

Effect of Promoters on the Catalytic Activity of the Isomerization Catalyst

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Abstract

The crystalline zeolite, namely faujasite type Y with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 5 was used as raw material for preparation of isomerization catalysts.

A 0.5 wt % Pt/HY-zeolite catalyst was prepared by impregnation of the decationized HY-zeolite with chloroplatinic acid.

The decationized HY-zeolite was treated with HCl, HNO_3 and HI promoters using different normalities and with different concentrations of Sn, Ni and Ti promoters by impregnation method to obtain acidic and metallic promoters' catalysts, respectively. A 0.5 wt% of Pt was added to above catalysts using impregnation method.

Isomerization of n-hexane was carried out at different prepared catalysts. The isomerization temperature varied from 250–325° C over weight hourly space velocity (WHSV) 1.6 h^{-1} . The pressure and hydrogen to feed mole ratio were kept constant at 1bar and 2 mol/mol, respectively.

The comparison between the above prepared catalysts shows that the total isomer yield during the process with Sn-Pt /HY- zeolite catalyst was higher than the other catalysts and, reached to 63.95% vol.

A 0.5 wt% of W and Zr was added to Sn-Pt/HY-zeolite catalyst by impregnation method to obtain W and Zr co-metal promoters catalysts. Isomerization of n-hexane was investigated using W and Zr co-metal promoters catalyst at the same operating conditions and the yield of isomers reached to 81.14% vol.and 79.07%vol.,respectively.

Keywords: isomerization, catalyst, catalytic activity, promoters.

Introduction

Isomerization is a catalytic process involves rearrangement of the molecular structure of a hydrocarbon without gain or loss of any of its components [1], in order to increase octane number of hydrocarbon fraction.

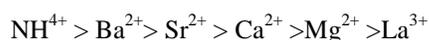
The main commercial applications during World War II and in a limited way thereafter were the isomerization

of butane to isobutane, pentane to isopentane [2,3], and naphtha or normal hexane fractions into a higher octane number gasoline. In these processes aluminum chloride is used with anhydrous hydrochloric acid as a liquid slurry or complex, on a granular alumina or bauxite support and dissolved in molten antimony trichloride. In all processes the feed must be dried so that moisture is not carried into the acid zone, but corrosion may be severe.

A refinery after 1956 almost completely utilizing all available cracked gases by polymerization and alkylation, and low octane gasoline is being upgraded by catalytic reforming. Thus, other means of upgrading octane number, notably isomerization, will be explored in an effort to upgrade pentane and hexane.

The isomerization process after 1957 was used the system of dual function catalyst (silica alumina) and hydrogenation catalysts such as nickel-silica-alumina or platinum-silica-alumina or similar catalyst which contains both metallic sites and acidic sites [1]. Recently, modern isomerization process uses zeolite bi-functional catalyst [4].

Gray and Cobb [5] studied mordenite catalysts with various cations prepared by a reflux ion exchange technique using chloride or nitrate salts and were tested for activity in the hydroisomerization and hydrocracking of n-pentane. The extent of sodium ion exchange possible followed the order:



Maximum catalyst activities for H-M, Ca-M and La-M occurred at calcination temperature of 510, 525 and 400° C, respectively.

Zhorov, Kartashev and Panchev [6] studied the isomerizing activity of decationized mordenite and faujasite in the isomerization activity of cyclohexane and n-hexane in isothermal reactor at 200-300° C and space velocity of 1.5 h⁻¹. The catalyst activated at 450° C for 5 h in air flow and dealuminized using EDTA and HCl. They found that type Y Zeolite was more active and selective in the isomerization of n-paraffins than mordenite but the latter was more selective for isomerization of naphthenes.

Prins, Massoth and Somorjai [7] studied the isomerization reaction of n-pentane and n-hexane over LaY, NaY, SrY, Ni-LaY, Ni-NaY and Ni-SrY zeolites and observed that the obtained data deviated from the ideal second-order kinetic model.

Lee and Woo [8] studied the isomerization of butane, pentane and hexane over HY, TiY, H-ZSM-5 and Ti ZSM-5 zeolites in the temperature range of 277-352° C and at atmospheric pressure. They found that the isomerization reaction of butane, pentane and hexane is first order reaction.

The aim of this investigation is the study of the effect of different catalyst promoters loaded on Pt/HY zeolite catalyst on the n-hexane isomerization.

Experimental Work

Feedstock

n-Hexane supplied from Reidel de Haen was used as raw material for isomerization activity test. The properties of n-hexane are shown in Table 1.

Table 1 n-Hexane Properties

Specification	Value
Molecular Weight	86.17
Purity (%)	99.8
Density (g/cm ³)	0.659
Boiling point (°C)	68.8

Catalyst preparation

Preparation of HY-zeolite

25 g of NaY-zeolite was slurried in 0.5 liter of 4N ammonium chloride [9] aqueous solution and left overnight for the ion exchange completion. The exchanged zeolite was filtered off, washed with deionized water and dried at 110° C overnight [10]. The dried exchanged zeolite was calcined initially at 150° C then the temperature increased to 525° C with a rate of 75°C/h [11]. During calcination, NH₃ and water are liberated and decationized HY-zeolite powder is formed. The prepared HY-zeolite was reduced with hydrogen at 380° C [12] for three and half hours at hydrogen linear velocity 3.38 × 10⁻⁴ m/s. The prepared catalyst powder was then fabricated as a spherical shape with 20% sodium silicate as a binder and calcined at 400° C for 5 hours.

Preparation of decationized 0.5%wt Pt/HY-zeolite

A 25 g of prepared HY-zeolite powder was used for the preparation of 0.5% Pt/HY-zeolite by impregnation method using impregnation apparatus shown in the Fig 1.

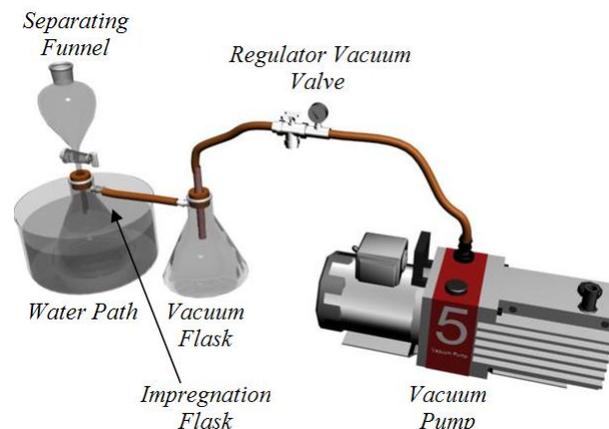


Fig. 1 Impregnation apparatus

1.3688 g of HCl was mixed with a solution of 0.3125 g of chloroplatinic acid (H₂PtCl₆) and 82 ml of water. The

resultant solution is added drop by drop to 25 g of prepared HY-zeolite with continuous agitation. Then, the sample mixed by using a magnetic stirrer for 2 hours to have a homogeneous distribution of chloro platinic acid. Then, the slurry was dried at 110°C overnight and calcined at 400° C for 5 hours. The calcined catalyst was reduced with hydrogen at 380° C for three and half hours at a hydrogen linear velocity 3.38×10^{-4} m/s. The prepared catalyst powder Pt/HY-zeolite was then formulated as a spherical shape with 20% sodium silicate as a binder and calcined at 400° C for 5 hours.

Preparation of decationized Pt/HY-zeolite with different acidic promoters

HCl, HNO₃ and HI used in different normalities to obtain HY-zeolite catalyst with different acidity. A 25 g of decationized HY-zeolite is added to solutions of 2, 4, 6 and 8 N of HCl, HNO₃ and HI, respectively. Then, the samples were filtered off through Buchner funnel and washed with deionized water to be free of anions, and dried at 110°C overnight. A 1.3688 g of HCl was found necessary to add in the solution of 0.3125 g of chloroplatinic acid and 82 ml of water to get a macroscopic homogeneous distribution of Pt inside the HY-zeolite pores. Then the resulted solution was added to each sample of the promoted catalysts as a drop by drop with continuous agitation and then mixed by using a magnetic stirrer to have a homogeneous distribution of chloroplatinic acid. Evaporation of samples was carried out at 140° C for 1 hour. The impregnated powders were then dried at 110° C overnight, and calcined at 400° C for 5 hours. The calcined catalysts were reduced with hydrogen at 380° C for three and half hours at hydrogen linear velocity 3.38×10^{-4} m/s. The prepared catalyst powders were then formulated as a spherical shape with 20% sodium silicate as a binder and calcined at 400° C for 5 hours.

Preparation of decationized Pt/HY-zeolite with different metal promoters

The decationized HY-zeolite was used to prepare catalysts containing different concentrations of Sn, Ti and Ni. A 25 g of decationized HY-zeolite was charged into impregnation apparatus. Evacuation is operated to remove the air from the pores of the carries HY-zeolite. The impregnation solutions are prepared by dissolving different quantities of SnCl₄, TiCl₂ and NiCl₄ in different quantities of decationized water. The impregnation process was accompanied with shaking for 4 hours at mixed temperature of 20° C. The impregnated products are then dried at 110° C overnight and dried catalysts are calcined at 400° C for 5 hours. A 1.3688 g of HCl adds to the solution of 0.3125 g of chloroplatinic acid H₂PtCl₆ and 82 ml of water to get macroscopic homogeneous

distribution of Pt inside the HY-zeolite pores. Then, the total solution was added to each sample of above prepared catalysts as a drop by drop with continuous agitation and then mixed by using a magnetic stirrer to have a homogeneous distribution of impregnation solution. The impregnated powders were then dried at 110° C overnight, and calcined at 400° C for 5 hours. The calcined catalysts were reduced with hydrogen at 380°C for three and half hours at a linear velocity of hydrogen 3.38×10^{-4} m/s. The prepared catalyst powder was then formulated as a spherical shape with 20% sodium silicate as a binder and calcined at 400° C for 5 hours.

Preparation of decationized Pt/HY-zeolite with different co-metal promoters

The decationized HY-zeolite was used to prepare two catalysts with tungsten and zirconium promoters. The first one containing 0.5 wt% Pt, 2 wt% Sn and 0.5 wt% W, while the second catalyst contains 0.5 wt% Pt, 2 wt% Sn and 0.5 wt% Zr. The first co-promoter solution was prepared by dissolving 2 g of ammonium meta tungsten in 15 ml of the decationized water, while the second co-promoter solution was prepared by dissolving 0.833 g of Zirconium tetra chloride in 20 ml of decationized water. The catalyst (W-Sn-Pt/HY-zeolite) was prepared by adding the first co-promoter solution to above prepared Sn-Pt/HY-zeolite as a drop by drop with continuous agitation and then mixed by using magnetic stirrer, while the catalyst (Zr-Sn-Pt/HY-zeolite) was prepared by adding the second co-promoter solution to above prepared Sn-Pt/HY-zeolite using the same previous procedure. The impregnated material then dried at 110°C, calcined at 400° C for 5 hours, and reduced with 3.38×10^{-4} m/s of hydrogen at 380° C for three and half hours. The prepared catalysts were then formulated as a spherical shape with 20% sodium silicate as a binder and calcined at 400° C for 5 hours.

Isomerization unit

The isomerization experiments were carried out in a laboratory unit. The process diagram of this unit is shown in Fig. 2. The unit consists of heater storage, reactor, chiller and condenser.

The reactor of this unit is a stainless steel tube with 80 mm inside diameter, 2 mm wall thickness and 750 mm length. It was packed with 25g of catalyst between two layers of inert material. The reactor is heated and controlled automatically by temperature controller.

Isomerization Operating Conditions

Isomerization of n-hexane was carried out using different prepared catalysts. The temperature range varied from 250 to 325° C. The pressure, weight hourly space

velocity and hydrogen/hydrocarbon mole ratio were kept constant at 1 bar, 1.6 h^{-1} and 2 mol/mol, respectively.

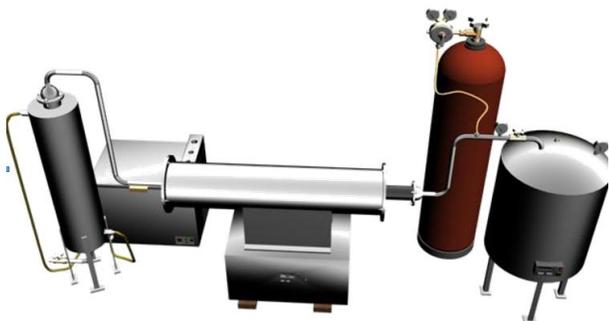


Fig. 2 Isomerization unit

Results and Discussion

Comparison between HY-Zeolite and 0.5%wt Pt/HY-Zeolite Catalysts

Figure 3 shows the effect of temperatures on the isomerization activity (total isomer yield) using HY-zeolite catalyst, and Pt/HY-zeolite catalyst.

The comparison between two curves shows that the total isomer yield of Pt/HY-zeolite was higher than that of HY-zeolite.

The mechanism of n-paraffin isomerization as mentioned by Gates et.al. [13] has three steps, n-paraffin's is dehydrogenated to n-olefins which occur on the metal sites, n-olefins isomerize to iso-olefins which occur on the acid sites and of iso-olefins hydrogenated to isoparaffin which occur on the metal sites again. Therefore, the increasing in the total isomer yield may be due to the addition of platinum which activates the hydrogenation/ dehydrogenation activity [1].

Furthermore, both curves show that as temperature increases the rate of isomerization reactions increases too.

Effect of Acidic Promoters on the Catalytic Activity

Figures 4 to 6 show that the effect of temperature on the isomerization activity using HCl, HNO₃ and HI promoters with different concentrations on HY-zeolite and Pt-HY-Zeolite. These figures show that the activity increases after the addition of HI, HCl and HNO₃ compared with HY-zeolite and Pt/HY-zeolite without promoters; and with increasing the concentration of the acid promoters.

This may be due to the active acid sites increasing after the addition of the acid promoters and that may be lead to enhance the isomerization of n-olefins to iso-olefins which occurs on the acid sites.

These figures also show that the activity increase with increasing the reaction temperature exception one curve in figure 4 in which the catalytic activity increases until 300° C and then decrease. This may be due to the considerable enhancing effect of acidic promoters which emerged when the HY-zeolite had been adsorbed them at higher temperature when the OH groups (causing the catalytic activity of HY-zeolite) will be supplied by the dissociation of the acidic promoters added. The ability of acidic promoters to enhance the activity of the HY-zeolite at high temperatures can be attributed to the newly formed OH groups [14].

It's clearly shown from Fig.s 4-6 that the higher activity (total isomer yield) was obtained using HI. This may be due to the reverse reaction of HI in its aqueous solution. HCl and HNO₃ are completely dissociated in its aqueous solution, while HI is partially dissociated in its aqueous solution [15]. When the temperature increases in calcination Cl⁻, I⁻ and NO₃⁻ an ions are liberated from HCl, HI and HNO₃, respectively with some H⁺ ion causing a decrease in isomerization activity.

Effect of Metal Promoters on the Catalytic Activity

Figures 7 to 9 show the effect of temperature on the isomerization activity at different concentrations of metal promoters supported on Pt/HY-zeolite. These figures show that the total isomer yield increases after the addition of Sn, Ni and Ti compared with HY-zeolite, Pt/HY-zeolite and acidic promoters supported on HY-zeolite, and the activity increases with increasing the concentration of metal promoter. This result may be due to the metal hydrogenation/ dehydrogenation activity increasing after addition of metal promoters. Also these figures show that the increasing in temperature increases the catalytic activity then the activity begin to decrease exception some curves in the above figures in which the catalytic activity increases with increasing temperature .

It is generally accepted that the catalytic activity of HY-zeolite is caused by the OH groups playing the role of Bronsted acid sites. The OH concentration decreases considerably when the HY-zeolite had been treated at the high temperatures which lead to a decrease in the catalytic activity. These results are in agreement with Otsuka, et.al.work [15].

Higher activity (63.95% yield) was obtained with Sn promoter. This may be due to Ni and Ti mild hydrogenation/dehydrogenation activity, while Sn has strong hydrogenation activity as mentioned also by Recharadson [16] .

Effect of Co-Metal Promoters on the Catalytic Activity

Figure 10 shows the effect of temperature on the isomerization activity using co-metal promoters (W and Zr) supported on HY-zeolite. This figure and the previous figures show that the activity increases after the addition of Zr and W compared with HY-zeolite, Pt/HY-zeolite, acidic promoters supported zeolite and metal promoters supported on HY-zeolite. This result may be due to the increasing of the hydrogenation/ dehydrogenation metal function of the catalyst.

Figure 10 also shows that the activity increases with increasing the reaction temperature up to 275° C then begins to decrease, and the W promoted catalyst gives higher isomer yield than Zr promoted catalyst and the maximum isomers yield with W promotor reaches to 81.14% vol. at 275° C.

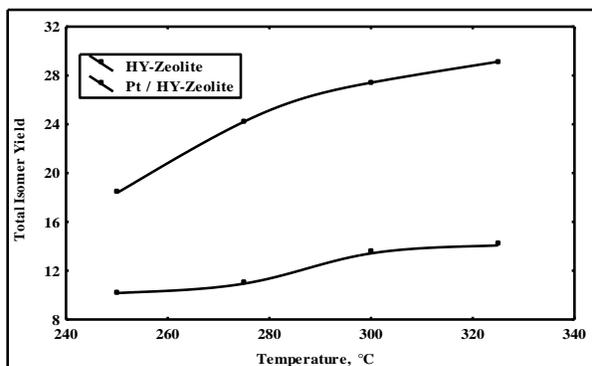


Fig. (3) Effect of Isomerization 0.5%wt Temperature on the Catalytic Activity Using HY-Zeolite and Pt / HY-Zeolite

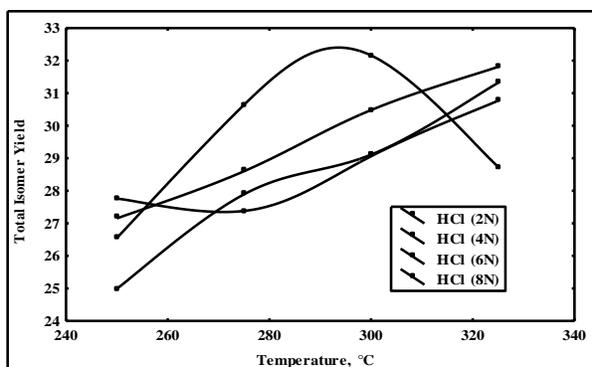


Fig. (4) Effect of Isomerization Temperature on the Catalytic Activity Using HCl-Pt / HY-Zeolite

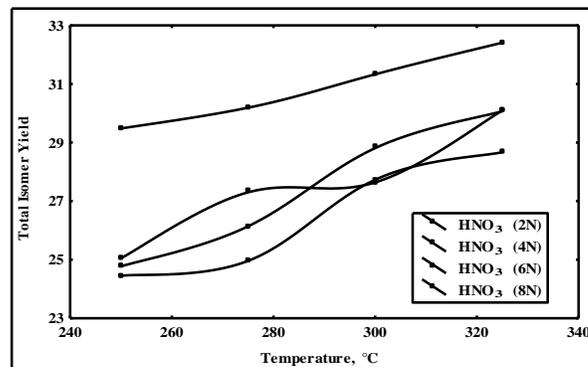


Fig. (5) Effect of Isomerization Temperature on the Catalytic Activity Using HNO₃-Pt / HY-Zeolite

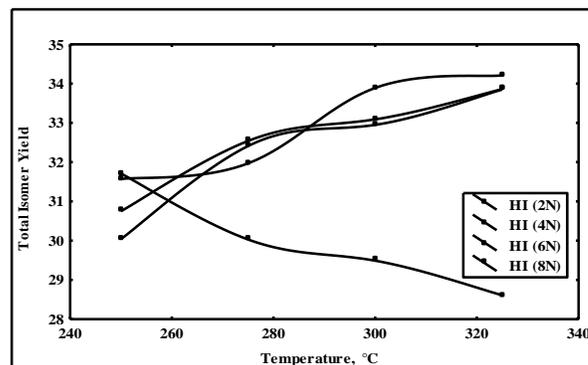


Fig. (6) Effect of Isomerization Temperature on the Catalytic Activity Using HI-Pt / HY-Zeolite

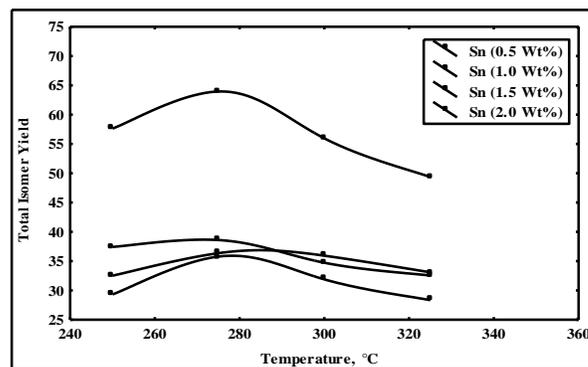


Fig. (7) Effect of Isomerization Temperature on the Catalytic Activity Using Sn-Pt / HY-Zeolite

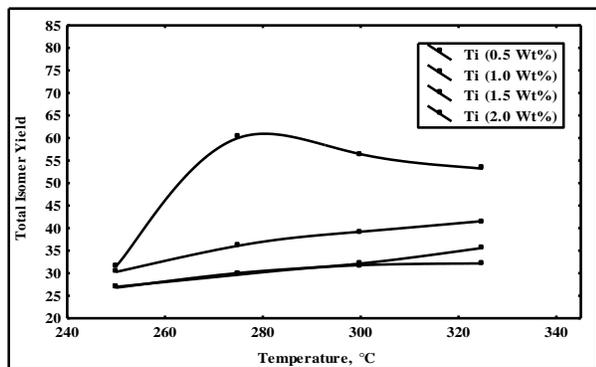


Fig. (8) Effect of Isomerization Temperature on the Catalytic Activity Using Ti-Pt / HY-Zeolite

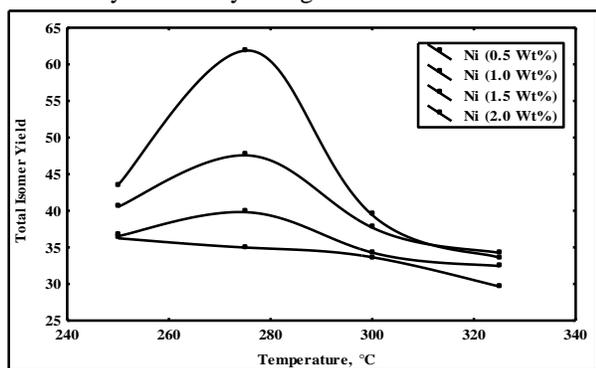


Fig. (9) Effect of Isomerization Temperature on the Catalytic Activity Using Ni-Pt / HY-Zeolite

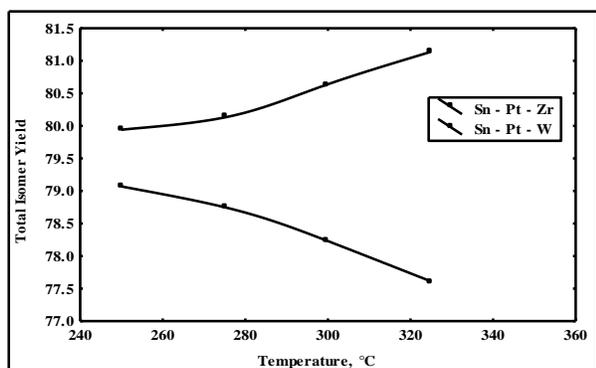


Fig. (10) Effect of Isomerization Temperature on the Catalytic Activity Using Co promoters Catalysts

Conclusions

1. HI promoter enhances the catalytic activity higher than HCl and HNO₃ promoters.
2. The metal promoters varied in increasing of catalytic activity and addition of Sn promoter gives higher activity (63.95% yield) than Ni and Ti.
3. The temperature 275° C gives the higher isomerization activity (the higher isomer yield) for metal sites promoters.

4. The addition of promoters have an important influence on the catalytic activity (total isomer yield) of isomerization of n-hexane reaction, and this influence is varied from one type of promoters to another.
5. The enhancement of isomerization activity at 275° C take the order:
6. Co-metal promoters > Metallic promoters > Acidic promoters (maximum yield 81.14% vol.) (maximum yield 63.95% vol.) (yield 29.98% vol.)

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