



Experimental Study of Iraqi Light Naphtha Isomerization over Ni-Pt/H-Mordenite

Halah M. Hussain and Abdulhaleem A.K. Mohammed

Alfaraby University College / Baghdad-Iraq

Abstract

Hydroisomerization of Iraqi light naphtha was studied on prepared Ni-Pt/H-mordenite catalyst at a temperature range of 220-300°C, hydrogen to hydrocarbon molar ratio of 3.7, liquid hourly space velocity (LHSV) 1 hr⁻¹ and at atmospheric pressure. The result shows that the hydroisomerization of light naphtha increases with the increase in reaction temperature at constant LHSV. However, above 270 °C the isomers formation decreases and the reaction is shifted towards the hydrocracking reaction, a higher octane number of naphtha was formed at 270 °C.

Keywords: Iraqi light naphtha isomerization, Nickel-Platinum over H-mordenite.

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1- Introduction

The utilization of an upgraded low-value refinery stream to the gasoline pool might present a solution to the problem, as it can considerably lower the cost of gasoline production, while loses only some of its original quality, but still remains environmentally friendly. The use of bifunctional zeolite catalysts specifically designed to enhance the octane number of light naphtha through the hydroisomerization process has already been marketed.[1].

However, this application has not yet been commercially extended to include the treatment of heavy naphtha, which usually contains normal alkanes from the Heptane range to Decane [2].

Isomerization, cracking and alkylation are acid-induced reactions. The catalyzed hydrocarbon reactions are of great importance nowadays and it is not surprising that many studies have been devoted to this subject. However, important questions remain regarding the mechanism and effect of catalytic pore structure on the activity and selectivity to answer. [3].

Isomerization of n-paraffin to branched paraffin is important in petroleum refining industry for improving motor fuels properties such as high gasoline octane number [4], diesel fuel with high cetane number, low pour point and high viscosity index. To accomplish high isomerization selectivity; balance between the active component (metal) and acid functions is needed [5].

More studies about isomerization to produce high quality gasoline such as Vaudagna, [6] indicated that loading of Pt on WO₃/ZrO₂ have positive effect on the rate and selectivity of alkanes isomerisation in the presence of hydrogen.

The Pt metal was impregnated into the WO₃/ZrO₂, so that the catalysts contain 0.4wt. % of Pt and the Pt/WO₃/ZrO₂ calcined to a temperature of 830 °C (at 20 C min⁻¹) for 3 hours. The specific surface area was found to increase to more than 350m²/g.

Al-Hassany M. [7] studied that Light naphtha treatment achieved over 0.3wt%Pt loaded-alumina, HY-zeolite and Zr/W/HY-zeolite catalysts at temperature range of 240-370 °C, hydrogen to hydrocarbon mole ratio of 1-4 with liquid hourly space velocity (LHSV) 0.75-3 hr⁻¹, and at atmospheric pressure. Results showed that Pt/Zr/W/HY is the best catalyst for producing isoparaffines due to its higher acidity compared with Pt/HY. The Pt/Zr/W/HY catalyst showed lower activity for aromatization of naphtha to cycloparaffins and benzene selectivity than Pt/HY.

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/ HY.

Al-Saraj M A A. et al. [8] studied light naphtha isomerization over 0.3wt. % Pt / HMOR was the catalyst. The operating condition was performed for all temperature experiments from 200 to 350 ° C, pressure - range from 3 to 15 bar, LHSV - range from 0.5-2.5hr⁻¹, and from hydrogen to naphtha - a ratio of 300. The results show that the isomerization of the Iraqi light naphtha increases with increasing reaction temperature and decreases with an increase in LHSV. High research octane number (93)was formed at 240 ° C.

In this work the catalytic activity of the promoted prepared catalyst (Pt-Ni/H-mordenite) using light naphtha isomerization was studied at different operating conditions and the chemical composition of produced gasoline using PONA analysis was determined.

2- Experimental Work

2.1. Materials

a. Feedstock

Iraqi light naphtha supplied from Al-Dora Refinery was used as a feedstock in hydroisomerization experiments. The physical properties and PONA analysis of Iraqi light naphtha are listed in Table 1.

Table 1. Physical Properties and PONA analysis of Iraqi light naphtha

| Physical properties | value |
|--|----------------------|
| Specific gravity at 60 ^o /60 ^o F | 0.6631 |
| API gravity | 80.6 |
| Kinematic viscosity at 25 °C, m ² /s | 7.2*10 ⁻⁷ |
| Research Octane number | 60 |
| Sulfur content ppm | 1.5 |
| Chemical Composition | Wt.% |
| n-Paraffin | 42.9 |
| i-Paraffin | 42.1 |
| Olefin | 0.3 |
| Naphthene | 9.1 |
| Aromatic | 5 |

b. Chemicals

The chemicals used for experimental work are tabulated in Table 2.

Table 2. The chemicals used for experimental work

| Chemical | Source(company) | Purity |
|---------------------|---------------------------|--------|
| Sodium Hydroxide | Alpha Chemika | 99% |
| Sulfuric Acid | Sigma Aldrich | 98% |
| Sodium aluminate | Sigma Aldrich | 50-56% |
| Ammonium Chloride | BDH Limited Pool, England | 99% |
| Nickel nitrate | Himedia, India | 97% |
| Cloro platinic acid | Sigma Aldrich | 40% |
| Hydrogen gas | Al-Dura Power station | 99% |
| Nitrogen gas | Al-Khalej Plant | 99% |

2.2. Synthesis of Na-mordenite (Na-MOR)

Na-MOR was synthesized from nano-silica. 38.90 g of NaOH was dissolved in 249.3 ml of water and then divided into two equal portions. In one portion, 5.56 g of nano-silica was completely dissolved. To the other portion, 10.19 g of NaAlO₂ was added to prepare a clear aluminate solution. Then the silicate solution was slowly poured into the aluminate solution with vigorous stirring, and a homogenous gel resulted.

The resultant gel was stored in a water bath at room temperature ($T = 25 \pm 2^\circ\text{C}$), in a sealed poly tetra fluoro ethylene (PTFE) bottle under stirrer at 250 rpm for 3 days at pH 14. The solid product was separated by filtration (Whatman No. 41 filter paper) using a Buckner funnel with the aid of a vacuum pump, then washed more times by distilled water until the pH value dropped to 8.69. The product was left at room temperature overnight, dried at 110 °C for 2 hr and calcined at 400 °C for 2 hr. [9].

2.3. Synthesis of H-mordenite (H-MOR)

The hydrogen form of zeolite H-MOR was obtained from Na-MOR exchange with a solution of 4 N NH₄Cl. Zeolite Na-MOR was slurred in an ammonium chloride solutions with mixing at 70 °C for 2 hr and then left at room temperature overnight for ion exchange completion.

After that the exchanged zeolite was filtered off, washed with distilled water. The product was left at room temperature overnight, dried at 110 °C for 2 hr and calcined at 400 °C for 2 hr. [10]

2.4. Preparation of Ni-Pt/H-MOR by impregnation method

100g of H-MOR-zeolite as a powder was mixed with 10 wt. % bentonite clay as binder. The resulting mixture was mixed with water to form a paste. Extrudates with 3-7 mm were formulated and dried over night at 110 °C and then calcined at 400 °C for 2 hr.

To prepare 0.15wt % of Pt on 50 g of H-MOR pellets the carrier catalyst H-MOR was dried at 110 °C with air for two hours and placed in impregnation under vacuum, then the solution of chloroplatinic acid (0.205 g H₂PtCl₆ and 30 ml deionized water) was added drop by drop under magnetic stirring then the vacuum cut off and the sample left under mixing for about 2 hr to have a homogenous distribution of metal precursors. The product was slurry filter washed with distilled water, dried at 110 °C overnight and calcined at 400 °C for two hours at a rate of 2 °C /min [11]. After calcination the catalyst was reduced by hydrogen at 350 °C for 3 hours. For preoare Ni-Pt/H-MOR catalyst containing 0.215 wt. % of Ni, 50 g of Pt/H-MOR was impregnated with 0.2 M Ni (NO₃)₂.2H₂O aqueous solution at 40 °C for 2 hours. The obtained filtrated, dried and calcined at 400 °C for 2 hours.

2.5. Catalytic Activity Test

The catalytic activity test was achieved in a continuous flow at fixed-bed reactor. Figure 1 shows the process flow diagram of unit. 30 g Ni-Pt/H-MOR was charged to the reactor between two layers of inert ceramic particles. The platinum containing catalyst was reduced with H₂ at 350 °C for 3 hr.

The catalytic reaction was carried out with LHSV of 1 hr⁻¹, at temperature range of 220-300 °C, hydrogen to feed mole ratio of 3.7 and at atmospheric pressure.

The reactor was flushed with nitrogen to purge the air from the system.

Meanwhile, the reactor is heated to the desired temperature. After reaching the reaction temperature, the nitrogen valve was closed.

A pre-specified flow rate of light naphtha was set on. Vaporization of the feed occurs in the evaporator.

The vapor of light naphtha was mixed with specified flow rate of hydrogen in the mixing section. The mixture entered the reactor from the top, and reacted on the surface of catalyst. The final condensed product was collected only after steady state operation was established while initial products were discarded.

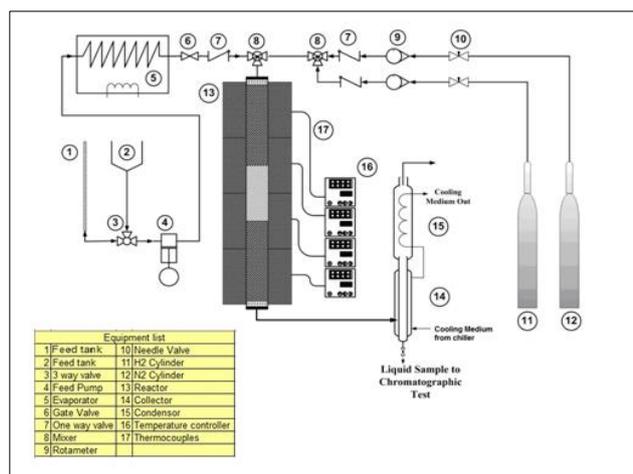


Fig. 1. Process flow diagram of the catalytic experimental unit

3- Results and Discussion

3.1 Characterization of Na-MOR and H-MOR.

a. XRD Analysis

Fig. 2 shows that the X-ray diffraction patterns of synthesized Na-MOR. These crystal was similar to that obtained by R. Szostak [12] and M. Mohamed et al, [13]. This means that the synthesized sample is Na-MOR crystals.

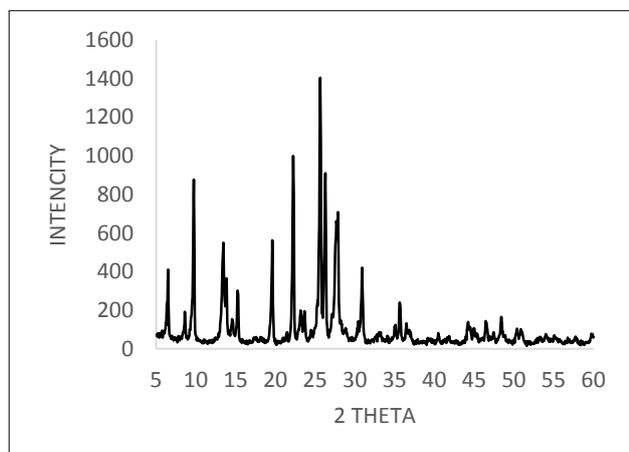


Fig. 2. X-ray powder pattern of prepared Na-MOR zeolite

The exchange technique was used in this work is one step impregnation under a constant temperature to convert Na-MOR zeolite to H-MOR zeolite. Fig. 3, illustrates the XRD patterns of the synthesized zeolite H-MOR. XRD phase is found to match with the show peaks at $2\theta = 6.57, 9.77, 19.65, 22.36, 25.72$ and 26.36 . These peaks are characteristic for H-MOR zeolite. It can be seen from Figure 4, that the synthesized sample showed the formation of H-MOR phase [13]. The relative crystallinity of H-MOR was calculated by equation 1 and it was 118 %.

$$\text{Relative crystallinity of zeolite} = \frac{S_x}{S_y} * 100 \quad (1)$$

Where:

S_x = sum of integral peak intensities for the prepared catalyst.

S_y = sum of integral peak intensities for the standard catalyst.

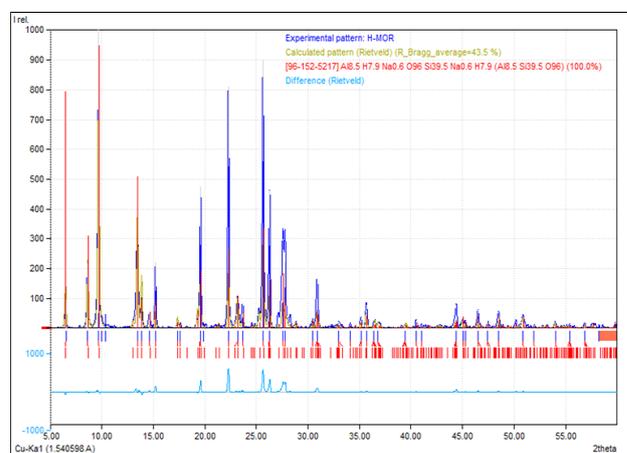


Fig. 3. X-ray powder pattern of prepared H-MOR zeolite

b. Surface Area and Pore Distribution Analysis

H-MOR was characterized using N_2 sorption to determine their surface area and pore volume. Surface area and pore volume depend mainly on the structure of the solid. It was found that the BET surface area and pore size of H-MOR were $336.7 \text{ m}^2/\text{g}$ and 2.49 nm , respectively. The surface area obtained in this work was higher than those obtained by Hisham M. et al, ($52.14 \text{ m}^2/\text{g}$) [14] and Heman et al, ($254.38 \text{ m}^2/\text{g}$) [15].

3.2. Isomerization Conversion

Isomerization conversion was determined by equation 2, while percentage decreasing of naphthenic and aromatic calculation by equation 3.

$$\text{Isomerization conversion} = \frac{\text{feed-out}}{\text{feed}} * 100\% \quad (2)$$

$$\text{Percentage decreases} = \frac{\text{feed-out}}{\text{feed}} * 100\% \quad (3)$$

Table 3 shows the chemical composition of produced gasoline using PONA analysis in order to evaluate the catalyst performance. The hydroconversion involves three main reactions hydroisomerization, dealkylation and hydrogenation.

Table 3. PONA analysis for isomerization of Iraqi light naphtha at LHSV = 1 hr⁻¹ and different T

| wt. % | T °C | 220 °C | 240 °C | 270 °C | 300 °C |
|------------|------|--------|--------|--------|--------|
| n-paraffin | | 29.4 | 28.1 | 26.1 | 28 |
| i-paraffin | | 57.2 | 62.7 | 65.2 | 62.7 |
| Olefin | | - | 0.2 | 0.2 | 0.2 |
| Naphthen | | 8.7 | 5.8 | 5.4 | 5.8 |
| Aromatic | | 4.7 | 3.2 | 3.1 | 3.3 |

Fig. 4 shows the effect of temperature on the isomerization reaction.

The isomerization conversion, as shown in this figure, increases with temperature increasing up to 270 °C. This is due to n-paraffin isomerization. This agrees with an investigation reported by Mohammed et al, [8] and Maha H. [7] obtained for hydroisomerization light naphtha using Pt-Ni/H-mordenite.

Furthermore, the lower reaction temperature increases the percentage of branch alkane at thermodynamic equilibrium as mentioned by Fahim M A et al. [16].

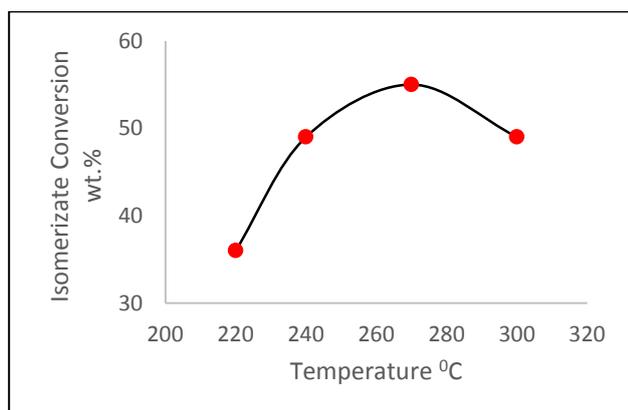


Fig. 4. Effect of temperature on isomerization conversion of Iraqi light naphtha on Pt-Ni/H-mordenite catalyst at LHSV = 1 hr⁻¹

Fig. 5 and Fig. 6 show the relationship between percentage change of naphthene and aromatic with temperature, respectively.

The increasing of temperature firstly, promote aromatic hydrogenation to cyclo-paraffin and cyclo-paraffin hydroisomerization to iso-paraffin and secondly, higher temperature change the thermodynamic equilibrium forward decreasing hydroisomerization as mentioned by Al-Hassany M. [7] at different temperature 220-300 °C, constant LHSV = 1 hr⁻¹ and H₂/hydrocarbon mole ratio = 3.7

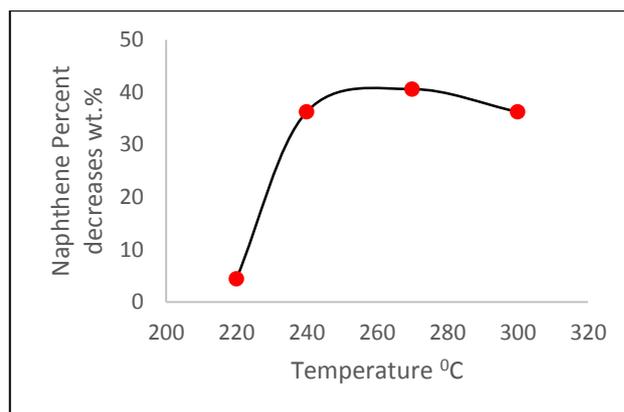


Fig. 5. Effect of temperature on naphthene percent decreases of Iraqi light naphtha on Pt-Ni/H-mordenite catalyst at LHSV = 1 hr⁻¹

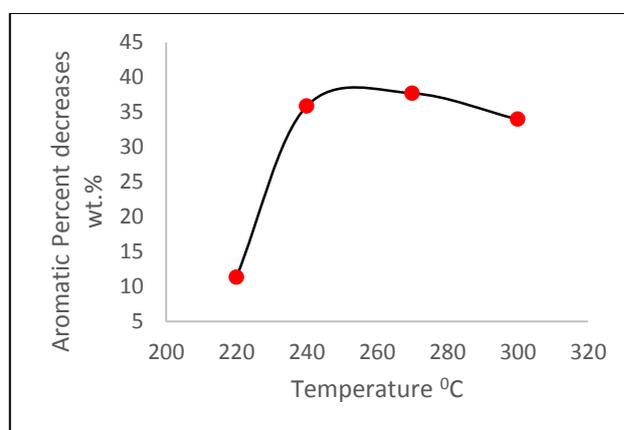


Fig. 6. Effect of temperature on aromatic percent decrease of Iraqi light naphtha on Pt-Ni/H-mordenite catalyst at LHSV = 1 hr⁻¹

Fig. 7 shows the octane number of produced light naphtha at different temperature. This figure shows that the octane number of produced light naphtha (isomerization) more higher than the light naphtha (RON = 60) and the maximum octane number (92) obtained at 270 °C. The isomerization obtained at 270 °C can be easily used as high octane component for producer lead free automobile gasoline.

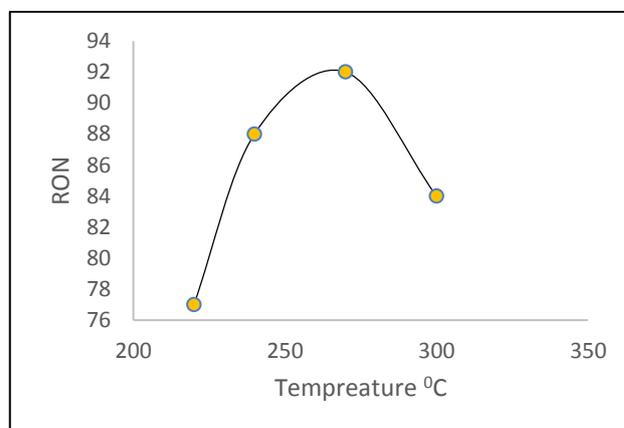


Fig. 7. The high of temperature on the RON at LHSV 1 hr⁻¹

4- Conclusions

The prepared catalyst Ni-Pt/H-mordenite exhibits a high hydroisomerization activity within the studied range of operating conditions. The hydroisomerization reaction is temperature dependent, and the lower temperature the greater hydroisomerization selectivity and in turn high RON value. The isomerizate at 270 °C and LHSV = 1 hr⁻¹ has RON = 92 and can be used as component for lead free gasoline production.

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دراسة عملية لأيزوميته النفط العراقية الخفيفة على Ni-Pt / H-Mordenite

هالة محمد حسين و عبدالحليم عبدالكريم محمد

كلية الفارابي الجامعة-بغداد-العراق

الخلاصة

تمت دراسة عملية الازمرة من النفط العراقية على محفزالمحضر Ni-Pt / H-mordenite عند درجة حرارة تتراوح بين 220-300⁰ م ، نسبة الهيدروجين الى هيدروكربون 3.7 مع سرعة الفراغية 1 hr⁻¹ و في الضغط الجوي.

أظهرت النتائج ان تحول النفط يزداد مع زيادة درجة حرارة التفاعل عند ثبوت السرعة ، في حين أن تكوين أيزومرات أعلى عند 270⁰ م ، يتم تحويل التفاعل نحو تفاعل التكسير بالهيدروجين. ارتفاع عدد الأوكتين النفط المتكون عند 270⁰ م.

الكلمات الدالة: أزمرة النفط العراقية الخفيفه, نيكل-بلاتينيوم على موردنايت.