EFFECT OF ZRO_2 , WO_3 ADDITIVES ON CATALYTIC PERFORMANCE OF PT/HY ZEOLITE COMPARED WITH PT/Γ-AL_2O_3 FOR IRAQI NAPHTHA TRANSFORMATION

Maha Al-Hassany
Asst. lecturer/ Chemical Engineering Department/
College of Engineering/ University of Baghdad

ABSTRACT

Light naphtha treatment was achieved over 0.3wt%Pt loaded-alumina, HY-zeolite and Zr/W/HY-zeolite catalysts at temperature rang of 240-370°C, hydrogen to hydrocarbon mole ratio of 1-4 0.75-3 wt/wt/hr, liquid hourly space velocity (LHSV) and at atmospheric pressure.

The hydroconversion of light naphtha over Pt loaded catalyst shows two main reactions; hydrocracking and hydroisomerization reactions. The catalytic conversion of a light naphtha is greatly influenced by reaction temperature, LHSV, and catalyst function. Naphtha transformation (hyroisomerization, cracking and aromatization) increases with decreasing LHSV and increasing temperature except hydroisomerization activity increases with increasing of temperature till 300°C then began to decrease due to the formation of hydrocracking reaction. The investigation of Pt containing catalysts under study shows a very high hydrogenlysis activity , due to presence of metal component (i.e. Zr, W) which enhances the rate of paraffin isomerization and cracking.The hyroisomerization and the hydrocraking activities can be arranged as follows,.

Pt/Zr/W/HY > Pt/HY > Pt/γ-Al_2O_3

The results showed that, Pt/γ-Al_2O_3 has higher activity for the direct dehydrogenation of C_6 and C_7 paraffin's present in naphtha to aromatics than Pt/HY and Pt/Zr/W/HY. This was due to pore volume catalyst ,the aromatics compounds increased as the pore volume increased.

الخلاصة

في هذا البحث تم دراسة تأثير إضافة الزركونيوم و التانكستن على حفاز البلاتين المحمل بالزيولايت و مقارنته بالالومينا للنفثا درس تحول النفثا على حفازات محتوية على بلاتين، زركونيوم، تانكستن محملة على زيولايت و بلاتين محمل على الالومينا بين درجات حرارة من 240-370درجة مؤية و معدلات سرع فراغية 0.75-3 و نسبة الهيدروجين الى النفثا من 1-4 نسبة مولية . وجد ان هناك تفاعلين أساسيين لتحولات النفثا و هي التكسير و الأزمرة و التي بدورها تتاثر بدورها بدرجة الحرارة و السرع الفراغية . اظهرت النتائج ان تحول النفثا يزداد بقلة السرع الفراغية و زيادة درجة الحرارة وجد إن تحولات المركبات مثل البنتان الهكسان العاديان الى المتشابهات الاكثر تشبعا تزداد بزيادة درجة الحرارة لحد 300 درجة مؤية ثم تبدا هذه التحولات بالنقصان بسبب تاثير تحولات التكسير و قد وجدت برافينات الهكسان و الهبتان صعوبة في التحول الى مركبات عطرية بواسطة حفاز البلاتين، زركونيوم، تانكستن المحمل على زيولايت اذا ما قورن بالحفاز بلاتين محمل على الومينا و ذلك بسبب حجم المسام حيث ان المركبات

الارماتية تزداد بزيادة حجم المسام.

INTRODUCTION

Octane number in gasoline is conventionally boosted by addition of aromatics and oxygenated compounds. However, as a result of increasingly stringent environmental legislation the content of these compounds in gasoline is to be reduced and thus industry has been forced to investigate alternative processes to reach the required octane levels (Rafael et al., 2008).

The gasoline pool composition affect it research octane number (RON). To increase the octane number of the light straight run naphtha, it must be isomerized and as a result RON increases. This increase is achieved by isomerizing n-pentane and n-hexane (the main component of (LSR) naphtha) to the corresponding isomers. (Srikant, 2003).

Isomerization reaction are commercially performed using bifunctional catalyst consisting of a metal support like alumina or HY zeolite. (Gauw et al., 2002). Bifunctional metal/acid zeolite catalysts are used in a various industrial process, viz., hydroisomerization of C_5-C_6 alkanes, hyrocracking, dewaxing etc. On these catalysts the alkanes transformation involves hydrogenation and dehydrogenation steps on the metallic sites, isomerization or cracking step on the acid sites and diffusion steps of the oleffinic intermediates from the acid to metallic sites and vice versa. That is why their activity, stability and selectivity depend on the characteristics of the acid and of the metallic sites, in particular on the balance between the acid and the hydrogenation functions, and on the characteristics of the zeolite pores (Alvarez, et al., 1996; Ward, 1999).

Many authours such as (Jeong et al., 1997 and Lawlor et al., 1998) show that, the maximum isomer yield is reached when the metal and acidic functions of the catalysts were balanced. Also show that Pt/HY has good activity and selectivity for naphtha isomerization at high reaction temperature. Therefore, tha main aim of the present work is to study the enhancement of catalytic performance by co-impregnation with Zr and W using 0.3wt%Pt/HY zeolite catalyst in order to obtain a maximum isomerization yield.

EXPERIMENTAL

- Catalyst preparation In this study three types of catalysts were used, and these catalysts are as follows:
- HY-zeolite (CBV 600) catalyst powder was supplied from zeolyst International Company and used as support for catalyst preparation.

- 100 gm of HY-zeolite powder was mixed with 30% montmorillonite clay as a binder. The resulting mixture was mixed with water to form a paste. An extrudates with 0.3cm×0.5cm were formulated and dried overnight at 100°C, then 0.3wt%Pt/HY zeolite was prepared by impregnation method with proper solution of hexachloropatinic acid containing of 0.1590 gm of hexachloropatinic acid and 8 ml deionized water for 20 gm catalyst . The impregnated extrudates were then dried at 110°C overnight then calcinated at 300°C for 3 hours in a furnace with dry air.

- WO_3/ZrO_2/Pt/HY catalyst was prepared by co-impregnation with proper solution of ammonium meta tungsten (Sigma Aldrich) and zirconium tetra chloride (BDH) and deionized water containing of 0.3880 gm zirconium tetra chloride and 0.8615 gm ammonium meta tungsten and deionized water till the volum of solution equal to pore volume of 40 gm (i.e.32 ml) of Pt/HY zeolite. The impregnated extrudates were then dried at 110°C overnight and calcinated at 700°C for 2 hours in a furnace with air.

- Pt/γ-Al_2O_3: commercial Pt/γ-Al_2O_3 supplied form Al- Dura refinery with surface area of 204 m^2/g, pore volume of 0.45 ml/g and density of 0.62 g/cm^3 was used as a support.

FEEDSTOCK

The feedstock used in hydroisomerization runs was light straight run (LSR) naphtha supplied from Dura rifinery and its properties listed in Table (1).

Table (1) Properties of LSR naphtha.

Composition	Wt%
i-C_4	1.5
n-C_4	3.8
i-C_5	4.9
n-C_5	4.7
i-C_6	8.5
n-C_6	41.6
Cyclo-C_6	5.7
i-C_7	4.9
n-C_7	5.8
Cyclo-C_7	8.7
n-C_8	3.2
Benzene	2.9
Toluene	3.8
API Sp. Gr. @ 60°/60°F	74.8

Some properties of prepared catalyst, and support are tabulated in Table (2).

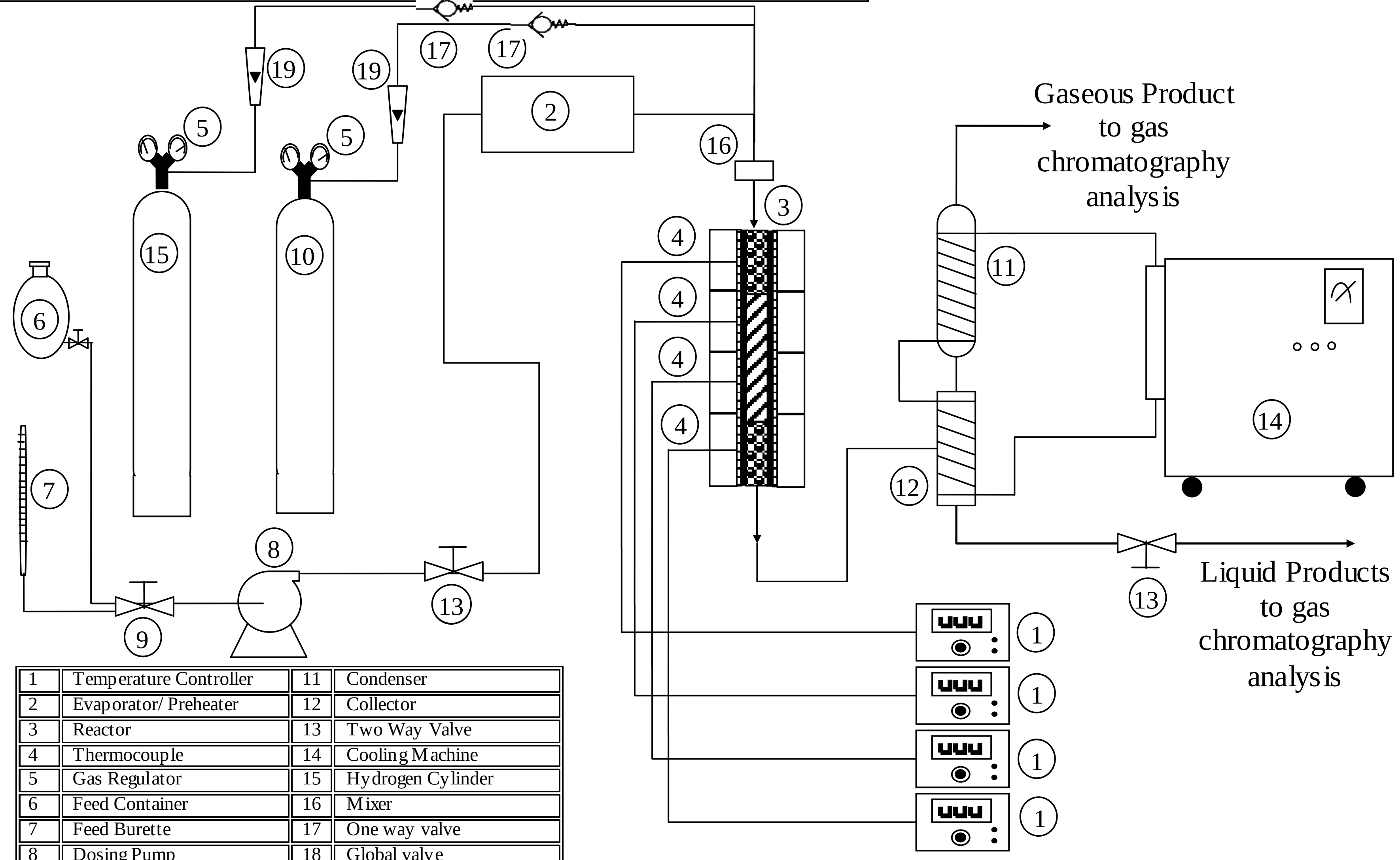
Table (2): Properties of prepared catalysts.

Catalyst	0.3wt%Pt/γ-Al_2O_3	0.3wt%Pt/HY zeolite	0.3wt%Pt/Zr/W/HY zeolite
Surface are, m^2/g	207	435.6	415.8
Bulk density, g/cm^3	0.62	0.466	0.488
Pore volume, cm^3/g	0.45	0.374	0.308

CATALYTIC ACTIVITY TEST

The catalytic activity test was achieved in a continuous down flow fixed-bed reactor. The reactor was carbon steel tube with an outside diameter of 1.9 cm, 2mm thick and 80 cm long.Fig.1 shows the process flow diagram. The platinum containing catalysts were reduced with H_2 at 350°C for 3 hr (Masologites and George, 1987 and Jan-Ku, et al., 1988).

The catalytic reaction were carried out with LHSV of 1-4 h^{-1}, at temperature range of (240-370°C), hydrogen to feed mole ratio of 1-4 and at atmospheric pressure. Liquid products were trapped by condenser at -10°C. Sample were collected periodically and analyzed by gas chromatography. The gas chromatography model 438 Aa-VSA, supplied by Agilent Technologies Company. This devised equipped with capillary column of 0.25mm diameter, 100m length and packed with CP-SIL-SCB and FID detector.



1	Temperature Controller	11	Condenser
2	Evaporator/ Preheater	12	Collector
3	Reactor	13	Two Way Valve
4	Thermocouple	14	Cooling Machine
5	Gas Regulator	15	Hydrogen Cylinder
6	Feed Container	16	Mixer
7	Feed Burette	17	One way valve
8	Dosing Pump	18	Global valve
9	Three Way Valve	19	Gas Rotameter
10	Nitrogen Cylinder		

Fig. 4.3, Flow diagram of the **continuous laboratory reaction unit**.

RESULTS AND DISCUSSION

In the present work ,the hydroconversion of light naphtha feedstock on the catalyst shows two essential reactions; hydrocracking and hydroisomerization. Other reactions, such as cyclization and aromatization were significantly different with all three catalysts.

Cracking activity

The results shown in Figs 2-5 that a certain amount of cracking products with the amount formation of C_1-C_4 were obtained between 240-350°C reaction temperature and LHSV of 0.75-3 h^{-1}. It can be clearly show that the amount formation of C_1-C_4 products are the lowest for Pt/γ-Al_2O_3 and highest for Zr/W/Pt/HY zeolite, throughout all experiments. The cracking yields are increased by increasing temperature and decreasing LHSV for all catalysts but are still the lower for Pt/γ-Al_2O_3 therefore; the cracking activity sequence can be arranged as follows:

$$Zr/W/Pt/HY > Pt/HY > Pt/\gamma\text{-}Al_2O_3$$

The increasing of transformation of naphtha on Zr/W/Pt/HY may be due to slightly enhancement of acid sites. According to Table 2, the pore volume of Zr/W/Pt/HY is lower than other catalysts. A decreases in a pore volume leads to increasing in ΔH_{ads}. An increase in ΔH_{ads} indicates of increasing of surface coverage, resulting in an increase in the number of molecules available for reation. Such explication are agree with Eder et al., 1997.

The results indicate that the low LHSV is favored for high conversion of naphtha, this means that increasing the residence time, which offer a plenty of contact time of feedstock to react on the catalyst (Jolly et al., 1999).

The change in the number and the strength of acid sites on Zr/W/Pt/HY is directly affects the state of the metal sites (Yan Liu et al., 2006). The combination of these two parameters influences the cracking activity due to the presence of metal component which enhance the rate of paraffin isomerization and cracking; paraffin can be dehydrogenated on a metal site and the resultant alkenes are much easier crack or isomerized depending on the acid strength of the catalysts.

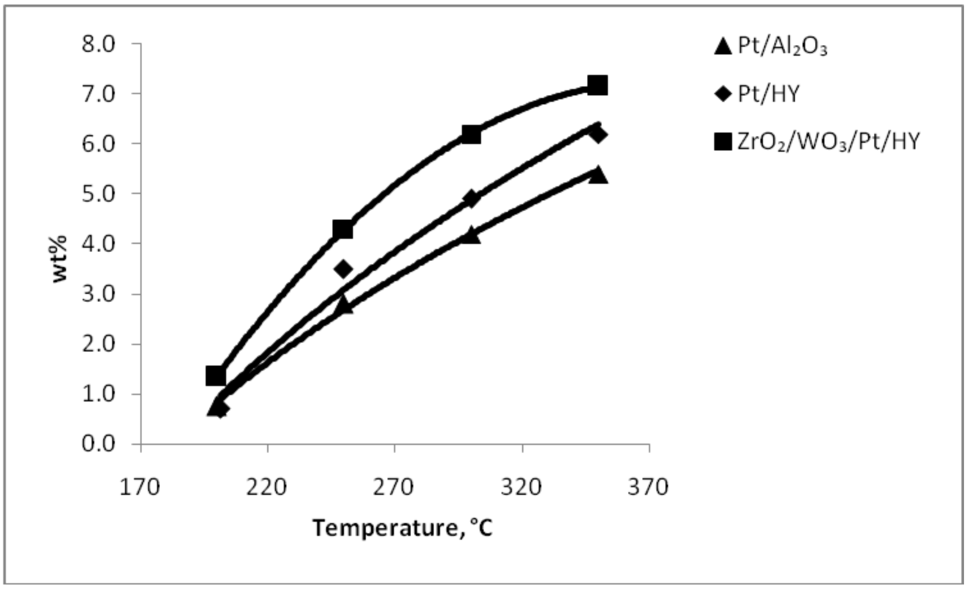


Fig.2, The effect of temperature on hydrocracking product at LHSV=0.75 h^{-1}.

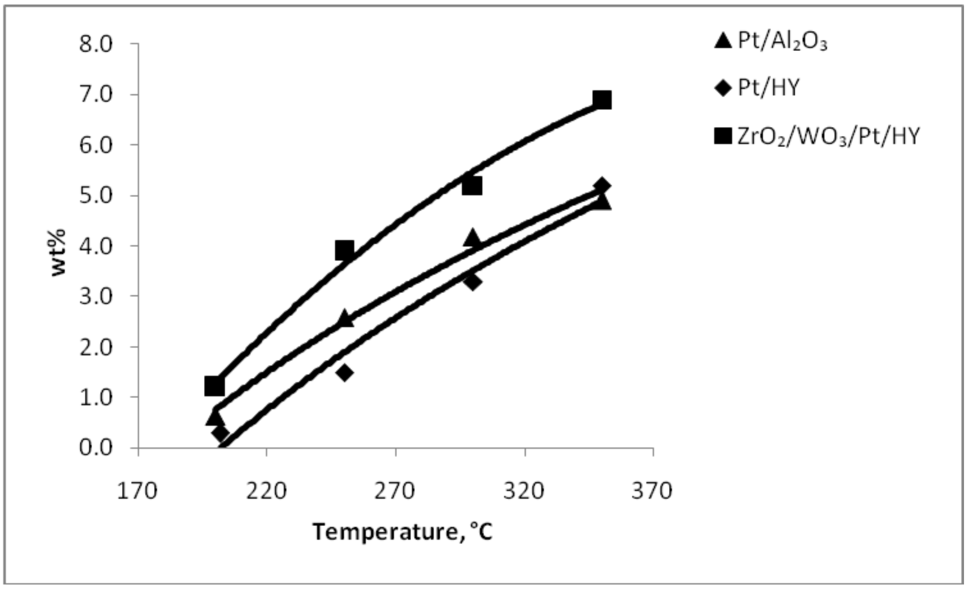


Fig.3, The effect of temperature on hydrocracking product at LHSV=1 h^{-1}.

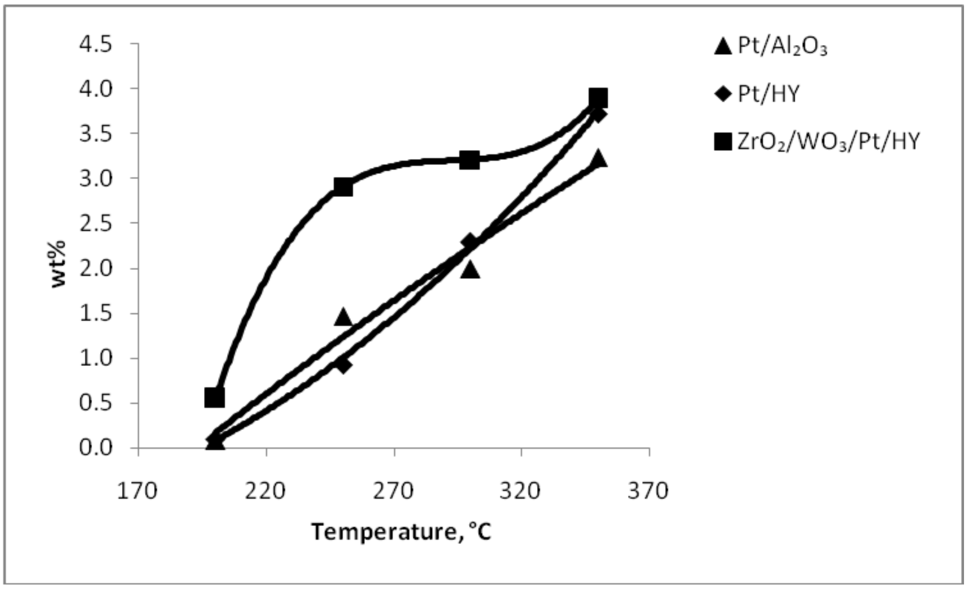


Fig.4, The effect of temperature on hydrocracking product at LHSV=2 h^{-1}.

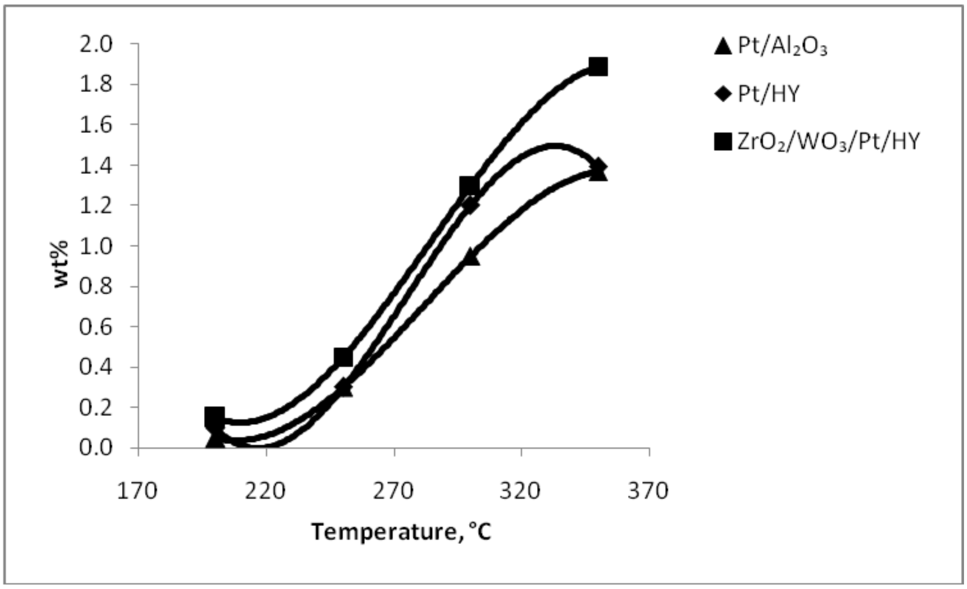


Fig.5, The effect of temperature on hydrocracking product at LHSV=3 h^{-1}.

HYDROISOMERIZATION ACTIVITY

The hydroisomerization of light naphtha over Pt loaded catalyst types is influenced by the LHSV, reaction temperature and the support base, as shown in Figs.6-9. All results indicate that, the low LHSV is favored for hydroisomerization of naphtha as discussed previously. Also the results show a remarkable rise in an isomerization activity, for all the tested catalyst and as the temperature raises till 300°C, and then isomerization activity began to decrease due to the cracking activity.

Since isomerization reaction is slightly exothermic, a low temperature favors the production of light naphtha isomers with high octane level. The data illustrated in a Table 2 and Figs. 6-9 indicate that Pt/ Zr/W/ HY zeolite produced the highest light naphtha isoparaffins through the temperature range 240-370°C as a compared to the other catalysts.

It is will known that HY zeolite has much stronger acidity than amorphous alumina, by the fact that the production of carbenium ion is energetically favored over that of carbonium ions. At higher temperature, i.e. above 300°C, the formation of carbonium is much faster than the carbenium ion and lead to the formation cracked product at the dehydrogenated site. That due to the fact of cracking reaction are endothermic, so a high temperature favors the production of cracked hydrocarbon (Gluseppe et al.,1986).

At a high temperature operation (>300°C) and from analogy to liquid phase, super acid chemistry, the monomolecular or protolytic cracking mechanism was originally proposed to proceed through a non-classical, penta-coordinated carbonium ion resulting from the proton attack of C-C or C-H bonds. Recent compulational and experimental of studies have suggested a distorted, strongly surface-coordinated transition state as opposed to a stable, carbonium ion intermediate. This perhaps explains why carbonium ions have not been directly observed in a zeolite. Monomolecular cracking become important under the limiting conditions of very low alkene coverage which implies high temperature, low partial pressure and low conversion of naphtha. (Hello et al., 2002) and (Willimas et al., 2000).

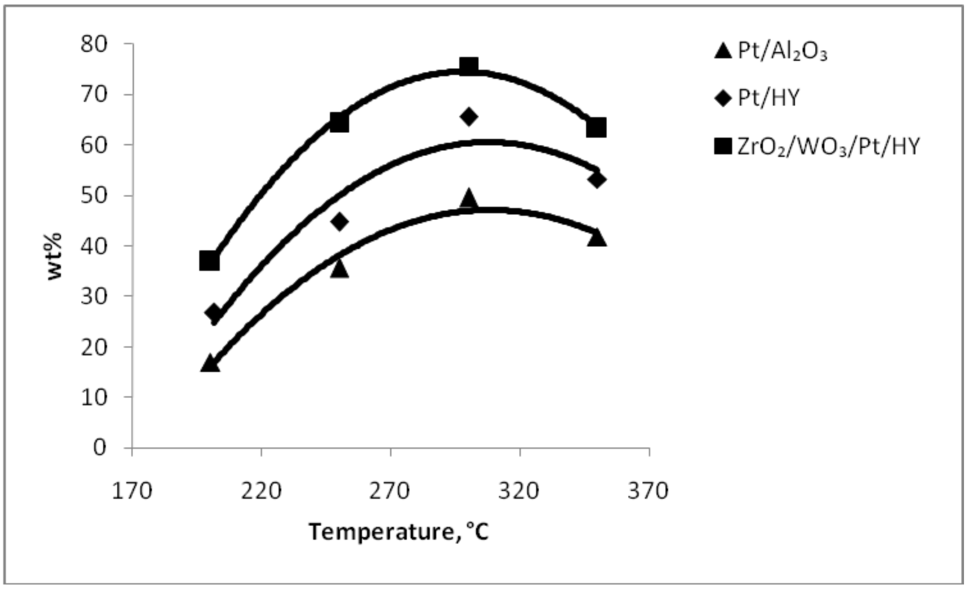


Fig.6, Isomers yield versus reaction temperature at LHSV=0.75 h^{-1}.

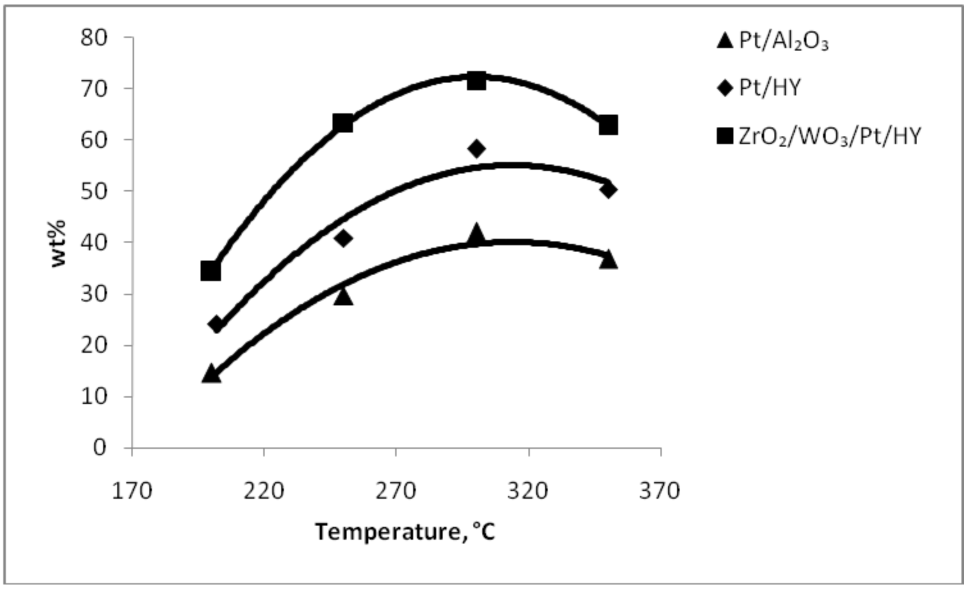


Fig.7, Isomers yield versus reaction temperature at LHSV=1 h^{-1}.

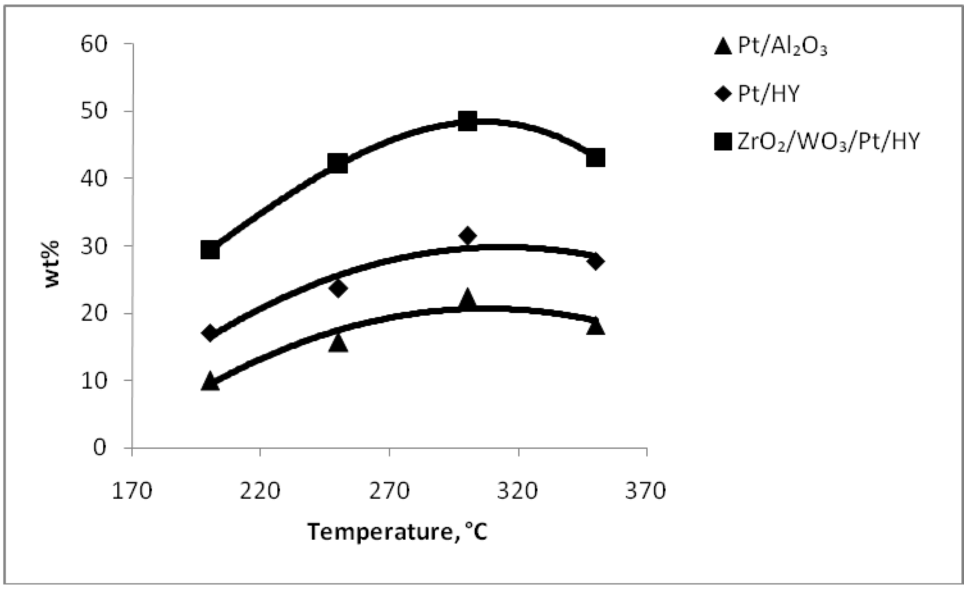


Fig.8, Isomers yield versus reaction temperature at LHSV=2 h^{-1}.

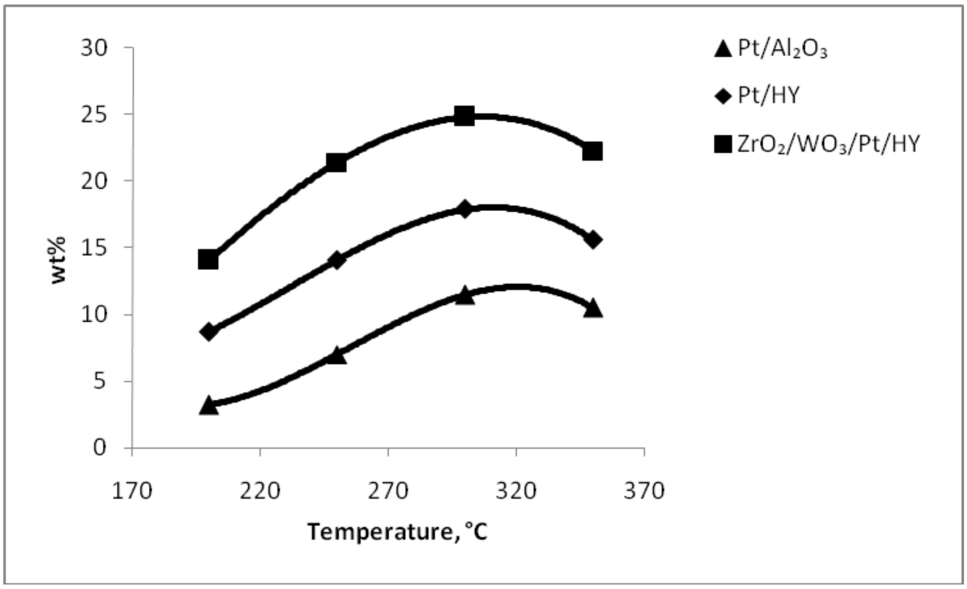


Fig.9, Isomers yield versus reaction temperature at LHSV=3 h^{-1}.

HYDROCYCLIZATION AND AROMATIZATION ACTIVITIES

It is well known that Pt/γ-Al_2O_3 has higher activity for the direct dehydrogenation of naphthenes to benzene than Pt/HY catalyst as shown in the figs 10-17. The production of benzene by the enlargement of C_5 cyclic ring to a C_6 cyclic ring.

The kinetic diameter of hexane is 4.8 Å, with an increase of about 0.7 Å for every additional increase in branch length, the kinetic diameters of benzene and cyclohexane are 6.75 and 6.9 Å respectively (Jan Ku et al., 1988). The fact that the hydrocarbons have a kinetic diameter greater than half the effective pore diameter of Zr/W/Pt/HY and Pt/HY as shown in Table 2 implies that any strongly adsorbed C_6 would create a barrier to diffusion of other C_6 .Thus strongly adsorbed C_6 cyclic can induce resistance to the mass transfer of a n-hexane to the pore interior, resulting in an induced pore blockage. With the Zr/W/Pt/HY and Pt/HY zeolite catalysts, an initial increase in a catalyst activity can be observed after 3 hours reaction, the activity is very stable (are practically identical before and after the various changes in operating conditions). While the Pt/γ-Al_2O_3 bed appears white at the inlet and increasingly dark colored, indicating coke formations, toward the reactor exit.

It was found that Zr/W/Pt/HY and Pt/HY stimulate to a much higher extent than Pt/γ-Al_2O_3, the skeletal isomerization reaction of C_5/C_6 and in a lower extent the production of benzene by enlargement of C_5 cyclic ring to a C_6 cyclic ring. In contrast, Pt/γ-Al_2O_3 enhances to a greater extent the direct dehydrogenation of C_6 to benzene than the other catalysts (Mohamed and Ahmed, 2004),

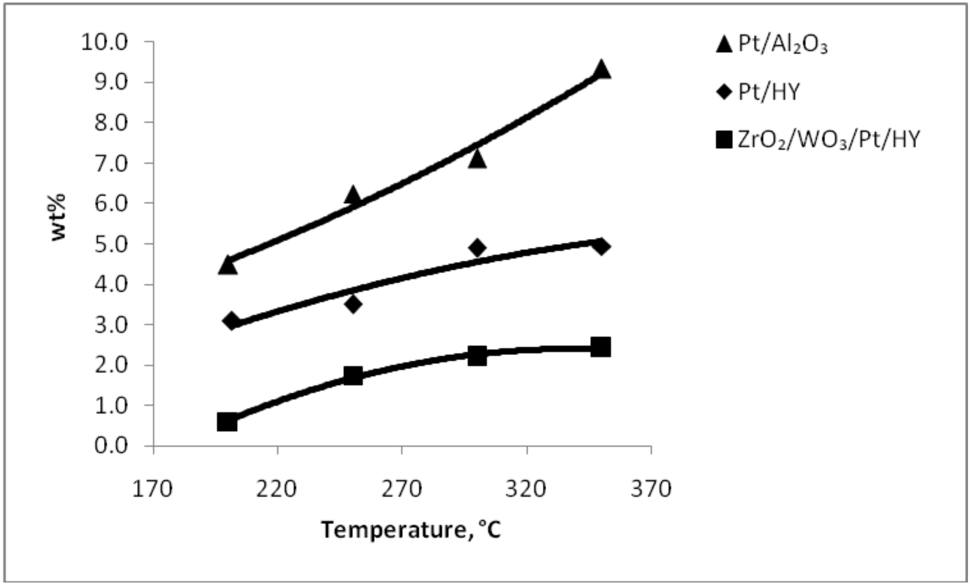


Fig.10, Percent of hydrocyclization products versus reaction temperature at LHSV=0.75 h^{-1}.

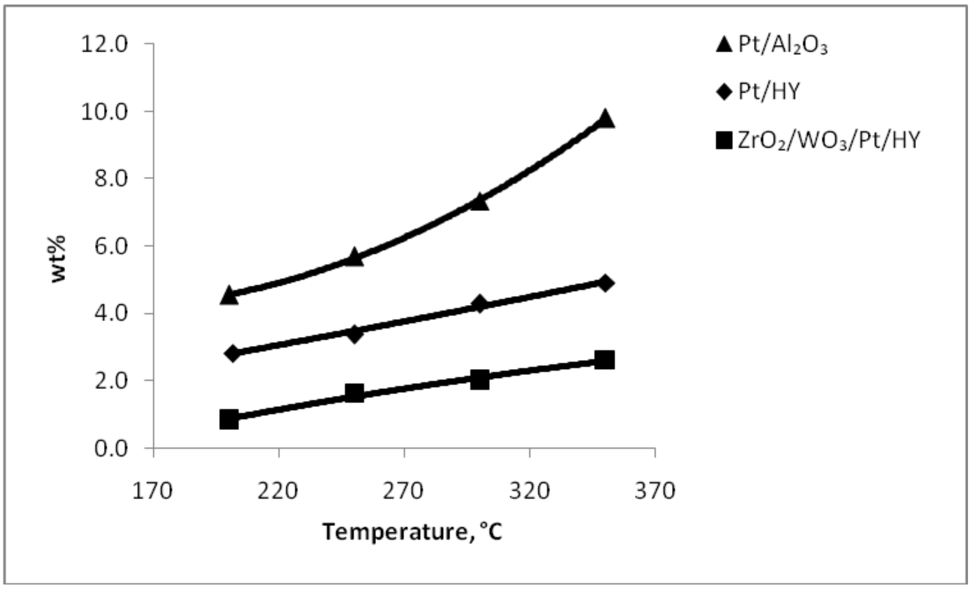


Fig.11, Percent of hydrocyclization products versus reaction temperature at LHSV=1 h^{-1}.

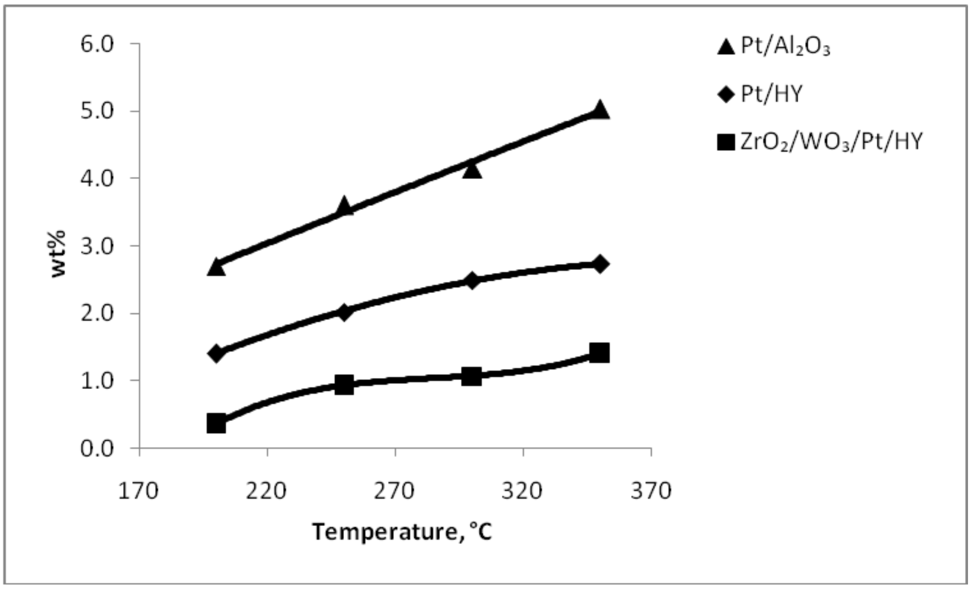


Fig.12, Percent of hydrocyclization products versus reaction temperature at LHSV=2 h^{-1}.

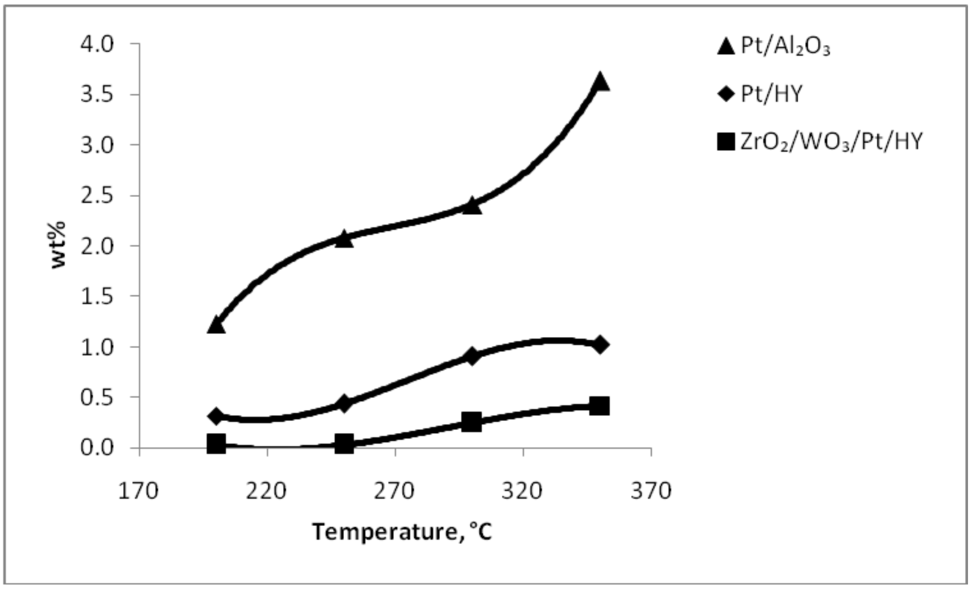


Fig.13, Percent of hydrocyclization products versus reaction temperature at LHSV=3 h^{-1}.

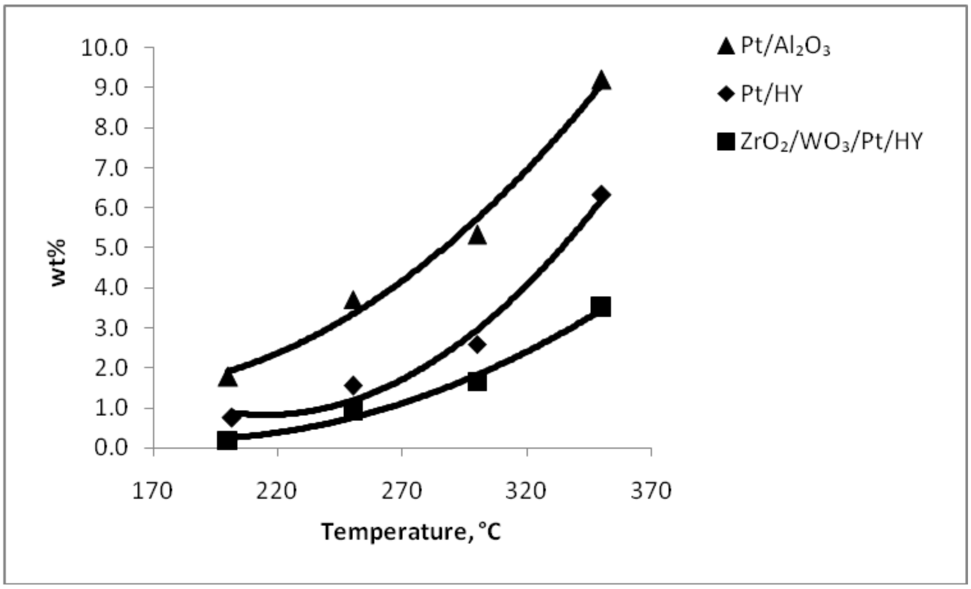


Fig.14, Percent of aromatics versus reaction temperature at LHSV=0.75 h^{-1}.

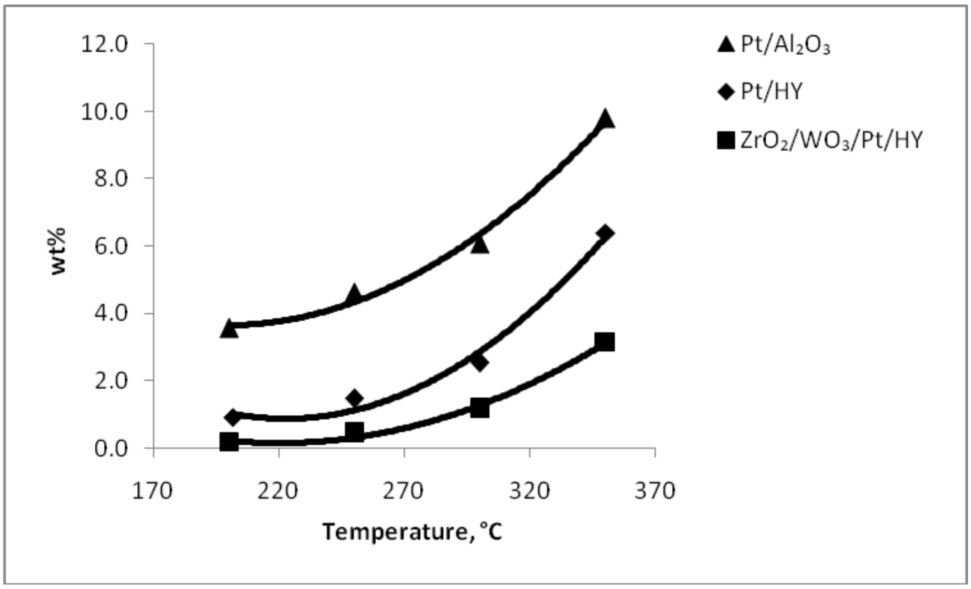


Fig.15, Percent of aromatics products versus reaction temperature at LHSV=1 h^{-1}.

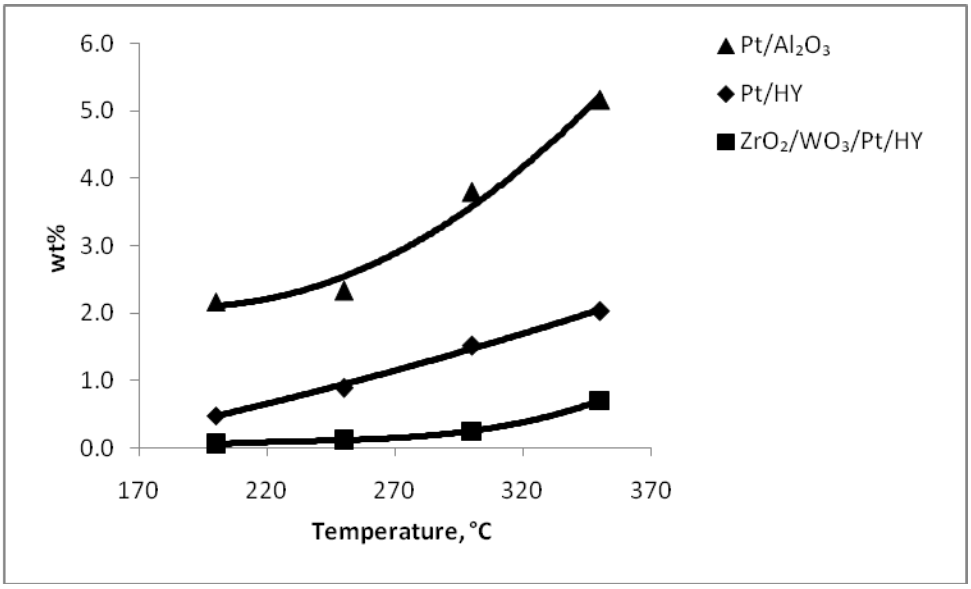


Fig.16, Percent of aromatics products versus reaction temperature at LHSV=2 h^{-1}.

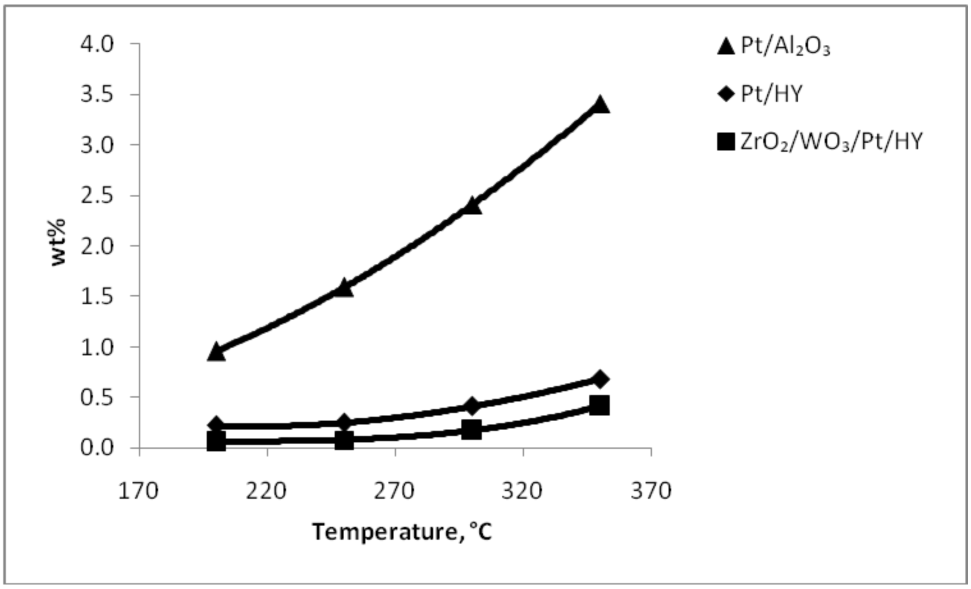


Fig.17, Percent of aromatics products versus reaction temperature at LHSV=3 h^{-1}.

CONCLUSION

It is found that Pt/Zr/W/HY is the best catalyst for producing isoparffines due to its higher acidity compared with Pt/HY and Pt/ γ-Al_2O_3 .The Pt/Zr/W/HY catalyst showed lower activity for aromatization of naphtha to cyclopareffins and benzene selectivity than Pt/HY and Pt/ γ-Al_2O_3 due to their pore volume.

A smaller pore volume leads to lower aromatization activity and higher isomerization and cracking activity.

The maximum isoparaffins extent was achieved and reached 78% at 300°C and LHSV of 0.75 hr^{-1} on Pt/Zr/HY and aromatics extent was reached 10% at 370°C and LHSV of 0.75 hr^{-1} on Pt/ γ-Al_2O_3.

REFERENCES

- Alvarez F., F.R.Ribeiro, G.Perot, Thomazeau, and M.Guisnet, 1996, “Hydroisomerization and hydrocracking of alkanes” , J.cat., 162, 174-180.
- Eder F., Stockenhuber M., Lercher J.A.,1997 , "On the role of pore size and tortuosity for sorption of alkanes in molecular sieves ", J. Phys. Chem. B: 101, 5411-5419 .
- Gauw F.J.M., Grandell J., Santen R.A., 2002, “The intrinsic kinetics of n-hexane isomerization catalyzed by Pt loaded solid acid catalyst”**,** J. Cat. 206, 295-304.
- Gluseppe E. Glannetto, Guy R. Perot, and Michel R. Gulenet, 1986, “Hydroisomerization and hydrocracking of n-alkanes.1. Ideal hydroisomerization PtHY catalysts”, Ind. Eng. Chem. Prod. Res. Dev., 25, 481-490.
- Hollo, J. Hancsok, D. Kallo, 2002, “Kinetics of hydroisomerizaion of C_5-C_7 alkanes and their mixture over platinum containing mordenite” A Applied Cat. A: General, 229, 93-102.
- Jan-Ku, Chen, A.M. Martin, Young Gull Kim and Vijay T. John, 1988, “*Mechanical study of isomerization of n-hexane”, Ind. Eng.* 27, 401-409.
- Jeong Kyu Lee, Hyun-ku Rhee, 1997, “Characteristics of Pt/HY-beta and Pt/H-mordenite catalyst for the isomerization of n-alkane”, Catalyst Today, 38, 235-242.
- Jolly, J.Saussey, M. Bettahar, J.C. Lavalley, 1997, “Reaction mechanisms and kinetics in n-hexane cracking”, 156, 71-96.
- Lawlor, Lawrence J., Marphy, William J., 1988, “Naphtha isomerization using a medium”, US patent, 4734539.
- Masologites., George,1987, “Method of treating a used Pt group alumina catalyst with a metal promoter”, US patent, 4070306.
- Mohamed L, Kh. and Ahmed H.S., 2004, “Isomerization of light over Pt containing support”, Egypt J. chem. 47, 3, 293-303.
- Rafael Roldan, Anderew M. Beale, Manuel S. S., Francisco., Romero, Cesar, Juan P., Gopinathan,2008, “Effect of the impreantion order on the nature of the metal particles”, J. Cat., 254 ,12-26.
- Srikant Gopal, 2003, “Synthesis, Modification, Characterization and catalytic study of zeolite” Ph.D. Thesis, university of cininnati.
- Ward, J.W.,1993,”Fuel Process Technol”,35,55.
- Williams B.A, W. Ji, Miller, Snurr, 2000, “Evidence of a different reaction mechanisms during the cracking of n-hexane” Applied Cat. A: General, 203,179-190.

- Yan Liu,Yejun Guan,Can Li, Juan L.,Geok J., Eng Chew, Fethi K.,2006,"Effect of ZnO additives and acid treatment on catalytic performance of Pt/W/Zr for heptane isomerization,"J. of cat.244,17-23.