IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.8 No.3 (September 2007) 43-48
ISSN: 1997-4884

University of Baghdad
College of Engineering

Study of Catalysts Deactivation in Isomerization Process to Produce High Octane Gasoline

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Abstract

In this study the isomerization of desulfuerized light Iraqi petroleum naphtha (Al-Dura Refinery) with boiling point range of 37 to 124 °C , 80.5 API specific gravity and 68.2 octane number has been investigated. Two types of catalysts were prepared (Pt/HX and Pt/SrX) by impregnation of 0.8 wt% Pt on 13X-zeolite. The catalyst activity and selectivity toward isomerization, and catalyst deactivation were investigated.

The isomerization unit consisted of a vertical tubular stainless steel reactor of 2 cm internal diameter, 3 cm external diameter and 68 cm height. The operating pressure was atmospheric for all experimental runs. The liquid flow of light-naphtha was 0.4 L/h, and the catalyst weight was 50 gm, H_2/H.C ratio used was 4 for all experimental runs. The isomerization process was studied at different temperatures of 250, 270, 275, 300, 325, and 350 °C . It was found that, the optimum isomerization temperature is 270 °C

The isomerization activities and selectivities as a function of time showed high activity at the beginning of the reaction and were deactivated rapidly. This indicates that the deactivation of Pt/HX and Pt/SrX results from the blocking of pore mouth by the deposited carbon. The following deactivation decreasing order, Pt/HX > Pt/SrX was found. On the other hand, Pt/HX catalyst shows higher activity and selectivity than that of Pt/SrX.

It was concluded that, only an average of 90 wt% of the carbon atoms feed into the reactor (light naphtha) is detected in the product stream due to formation of coke deposits which leads to catalyst deactivation. The results clearly showed that hydrogen is necessary for the hydrogenation of olefins in order to prevent oligomerization reaction that leads to coke formation and catalyst deactivation.

Keywords: catalytic isomerization, light-napgtha, Pt/HX and Pt/SrX catalysts, deactivation.

Introduction

Due to a heightened awareness of the environmental problem worldwide, expectations of clean and unleaded gasoline and world demand for gasoline have been increasing. Catalytic isomerization is regarded one of the most important processes in oil refineries which produce clean and high octane gasoline. Isomerization converts n-butane, n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number.The common feedstocke for isomerization process is the light straight run naphtha, which consists of the lighter fraction C5 /C6 [1, 2].

In general, a catalyst may lose its activity or its selectivity due to poisoning, fouling, sintering and loss of active species [1]. One of the most challenging tasks in the design and operation of industrial catalytic processes is the prevention, or at least the control, of catalyst deactivation. Loss of catalyst activity is often accompanied by a loss in selectivity. This leads to greater formation of undesired by-products such as carbon oxides, poor utilization of raw materials, waste of energy, and increased pollution [3,4]. Thus, solving deactivation problems is of paramount importance for the economic and ecologic performance of the process industry. Understanding deactivation mechanisms could ultimately lead to the design of inherently stable catalysts, with considerable benefits. Solving deactivation problems requires a detailed knowledge of the many causes and mechanisms involved [6,7, 8].

On the other hand, fouling formation is regarded one of the most important types of catalyst deactivation in isomerization process. Generally, the kinetics of a catalyst deactivation is a function of temperature, time, pressure and the concentrations of different substances [9, 10].

The principal differences between the various industrial processes of isomerization relate to the catalyst used; this will in turn affect the feed pretreatment steps and spent catalyst characterization. The two principal types of catalyst identified in the industry are: platinum on zeolite, which operates at temperatures above 200 °C, and platinum chloride on alumina, which operates at temperatures below 200 °C [11, 12]. The main advantage of zeolites over platinum on chlorinated alumina catalysts is that they have a much better resistance against feed impurities such as water, which obviates the need for expensive drying facilities. Moreover, in zeolite based processes it is unnecessary to continuously add chlorinating agents, remove hydrogen chloride from effluent streams and take precautions against corrosion. Many authors have investigated the catalyst deactivation phenomenon over Pt/Al_2O_3 catalyst using n-pentane, n-hexane, and n-heptane as a feedstock for isomerization reaction [11, 13, 14].

In order to design and optimize catalysts, a detailed understanding of the reaction mechanism, kinetic, deactivation and catalyst properties is of primary interest. The combination between catalyst performance and understanding of catalyst deactivation will enable the design of a new catalyst with reduced deactivation and increased activity and selectivity for desired products. Therefore, the present work aims to:

- provide a substantiated knowledge of the isomerization reaction based on bifunctional zeolite catalysts by using light-naphtha as a feed and determining the optimum process conditions.
- test the performance, deactivation rates and catalyst stability under optimum process conditions

Experimental Work

Catalytic unit

The experimental study was carried out to investigate the catalysts activity, selectivity and catalysts deactivation rate by building an experimental rig specified for isomerization reaction, as shown in Figure (1) which represents general view of experimental unit.

Figure (2) shows a schematic diagram of a fixed bed flow-type apparatus. The isomerization unit consists of a vertical tubular stainless steel reactor of 2 cm internal diameter, 3 cm external diameter and 68 cm height (reactor volume 214 cm^3). The reactor was heated uniformly using an electrical furnace. The temperature at the reactor center of the catalyst bed and at different points in reactor and system were determined by manufacturing an interface system, (Computerized Temperature Measurement System) which has ten calibrated thermocouple sensors type K (iron-constantan). The interface is programmed and run by a computer (P4).

The reactor is fitted with accurate means for control of pressure, gas and liquid flow rates. The experiments were conducted at atmospheric pressure. Feed mixtures of hydrogen and hydrocarbon were preheated to reactor temperature before entering the bed.

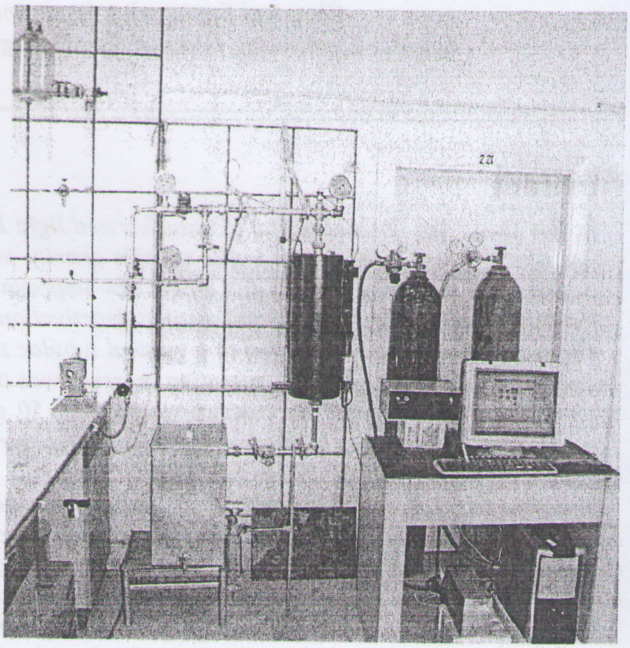

Fig.(1) General view of experimental apparatus

Materials

Two types of catalysts named Pt/HX and Pt/SrX were prepared. The preparation of the catalysts were carried out by impregnation of extrudates (3 x 5) mm of sodium type13X zeolite, Si/Al = 2.8 (Linde Company) with 0.8 wt% platinum.

Dried and desulfurized Iraqi light petroleum naphtha delivered by Al-Dura Refinery-Baghdad was used as a feedstock. Hydrogen gas was supplied from Al-Mansour plant (purity is 99.9 %). Various types of chemical compounds were used. Hexachloroplatonic acid H_2PtCl_6 (40%wt Pt), strontium chloride, ammonium chloride were obtained from Fluka AG.

The properties and chemical analysis of light-naphtha are tabulated in Tables (1) and (2) respectively. On the other hand, according to G.C. analysis shown in Table

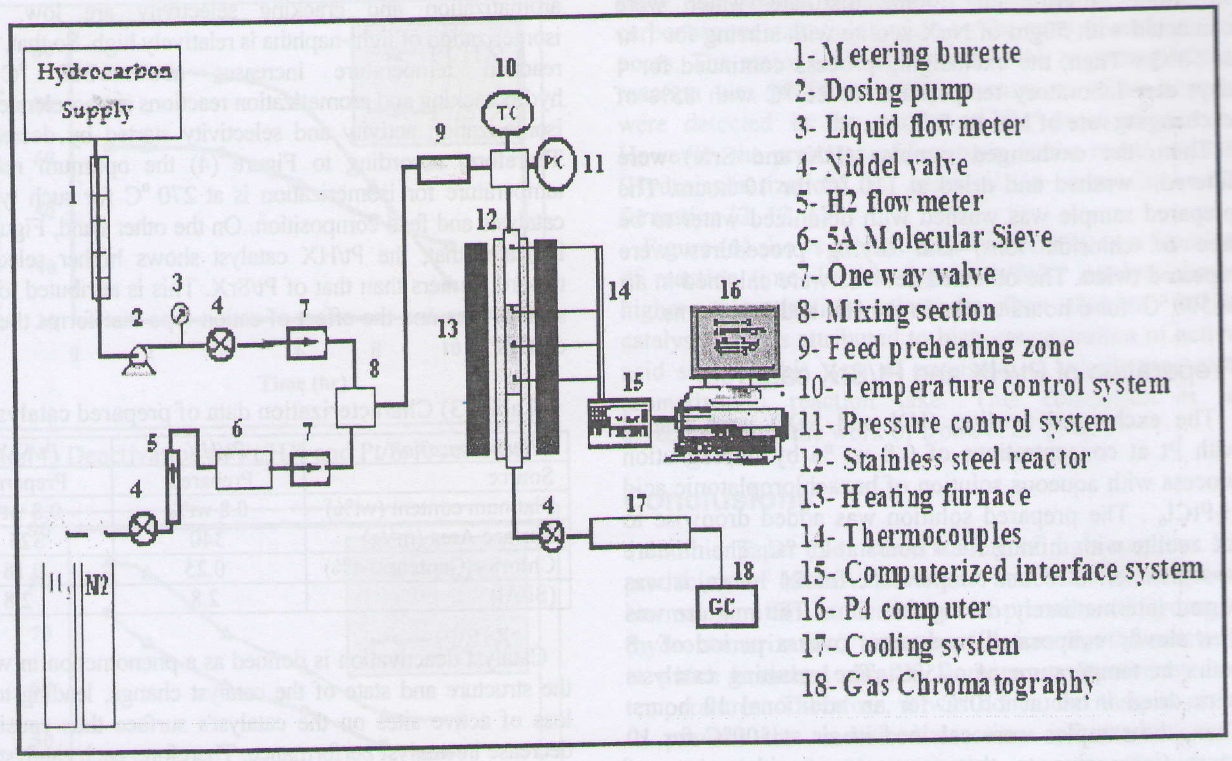

Fig. (2) Schematic diagram of the experimental apparatus.

(2), the main components of the light-naphtha feed are n-pentane and n-hexane (35.70 and 40.8 vol% respectively) which indicates that, the catalytic isomerization for such feed may be a dominant process. Therefore, such process can be used to improve the octane number when optimum operating conditions are applied.

Table (1) The properties of light-Iraqi petroleum naphtha

Property	Data
Sp.gr. at 15.6 °C	0.665
API	80.5
Distillation	
I.B.P.	37 °C
5 Vol.% distilled	42 °C
10 Vol.% distilled	48 °C
20 Vol.% distilled	52 °C
30 Vol.% distilled	56 °C
40 Vol.% distilled	60 °C
50 Vol.% distilled	65 °C
60 Vol.% distilled	68 °C
70 Vol.% distilled	76 °C
80 Vol.% distilled	82 °C
90 Vol.% distilled	86 °C
95 Vol.% distilled	92 °C
E.B.P.	124 °C
Total distillate	96 Vol.%
Total recovery Residue	0.7 Vol.%
Loss	3.3 Vol.%
Octane Number	68.2
Sulfur Content	< 3 ppm (Desulfurized)
Kinematic Viscosity at 25 °C	5.4×10^{-7} m^2/s

Table (2) Chemical analysis of light-Iraqi petroleum naphtha

Composition	wt%
n-Pentane	35.70
n-Hexane	40.80
Methyl CycloPentane	11.13
Benzene	1.40
Cyclohexane	2.82
n-Heptane	3.15
n-Octane	1.88
Toluene	1.54
C7 +	1.22
Total	99.64

Modification of 13X-Zeolite.

In order to modify the NaX zeolite specification, NaX zeolite were exchanged with two type of cations (Ammonium and Strontium). The Na+ ions were exchanged for NH4+ ions to obtain the HX by ion exchanging the original NaX zeolite with (3 N) ammonium chloride solution [4]. Thus 78.75gm of ammonium chloride in 500ml distillate water was contacted with 50gm of NaX zeolite with stirring for 1 hr at 50 °C . Then, the exchanging process continued for 4 days at laboratory temperature of 25 °C . The exchange result shows 82 % of exchanging rate of Na^+ by Sr^+.

On other hand, SrX form zeolite was prepared by ion exchanging the original NaX zeolite with (3 N) strontium chloride solution [5, 6]. Thus 80gm of strontium chloride in 500ml distillate water were contacted with 50gm of NaX zeolite with stirring for 1 hr at 50°C . Then, the exchanging process continued for 4 days at laboratory temperature of 25 °C with 85% of exchanging rate of Na^+ by Sr^+.

Then, the exchanged samples (HX and SrX) were filtered, washed and dried at 110 °C for 10 hours. The prepared sample was washed with deionized water to be free of chloride ions, and drying procedures were repeated twice. The obtained zeolites were calcined in air at 500 °C for 6 hours to obtain the HX and SrX forms.

Preparation of Pt/HX and Pt/SrX catalysts

The exchanged zeolites (HX and SrX) were loaded with Pt at concentrations of 0.8 wt % by impregnation process with aqueous solution of hexachloroplatonic acid H_2PtCl_6 . The prepared solution was added dropwise to the zeolite with mixing for 4 hours at 25 °C. The mixture was then left at room temperature for 24 hours, it was stirred intermediately during this time. The mixture was then slowly evaporated to dryness over a period of 8 hours at temperature of 75°C. The resulting catalysts were dried in air at 110°C for an additional 12 hours. Then, the samples were calcined in air at 500°C for 10 hours (increasing to that temperature with a rate of 0.5°C/min) and finally reduced at 350°C in flowing H_2 for 4 hours (4, 5). Then, the samples are referred to as Pt/HX and Pt/SrX catalysts.

Procedure

Before the experiments, the catalyst was dried at 110 °C in nitrogen flow for one hour and then reduced at 350 °C in hydrogen flow for three hours. The operating pressure were held constant at 1 bar for all experimental runs. The liquid flow of light-naphtha was 0.4 L/hr , and the amount of catalyst was 50 gm. A hydrogen/hydrocarbon molar ratio used was 4 for all experimental runs. The isomerization process carried out at a range of temperatures varied between 250, 275, 300, 325, and 350 °C .

The feed and the effluent reactor were analyzed in a gas chromatograph (Shimadzu GC-2014) FID using capillary column (S.G.E., length=25 mm, I.D.= 0.22 mm, film=0.2μm) and using N_2 as a carrier gas.

Results and Discussion

Table (3) shows the main characterizes of prepared catalysts (Pt/HX and Pt/SrX. It is clear that, Pt/HX catalyst shows a total surface area greater than that of Pt/SrX.

The reaction temperature influences isomerization activity and selectivity of the catalyst to a higher extent. Figure (3) shows the effect of reaction temperature on isomerization selectivity toward branched isomers hydrocarbons. It is noted that, at low reaction temperatures 225, 250, 275 °C the aromatization and cracking selectivity are low, while isomerization of light-naphtha is relatively high. So that, as the reaction temperature increases above 300 °C the hydrocracking and aromatization reactions are accelerated and isomerization activity and selectivity started by decreasing. Therefore, according to Figure (4) the optimum reaction temperature for isomerization is at 270 °C for such type of catalysts and feed composition. On the other hand, Figure (3) indicates that, the Pt/HX catalyst shows higher selectivity toward isomers than that of Pt/SrX. This is attributed to high surface area and the effect of cation type that forms the final catalyst.

Table (3) Characterization data of prepared catalysts.

Characterization	*Pt/HX*	*Pt/SrX*
Source	Prepared	Prepared
Platinum content (wt%)	0.8 wt%	0.8 wt%
Surface Area (m^2/g)	340	325
Chlorine Content (wt%)	0.25	0.18
(Si/Al)	2.8	2.8

Catalyst deactivation is defined as a phenomenon in which the structure and state of the catalyst change, leading to the loss of active sites on the catalyst's surface thus causing a decrease in catalyst performance. Therefore, each catalyst was subjected to an aging period. After a pretreatment at 350 °C in flowing hydrogen the catalyst was submitted to 10 hr of standard reaction conditions (T=270 °C and atmospheric pressure). The catalytic activity, expressed in terms of percentage iso-butanes, iso-pentanes and iso-hexanes yield, is plotted as a function of onstream time as shown in Figure (4). Both catalysts showed good stability, however, the activity of Pt/HX fell rapidly and it was even lower after 10 hr than that of Pt/SrX. The fast catalyst deactivation that was noted after few hours of reaction time can be attributed to a high hydrogenation-dehydrogenation capacity of platinum according to the conclusions submitted by the work of Tomp et al. [11] and Jorge et al. [12]. Also, Figure (4) indicates that, both catalysts lose approximately 35% of their initial activity.

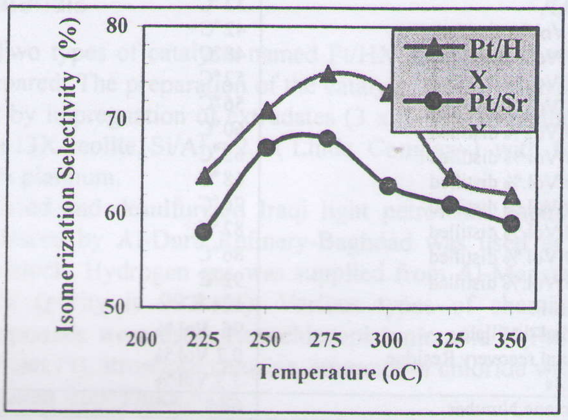

Fig. (3) The influence of reaction temperature on isomerization selectivity

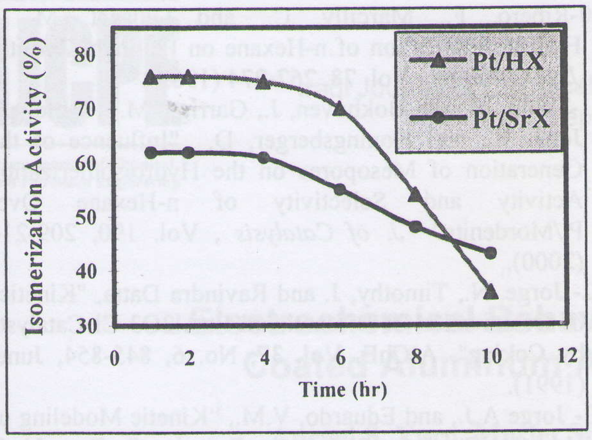

Fig.(4) Deactivation of Pt/HX and Pt/SrX catalysts

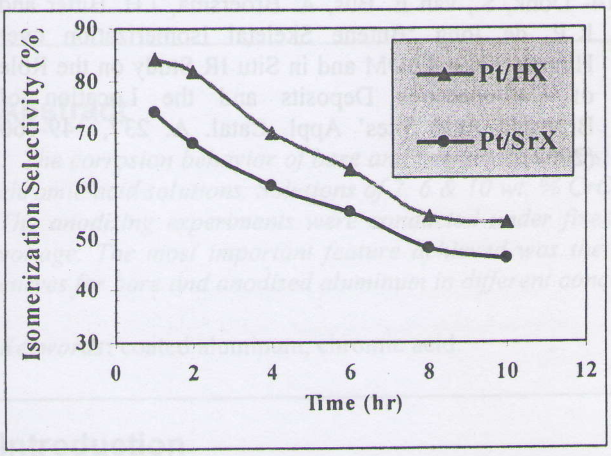

Fig.(5) Loses of catalysts selectivity with aging time

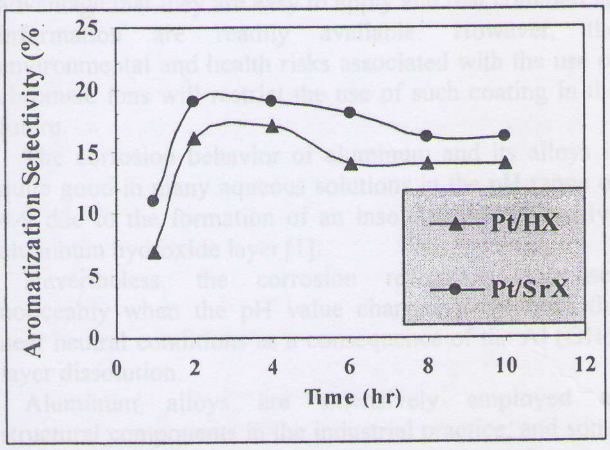

Fig.(6) Aromatization selectivity as a function of reaction time

On the other hand Figure (5) shows the isomerization selectivity toward paraffin isomers. The isomerization selectivity was reduced from 85% to 55% for Pt/HX catalyst and from 74% to 46% for Pt/SrX under 10 hours of reaction time. Both catalysts used in the present work show fast catalyst deactivation caused by deposition of carbonaceous materials (coke) on the catalyst surface and pores. The major product formed in the beginning of the reaction was iso-butane. Higher contents of iso-hexane were detected in the course of the deactivation run. However, the presence of hydrogen in the reaction zone (Hydroisomerization) is essential to minimize coke formation [2, 12, 13].

Figure (6) shows aromatization selectivity as a function of reaction time. In this figure, Pt/SrX catalyst shows higher aromatization selectivity than that of Pt/HX catalyst. This is attributed to high concentration of active acid sites in this type of catalysts, in which promoted aromatization reaction take. This conclusion is in agreement with the work of Donk et al. [14].

Conclusions

In this paper the isomerization of light-naphtha for producing of branched isomers has been investigated. Normal paraffin isomerization in presence of hydrogen (hydroisomerization) is an equilibrium limited reaction, in which branched paraffin isomers are favored by low temperatures. Therefore, it was concluded that, in order to prevent the undesired reactions of cracking and aromatization, the isomerization process should be carried out at 270 °C as an optimum operating temperature for both Pt/HX and Pt/SrX catalysts.

It was concluded that only an average of 90% wt of the carbon atoms feed into the reactor (light-naphtha) are detected in the product stream. This loss (~ 10%) is due to formation of coke deposits which lead to catalyst deactivation. On the other hand, the results clearly show that hydrogen is necessary for the hydrogenation of olefins in order to prevent oligomerization reaction that leads to coke formation and catalyst deactivation.

In spite of the presence of coke deposits poisoning of the metal sites, coke deposits also block the acid sites of a zeolite. The following deactivation decreasing order of catalysts Pt/HX > Pt/SrX was found. On the other hand, Pt/HX catalyst showed higher activity and selectivity than of Pt/SrX.

Acknowledgment

The authors gratefully acknowledge the financial support provided for this work by Ministry of Higher Education and Scientific Research/ Scientists and Creators Department-Baghdad.

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