

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.

Decationized HY-zeolite was prepared by treating Na Y-zeolite with solution of 4N ammonium chloride through ion exchange, drying at 110°C , and calcination initially at 150°C and the temperature increased to 525°C with a rate of $75^\circ\text{C}/\text{h}$ to liberate NH_3 and water. Then, HY-zeolite was reduced with hydrogen at 380°C , then fabricated as a spherical shape and calcined at 400°C .

A 0.5 wt % Pt/HY-zeolite catalyst was prepared by impregnation with chloroplatinic acid. The catalyst was dried at 110°C over night, calcined at 400°C and reduced with hydrogen at 380°C . The prepared catalyst powder was then formulated as a spherical shape with 20% sodium silicate.

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. The catalysts were then dried, calcined, reduced and formulated using the same steps in preparation of Pt/HY-zeolite catalyst.

تأثير المنشطات على فعالية العامل المساعد المستخدم في عملية

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الخلاصة

إن الزيولايت المتبلور والمسمى نوع Y الذي تكون فيه النسبة المولية من السيلكا إلى الألومينا ($\text{SiO}_2/\text{Al}_2\text{O}_3$) تساوي خمسة، قد تم استخدامه كإداة أولية لتحضير العوامل المساعدة المستخدمة في عملية الأزمنة .

إن الزيولايت الخالي من الكاتيونات (HY) قد تم تحضيره عن طريق الاستبدال الأيوني لأيون الصوديوم من الزيولايت (NaY) بعملية التبادل الأيوني مع محلول كلوريد الأمونيوم ذو تركيز 4 عياري لمدة 24 ساعة ومن ثم جفف بدرجة حرارة 110°C ، وصلب ابتداءً بدرجة حرارة 150°C وتم زيادتها تدريجياً إلى 525°C وبمعدل $75^\circ\text{C}/\text{h}$ لساعة لتحرير الأمونيا NH_3 والماء . بعد ذلك تم اختزال الزيولايت (HY) بالهيدروجين عند درجة حرارة 380°C . 0.5% نسبة وزنية من البلاتين المحمل على الزيولايت الخالي من الكاتيونات (Pt/HY-zeolite) قد حضر بطريقة التشبع مع حامض الهيدروكلوريك . جفف العامل المساعد بدرجة حرارة 110°C لمدة 24 ساعة ثم صلب بدرجة حرارة 400°C وتمت اختزاله بالهيدروجين عند درجة حرارة 380°C . بعد ذلك تم تشكيل مسحوق العامل المساعد بشكل كروي باستخدام 20% من سيليكات الصوديوم كإداة رابطة .

الزيولايت الخالي من الكاتيونات عمل بمحامض الهيدروكلوريك وحامض النتريك وحامض يوديد الهيدروجين كعوامل منشطة باستخدام عيارات مختلفة وكذلك عمل مع تراكيز مختلفة من القصدير والتيتانيوم والنيكل كعوامل منشطة أخرى بطريقة التشبع للحصول على عوامل مساعدة ذات منشطات حامضية وقاعدية على الترتيب . 0.5% نسبة وزنية من البلاتين أضيف إلى العوامل المساعدة المشار إليها أعلاه بطريقة التشبع أيضاً . تمت بعد ذلك تجفيف العوامل المساعدة وتصلبها واختزالها وتشكيلها باستخدام نفس الخطوات التي أتت في تحضير البلاتين المحمل على الزيولايت (Pt/HY-zeolite).

1. 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^(2,3), pentane to isopentane^(4,5,6), and naphtha or normal hexane fractions into a higher octane number gasoline. In these process aluminum chloride is used with anhydrous hydrochloric acid as a liquid slurry or complex⁽²⁾, on a granular alumina or bauxite support^(4,3) and dissolved in molten antimony trichloride.⁽⁵⁾ In all processes the feed must be dried so that moisture is not carried into the acid zone, but corrosion may be severe.⁽⁶⁾

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⁽⁷⁾.

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^(8, 1).

The aim of this investigation is studying the effect of different catalysts types of promoters on the n-hexane isomerization catalytic activity of Pt/HY-zeolite catalyst.

2. Experimental Work

Feed Stock

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

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

Catalyst Preparation:

Preparation of HY-zeolite

A 25 g of NaY-zeolite was slurried in 0.5 l of 4N ammonium chloride 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. 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 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.

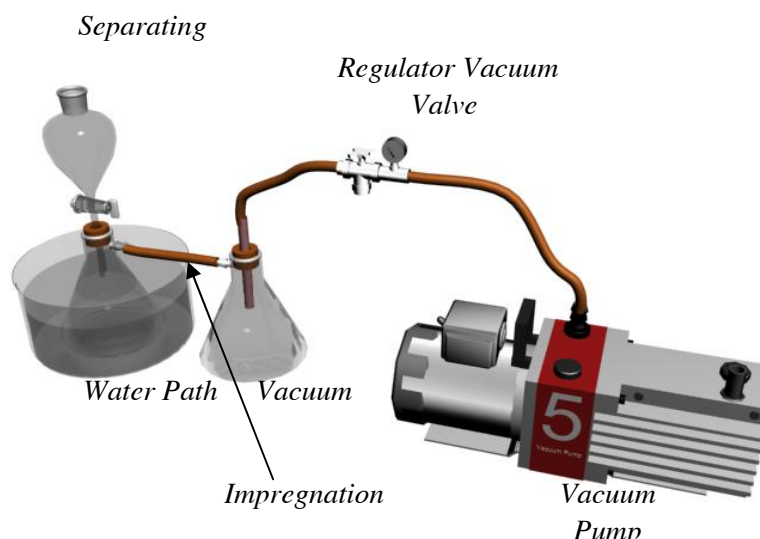


Fig. 1. Impregnation Apparatus.

A 1.3688 g of HCl was mixed with a solution of 0.3125 g of chloroplatinic acid (H_2PtCl_6) 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 platinumic 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, HNO_3 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, HNO_3 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 SnCl_4 , TiCl_2 and NiCl_4 in different quantities of decationized water. The impregnation process was accompanied with shaking for 4

hours⁽²⁰⁾ at mixed temperature of 20°C⁽¹⁷⁾. 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 H_2PtCl_6 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 unit consists of heater storage, reactor, chiller and condenser.

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.

3. Results and Discussion

3.1 Comparison between HY-Zeolite and Pt/HY-Zeolite Catalysts

Figure 2 shows the effect of temperatures on the isomerization activity (total isomer yield) using HY-zeolite catalyst, and the effect of temperature on the isomerization activity using 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 has three steps, n-paraffin's is dehydrogenated to n-olefins which occurs on the metal sites, n-olefins isomerize to iso-olefins which occurs on the acid sites and of iso-olefins hydrogenated to isoparaffin which occurs 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⁾.

Also both figures show that as temperature increases the rate of isomerization reactions increases too.

3.2 Effect of Acidic Promoters on the Catalytic Activity

Figures (3) to (5) show that the effect of temperature on the isomerization activity at different acid promoter concentrations and on 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; and with increasing the concentration of the acid promoters. This may be due to the active acid sites on which 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 3 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⁽¹⁷⁾.

It's clearly shown from figures 3 to 5 that are 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 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.

3.3 Effect of Metal Promoters on the Catalytic Activity

Figures 6 to 8 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 increases after addition of metal promoters. Also these figures show that the increasing in temperature increases the catalytic activity then the activity begin to decreases exception figures some curves in 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⁽¹⁴⁾.

Higher activity was obtained with Sn promoter. This may be due to Ni and Ti mild hydrogenation/dehydrogenation activity, while Sn has strong hydrogenation activity⁽²¹⁾.

3.4 Effect of Co-Metal Promoters on the Catalytic Activity

Figure 9 shows the effect of temperature on the isomerization activity using co-metal promoters supported on HY-zeolite. This figure 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 the hydrogenation/dehydrogenation metal function of the catalyst.

These figures also show that the activity increases with increasing the reaction temperature, and the W promoted catalyst gives higher isomer yield than Zr promoted catalyst.

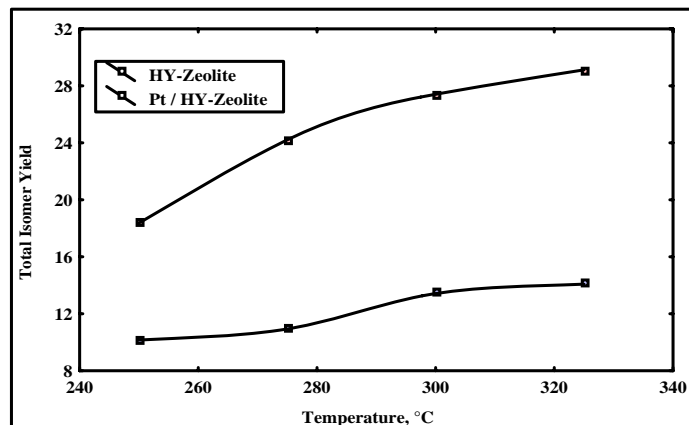


Fig. 2. Effect of Isomerization Temperature on the Catalytic Activity Using HY-Zeolite and Pt / HY-Zeolite

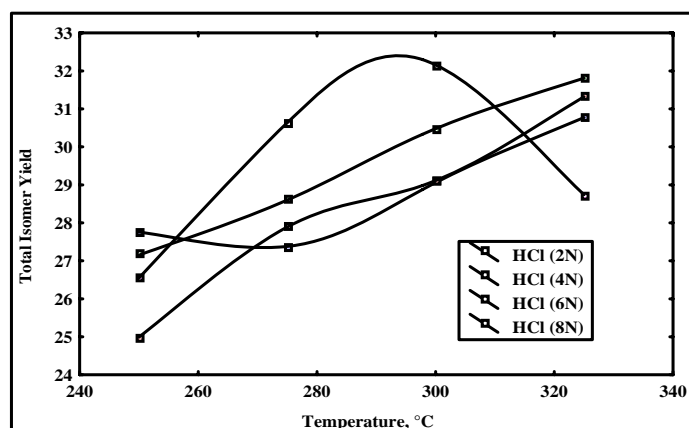


Fig. 3. Effect of Isomerization Temperature on the Catalytic Activity Using HCl-Pt / HY-Zeolite.

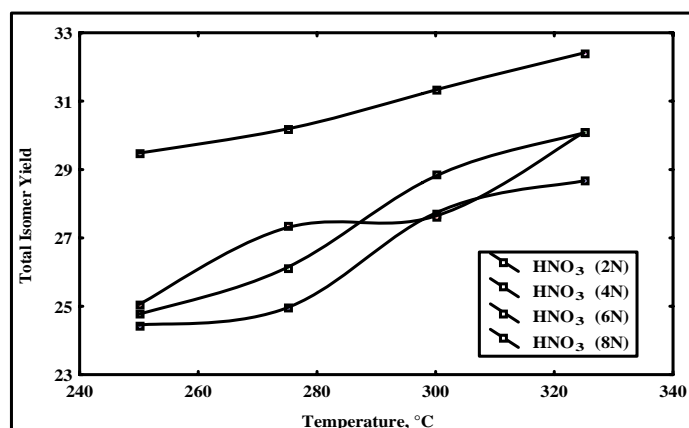


Fig. 4. Effect of Isomerization Temperature on the Catalytic Activity Using HNO₃-Pt / HY-Zeolite.

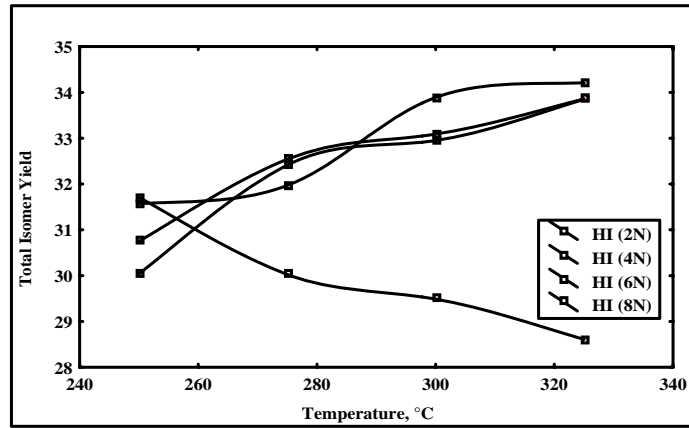


Fig. 5. Effect of Isomerization Temperature on the Catalytic Activity Using HI-Pt / HY-Zeolite.

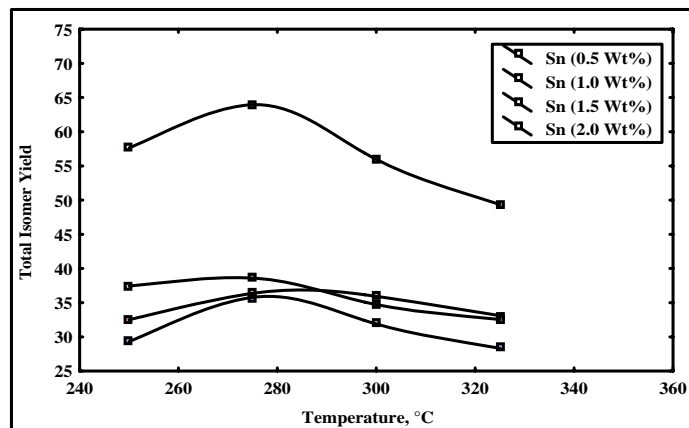


Fig. 6. Effect of Isomerization Temperature on the Catalytic Activity Using Sn-Pt / HY-Zeolite.

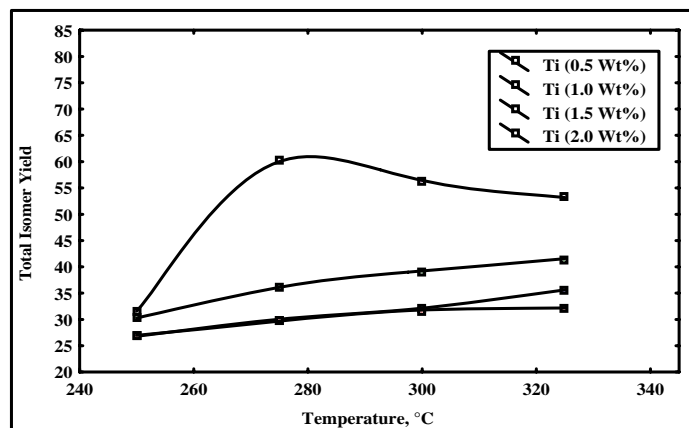


Fig. (7) Effect of Isomerization Temperature on the Catalytic Activity Using Ti-Pt / HY-Zeolite

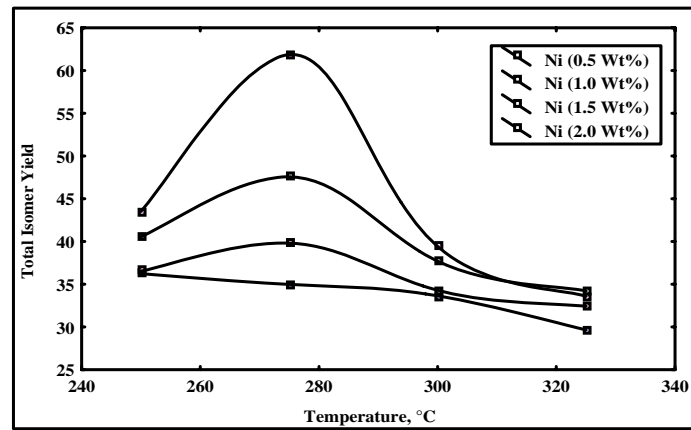


Fig. 8. Effect of Isomerization Temperature on the Catalytic Activity Using Ni-Pt / HY-Zeolite.

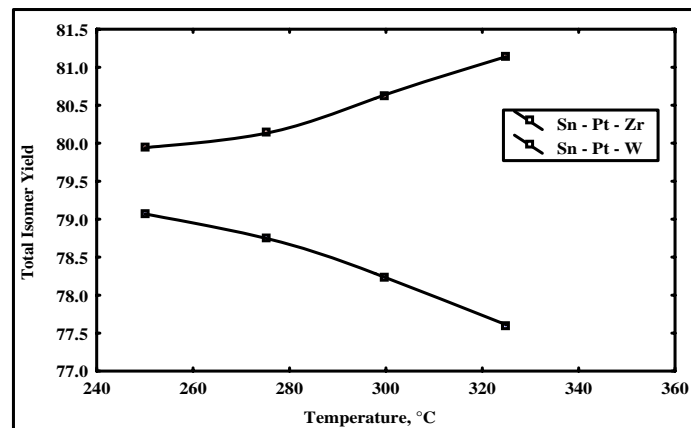


Fig. (9) Effect of Isomerization Temperature on the Catalytic Activity Using Co promoters Catalysts.

4. 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 than Ni and Ti.
3. The temperature 275°C gives the higher isomerization activity (the best 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 different from one type of promoters to another.

The enhancement of isomerization activity take the order:

Co-Metal promoters > Metallic promoters > Acidic promoters
 (81.14% vol.) (63.95% vol.) (29.98% vol.)

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