physical adsorption series with a BET method. The catalysts were outgassed at 200 °C prior to the surface area measurements.

#### 2.2. Catalytic tests for n-pentane isomerization

The isomerization of n-pentane was carried out in a stainless steel fixed-bed continuous flow reactor (i.d. = 4.5 mm). As can be seen in Fig. 1, a hot air furnace placed around the reactor provides the reaction temperature. The mixture of hydrogen and n-pentane was fed into the reactor simultaneously. The liquid n-pentane was injected by a syringe pump and the gas flow rates were controlled by electronic mass flow controllers. Prior to the reaction the catalysts were pelletized, crushed and sieved in the mesh size of 20–40. For each test 0.5 g of catalysts were loaded to the reactor and pre-treated in drying air flow (20 mL/min) at 400 °C for 2 h to remove the impurity absorbed on the surface of the catalyst. Then the metallic phase was reduced by a hydrogen flow (20 mL/min) at 450 °C for 2 h. Catalytic tests were performed at atmospheric pressure and the n-pentane conversion and selectivity of i-pentane as a function of time on stream over Pt/ H-ZSM-5 catalysts was investigated at 250 °C with weight hour space velocity (WHSV) of 0.3, and a H<sub>2</sub>/n-C<sub>5</sub> molar ratio of 3. Also, the effect of temperature on the isomerization of n-pentane over ZS-24-PtM catalysts was examined at the same reaction conditions. Reaction products were analyzed online using a Teif-Gostar GC-2550 TG gas chromatograph equipped with a flame ionization detector, capillary column (30 m, DB-1 column) and automatic valve for continuous analysis.

The reactor effluent stream was passed through a heated line to reach the automatic valve for analysis. Repeated experiments confirmed that the data obtained were closely reproducible. The conversion and selectivity of the products were calculated based on the carbon number of the components as defined by formulas given below

 $conversion (\%) = \frac{consumed n-pentane}{inlet n-pentane}$ 

 $selectivity(\%) = \frac{i\text{-pentane}}{consumed n\text{-pentane}} \times 100$ 

(Fig. 1)

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#### 3. Results and discussion

#### 3.1. Characterization results

#### 3.1.1. Influence of ion exchange in different autoclave modes

To investigate the effect of different autoclave modes on ion exchange, ZS-72 and ZR-72 samples were synthesized at static and rotatory modes respectively. The XRD patterns of these samples are shown in Fig. 2. It is evident that both samples have a typical MFI structure with high phase purity, but ZS-72 sample has more crystallinity. The physicochemical properties of all the samples at different steps are summarized in Table. 1. The average crystallite size obtained from the Scherrer equation showed a slight decrease in ZR-72 sample compared to ZS-72 sample.

#### (Fig. 2)

Comparing the Si/Al molar ratio of two samples revealed that this ratio decreased dramatically from 92 in ZS-72 to 25.5 in ZR-72 implying that rotation of autoclave during the crystallization time facilitated the entrance of aluminum atoms in zeolite structure (Table. 1). It is well-known that by entering the aluminum in the structure of zeolite, the structure is dissipated and consequently crystallinity is reduced. Also, as can be seen in Table 1, it led to a decrease in the size of zeolite crystals. These results were also confirmed by SEM micrographs in Fig. 3. So that, ZS-72 sample had a well-defined cubic structure with twinned morphology while in the case of ZR-72 many small and large amorphous particles could be seen. In addition, in the static mode, larger particles were formed which made the control of

their properties easier and led to twinned morphology with high crystallinity. Meanwhile, these larger particles caused to lower specific surface area of ZS-72 sample compared to other as shown in Table. 1.

#### (Table. 1)

Fig. 4 shows the FTIR spectra of the synthesized samples. The presence of the ZSM-5 zeolite in both samples is indicated by the infrared band at 545 cm<sup>-1</sup>, which has been assigned to the five-membered ring of the pentasil zeolite structure. The bands near 1080 (internal asymmetric stretch), 790 (external symmetric stretch), 540 (double ring vibration) and 450 cm<sup>-1</sup> (T-O bend) in both samples are the signature of ZSM-5 phase FTIR [10]. These patterns also confirmed the higher crystallinity of ZS-72 compared to that of ZR-72 sample due to its higher pick intensity.

## (Fig. 3)

#### (Fig. 4)

In catalytic applications, Na-form zeolites are usually converted to H-form using ion exchanging of the zeolite in acidic solutions to enhance their acidic properties. In general, this treatment leads to extraction of AI from the framework and increase in the Si/AI ratio, consequently. The created extra-framework aluminum species can act as Lewis acid centers and benefit certain catalytic applications especially in the isomerization of n-pentane. Contrary to published results in the literature, as can be seen in Table. 1, ion exchange of ZS-72 and ZR-72 samples led to a decrement in the Si/AI molar ratio. The reason for such a behavior was probably due to the presence of Trien and its effect on AI atoms in the structure of the zeolite. Trien acts as a chelation reagent of AI<sup>3+</sup> as a kind of mineralizer and affected the nuclei containing AI<sup>3+</sup> [12]. Meanwhile, AI is more difficult to extract. This fact can be explained by the negative charge associated with AI tetrahedra in the zeolite framework, hindering its extraction of AI through hydrolysis of Si-O-AI bonds by negatively charged hydroxyl groups [6]. Consequently, because of the strong position of AI<sup>3+</sup>, acid treatment leads to framework Si extraction, referred to desilication in the structure of zeolite alongside dealumination.

(Fig. 5)

As is evident in Fig. 5 removal of Si from zeolite structure influenced its morphology and crystallinity. These changes were not very significant in ZS-72-IX sample but in the case of ZR-72-IX sample, it was more striking. This behavior could be attributed to the lower Si/Al ratio and consequently higher Al content of ZR-72. The higher amount of Al makes zeolite structure unstable. The small particles existed in ZR-72 (Fig. 3b), due to the formation of amorphous silica species in the hydrothermal synthesis, disappeared after ion exchange and the surface of the particles also became rough. The disappearance of small particles during the desilication further confirmed that these particles should be amorphous silica. This also is based on the results revealed by the XRD analysis. XRD pattern of ZR-72-IX and ZS-72-IX samples showed that desilication during the ion exchanging might lead to a decrement in crystallinity. Additionally, some impurity peaks that were present in ZS-72 and ZR-72, had disappeared in ZS-72-IX and ZR-72-IX probably due to the removal of Si from the structure of the zeolite. The average crystallite size of both samples after ion exchange are listed in Table. 1. It was observed that the average crystallite size decreased after ion exchange in both samples indicating that treatment with acid not only increased the acid strength but also improved the diffusion properties.

The results illustrated that the rotation of autoclave during crystallization decreased the Si/Al ratio which consequently increased the acidity. On the other hand, it decreased the crystallinity of the zeolite structure. In order to overcome this problem and maintain the desired crystallinity in the low Si/Al ratios, the ZR-24 sample was synthesized in the rotary mode but for short crystallization time. Since by increasing the crystallization time, more Al entered the structure, the low Si/Al ratio was balanced by high crystallinity. As it was expected ZR-24 sample was

a typical twin hexahedron with perfect crystalline surfaces and highly ordered structures (Fig. 6a-b) with high Al content simultaneously (Si/Al  $\sim$  31). Also because of the higher crystallinity of this sample compared to ZR-72, it had a higher specific surface area (Table. 1). SEM images of ZR-24 after ion exchange are shown in Figure 6c. Ion exchange affected this sample to some extent, but the relatively complete crystalline structure of the zeolite was preserved.

#### (Fig. 6)

Also, the higher specific surface area of this sample in comparison with two other samples can be attributed to smaller particle size and a well-defined crystalline structure

(Table. 1). It can be said that with increasing the Si/Al ratio due to the lower content of Al, the effect of ion exchange on the structure of zeolite decreased. Also, comparing the ZS-72-IX, ZR-72-IX, and ZR-24-IX samples showed that the higher the original Si/Al ratio of the zeolite was, the greater the number of lost Si species. Moreover, the higher decline in Si/Al ratio illustrated that Si species were easier to remove from high Si content ZSM-5 zeolites which is in agreement with previous works over ZSM-5 [15].

#### 3.1.2. Effect of alkali treatment

ZS-72 sample was used to investigate the effect of alkaline treatment on the ZSM-5 zeolite synthesized in the presence of Trien. The XRD patterns of alkali-treated ZSM-5 zeolites are presented in Fig. 2. The intensity of most of the peaks was drastically decreased, which can be explained with a decrement in crystallinity by removal of Si from the framework. MFI major peaks in FTIR patent of treated zeolite showed that notwithstanding the severe changes in the structure, intrinsic crystalline structure of ZSM-5 remained but with lower crystallinity. This was shown by the presence of the infrared band at 550 cm<sup>-1</sup>, assigned to the five-membered ring of the pentasil zeolite structure (Fig. 4). As shown in Fig. 7a-b, alkaline treatment of the Na-ZSM-5 zeolite leads to the destruction of zeolite structure. Several large pores and holes appeared on the zeolite's surface. A part of the framework had also collapsed. Si/Al ratio of the sample was decreased drastically from 92 to 5.2 indicating that deep desilication occurred and it destroyed the zeolite framework. Average crystallite size of sample decreased from 53.6 to 45.18 after treatment. In general, the application of the alkaline treatment is discussed as a promising alternative to increasing porosity, [16] but contrary to what was expected as it is reported in Table. 1, specific surface area of AT-ZS sample showed drastic decrement. This behavior can be attributed to the structure collapse of AT-ZS. This result illustrates that crystallinity has an important role in the BET surface area of zeolite [5]. The high surface area of zeolites is primarily caused by a network of uniform micropores that provides shape selectivity opportunities [16]. It is worth noting that drastic changes in zeolite structure may be due to severe condition applied in this work. Treatment in the alkaline medium for a longer time and at higher concentration results in a higher degree of Si removal and consequently a decrement in crystallinity of zeolite. The decrease in the BET surface area after alkaline treatment also reported by Groen et al. They reported that BET surface area of FER zeolite decreased because of longer time and a higher concentration of NaOH led to a higher degree of Si removal. Also, they reported that a certain decrease of

the characteristic reflections was observed in all the zeolite examined but the main structure of zeolite preserved [17].

Fig. 7c gives SEM image of AT-ZS sample after ion exchanging which denoted as AT-ZS-IX. It can be seen that ion exchange led to the disappearance of edges and the structure of the sample became spongy. In addition, the particles became small upon the ion exchange. Likewise, the average crystallite size of the sample decreased after ion exchanging from 45.18 to 35.57.

#### (Fig. 7)

#### 3.1.3. Effect of platinum incorporation method

The method used in the incorporation of metal has a strong effect on metal particle size and structure [9]. Various techniques are available to introduce metals into zeolites, the most widely used being impregnation and ion exchange [18-20]. XRD patterns of the ZS-72-PtM and ZS-72-PtX samples are shown in Fig. 2. The platinum should be appeared at 20 =39.76 and, 46.24; however, a noise accompanied at these positions in addition to the low platinum concentration; therefore, no lattice fringes were observed in the figure from most of the nanoparticles, presumably because of their small sizes and random orientations. Also, these patterns showed that PtM had higher peak intensities and consequently higher crystallinity. It can be said that incorporation of Pt by impregnation method has a lower effect on the crystalline structure of zeolite compared to ion exchange method. SEM micrographs of both samples are shown in Figure 8. In the case of PtM sample, some bright spots were seen attributed to Pt particles. EDS analysis confirmed that these luminous spots were Pt particles which were not present in PtX sample. It was reported that in the impregnation, the relatively large metal particles were usually obtained while ion exchange resulted in a high initial dispersion and smaller particles which agree well with our results [18]. From obtained results, it can be concluded that higher dispersion of Pt was reached by ion exchange method whereas in impregnation method Pt particles remained large as they are explicit in SEM images. Babůrek et al also reported that Pt dispersion affected by Pt loading method and ion exchange method led to high Pt dispersion [21].

(Fig. 8)

#### 3.1.4. Catalytic isomerization of n-pentane

The n-pentane hydroisomerization experiments were carried out to compare the performance of synthesized catalysts. The conversion of n-pentane and selectivity toward ipentane over these catalysts are shown in Fig. 9 and 10 respectively. Obviously, the decrease of conversion and selectivity during the reaction time was virtually negligible over all the catalysts. Also, it can be seen that the conversions of n-pentane and selectivity of i-pentane over the different catalysts showed the great difference. The higher conversion of n-pentane was obtained over ZR-24-PtM catalyst. The reason for such a behavior is higher intrinsic acidity and higher crystallinity simultaneously. Acid strength, crystal/particle size and their morphology influence acidic zeolite activity and product selectivity [14,22]. It is generally acknowledged that the density of acid sites and the acid strength decreases with the increasing Si/Al molar ratios for ZSM-5 zeolites. On the other hand, with increasing Al atoms in structure, phase purity and crystallinity of ZSM-5 decreases. Comparing the performance of ZR-24-PtM and ZS-72-PtM catalysts showed that the first catalyst had higher conversion due to the lower Si/Al ratio and higher acidity. Also, smaller crystals offered shorter diffusion paths for the reactants and products and possessed a higher number of external active sites [22]. Comparing the performance of ZS-72-PtX and ZR-72-PtX shows that rotation during the crystallization time had a desirable effect on the catalytic performance of ZSM-5 catalyst. The better performance of the ZR-72-PtX catalyst could be explained in terms of the higher acidity and a more suitable specific surface area of this system. In fact, as mentioned above because of lower Si/Al ratio of ZR-72 and also higher BET specific surface area, the sample prepared in rotating mode showed higher conversion and selectivity compared to ZS-72 sample prepared in static mode. The less selectivity to i-pentane in the ZR-PtX catalyst can also be related to this higher strength of acid sites, which led to an increase in cracking products.

The significant changes in the acidity and the average crystallite size of ZSM-5 caused by alkali treatment may influence the catalytic activity. Thus, the hydroisomerization performance of alkaline treated Pt/ZSM-5 catalyst was examined, and the results are presented in Fig. 9 and 10. It is clearly observed that the alkaline treatment in the HZSM-5 zeolite catalyst synthesized in the presence of Trien enhances the n-pentane conversion remarkably. As can be seen in Table. 1 and mentioned above, the average crystallite size of ZS-72 sample reduced from 53.6 nm to 45.18 after alkali treatment. Smaller crystallite size suggested shorter diffusion paths, better performance of catalyst and higher conversion. Also,

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alkali treatment caused severe desilication and consequently drastic decline in the Si/Al molar ratio of ZS-72 sample from 92 to 5.5. The enhanced activity can be attributed to extraframework Al created during the alkaline treatment and desilication. Song et al whose alkaline treatment method was used in this work reported that the acidity of ZSM-5 was increased after alkaline treatment and their results showed that extra-framework Al formed in the alkali treatment and new stronger acid sites originated from treated ZSM-5 [14]. Moreover, some other papers reported the formation of strength acid sites with NaOH treatment [23]. Though there was a drastic change in the structure of ZSM-5, the increasing conversion with simultaneous high selectivity clearly showed that alkaline treatment was an effective method to improve isomer yield for ZSM-5 zeolite synthesized in the presence of Trien.

Comparing the activity results obtained from ZS-PtM and ZS-PtX samples showed that the conversion of n-pentane and selectivity of i-pentane for the catalysts prepared by impregnation method was greater than for the ion-exchanged counterparts. Based on the literature it is clearly observed that the preparation technique including ion-exchange and impregnation methods hardly affects the state of platinum in ZSM-5 [24]. These spectacular changes in conversion and selectivity are evident from Fig. 9 and 10. The Pt impregnated catalyst showed 22 times higher conversion compared to Pt ion exchanged one which has increased from 2.55 % to 50 % after 1 hour and there is a 37.5 % increase in i-pentane selectivity. Additionally, comparing the other results showed that all the catalysts in which Pt introduced by the impregnation method, showed higher conversion and selectivity compared to the one prepared by ion exchanging method. However, the selectivity for i-pentane over all the catalysts prepared by this method was identical and about 100 %.

Pt is assumed to play the dominant role in the activation of hydrogen which helps in the (de) hydrogenation reaction steps. This is important on the one hand in the proton transfer and formation and reactions of carbenium ions, and in suppressed deactivation of the catalysts, on the other hand. Also, according to Babůrek et al, higher dispersion of Pt enhanced the cracking reactions compared to the isomerization reaction and consequently selectivity was decreased over Pt ion-exchanged sample [21]. A similar effect was reported by Rodr'iguez-Reinoso et al. They reported high activity of small Pt clusters in the C-C bonds splitting. The dispersion effect is probably of more complicated nature, as also the Pt-H distances should be considered, which differs from large Pt particles located partially on

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the surface of the zeolite to small ones embedded predominantly inside the zeolitic cavities [25].

The catalysts, in terms of activity, can be listed as follow: ZR-24-PtM, AT-ZS-72-PtM, ZS-PtM, ZR-72-PtX, and ZS-72-PtX. The ZR-24-PtM sample due to higher acidity and crystallinity and also a method of Pt introduction exhibited a far superior activity. The effect of reaction temperature over the most active catalyst was investigated and the results are shown in Fig. 11. It can be seen that the conversion of n-pentane increased with temperature while the increasing of reaction temperature resulted in a substantial decrease of the selectivity to i-pentane. This behavior can be explained in terms of the exothermicity of the reaction. Since the reaction is equilibrium-limited, low temperature favors high concentrations of branched isomers and, furthermore, cracking products decrease with low reaction temperatures [26,27]. The highest yield of i-pentane over ZR-24-PtM was obtained at 250 °C.

(Fig. 10)

(Fig. 11)

#### 3.2. Our results compared with literature

As already mentioned, in recent years ZSM-5 zeolite has attracted more attention due to its unique characteristics for use as an acidic function in the bifunctional catalyst in the isomerization of linear alkanes. It is noteworthy that a strict comparison of our results with the results reported in the literature cannot be made, because of the difference in the amount of catalyst, weight percent of platinum in the catalyst, reactor configuration and reaction conditions. However, we have attempted to compare our data with comparable results from literature and results are summarized in Table. 2. It can be seen that most of the reported catalysts were active at 250 °C and higher temperatures and almost no data are reported below this temperature. In general, zeolite catalysts are active at higher temperatures, which is not suitable from the process and economic point of view. Whiles ZR-72-PtM synthesized in the present study, has the i-pentane yield of about 60 %. In fact, it can be claimed that it was a first ZSM-5 based catalyst which is highly active in n-pentane isomerization at 220 °C. Also, it is clear that the synthesized catalyst showed better performance compared to the others at higher temperatures. However, it was the first study on the catalytic use of ZSM-5

synthesized in presence of Trien by extended Charnell's method and its performance can be improved with further investigations. Research Octane Number (RON) of product stream is also calculated and reported in Table. 2. As seen, the RON of products is in a suitable range. It is important to mention that in the industrial isomerization the reactor outlet stream enters the adsorption column. These adsorption columns separate branched molecules from unconverted linear molecules that are transferred to the catalyst section in a recycle step which leads to higher research octane number.

#### 4. Conclusion

Presence of Trien led to decrease in Si/Al ratio of HZSM-5 obtained from ion exchange of Na-ZSM-5 zeolites synthesized by extended Charnell's method. Influence of ion exchange on the structure of zeolite affected by the mode of autoclave stirring and synthesis time as rotation of autoclave during the crystallization time facilities the entrance of Al atoms in zeolite structure and consequently led to lower Si/Al ratio. The new Pt/ZSM-5 nanocatalysts exhibited promising catalytic activity for the production of i-pentane from hydroisomerization of n-pentane. High n-pentane conversion and i-pentane selectivity of the synthesized Pt/ZSM-5 nanocatalyst showed that extended Charnell's method is a very useful method for preparation of zeolite for the catalytic application. Although, alkaline treatment causes a severe desilication and change in zeolite structure it significantly improved catalytic performance of Pt/ZSM-5 which can be attributed to the smaller crystallite size and lower Si/Al ratio and the higher acidity of the prepared sample. Impregnation method resulted in very high n-pentane conversion and i-pentane selectivity. By contrary, ion exchange method led to lower conversion and selectivity which could be related to higher dispersion of Pt. In this case, higher dispersion of Pt enhanced the cracking reactions and decreased selectivity and n-pentane conversion. Among the tested catalysts ZR-24-PtM showed the highest conversion of 75 % and selectivity of 97.6 % at 250 °C where a short crystallization time (24 h) in the rotary mode was applied and the introduction of Pt was done by impregnation method

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Sample	Average crystallite size	BET specific surface area	Si/Al		
ZS-72	53.6	236.05	92		
ZR-72	51.08	336.07	25.5		
ZR-24	26.48	342.5	31		
ZS-72-IX	44.0	-	42		
ZR-72-IX	33.5	-	20		
ZR-24-IX		-	24		
AT-ZS	45.18	52.53	5.5		
AT-ZS-IX	35.57	-	3.2		

Table. 1. Average crystallite size, specific surface area and Si/Al molar ratio of different samples.

T(°C)	C) 200				220			250				300				
Ref.	<b>X</b> <sup>1</sup>	<b>S</b> <sup>2</sup>	Y <sup>3</sup>	RON	X	S	Y	RON	X	S	Y	RON	X	S	Y	RON
	%	%	%		%	%	%		%	%	%		%	%	%	
[27]	-	-	-	-	-	-	-		10	60	6	-	40	30	12	-
[19]	-	-	-	-	-	-			-	-	-	-	22.1*	96.4*	21.3*	-
[28]	10	93	9.3	-	-	-	-	-	77.2	93.9	72.5	-	80	63	50.4	-
[25]	-	-	-	-	-		-	-	-	-	-	-	40	50	20	-
[29]	-	-	-	-		-	-	-	50	95	47.5	-	75	75	56.25	-
[8]	-	-	-	-	-	-	-	-	68	98.6	67	-	66	91.6	60	-
This	20	100	20	68	60	98.8	59.28	80	75	97.6	73.2	84.8	71.2*	89*	63.36*	84*
work																
<sup>1</sup> Convers	sion															

isomerization in the presence of Pt/ZSM-5 catalyst

Table. 2. Comparison of the results obtained in this study with the literature on n-pentane

<sup>2</sup>Selectivity

<sup>3</sup>Yield \* 280°C



Fig.1. Process flow diagram of experimental set-up for n-pentane isomerization



**Fig. 2.** XRD patterns of the samples: (a) ZR-72, (b) ZR-72-IX, (c) ZS-72-PtX, (d) ZS-72-PtM, (e) ZS-72, (f) ZS-72-IX, (g) AT-ZS-72 and (h) AT-ZS-72-IX.



Fig. 3. SEM micrographs of Na-ZSM-5 samples. (a) ZS-72 (b) ZR-72

PCCK



Fig. 4. FTIR spectra of ZSM-5 samples: (a) ZR-72, (b) ZS-72, (c) ZS-72-IX, (d) AT-ZS-72, (e) AT-

ZS-72-IX



Fig. 5. SEM micrographs of ion-exchanged samples (a) ZS-72-IX and (b) ZR-72-IX.

RCK



Fig. 6. SEM micrographs of (a-b) ZR-24 and (c) ZR-24-IX samples.



Fig. 7. SEM micrographs of alkaline treated and ion-exchanged alkaline treated ZSM-5 samples (a-b)

AT-ZS-72 and (c) AT-ZS-72-IX.



Fig. 8. SEM micrographs of Pt incorporated ZSM-5 samples (a-b) ZS-72-PtM and (c-d) ZS-72-PtX.



Fig. 9. Conversion of n-pentane as a function of TOS over various Pt/ZSM-5 catalysts



Fig. 10. Selectivity of i-pentane as a function of TOS over various Pt/ZSM-5 catalysts



Fig. 11. Effect of reaction temperature on conversion of n-pentane, selectivity to i-pentane and yield

of i-pentane

- ZSM-5 prepared by extended Charnell's method was used to synthesize catalyst first time.
- Catalysts synthesized by this method showed high activity and selectivity.
- Presence of Trien led to decrease in Si/Al ratio after ion exchange.
- Alkaline treatment improved catalytic performance.
- Impregnation method resulted in a higher activity and selectivity.

