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Synthesis and Characterization of Ni-WO3/Sulfated Zirconia Nano catalyst for Isomerization of N-Hexane and Iraqi Light Naphtha

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Abstract

This work deals with the preparation of Sulfated Zirconia catalyst (SZ) for isomerization of n-hexane model and refinery light naphtha, as well as enhanced the role of promoters to get the target with the mild condition, stability, and to prevent the formation of coke precursors on strong acidic sites of the catalyst. The prepared Ni-WO_3/Sulfated Zirconia catalyst was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Brunauer –Emmett-Teller (BET) surface area analysis, Thermogravimetric Analysis (TGA), and atomic force microscopy (AFM) Analyzer. The results illustrate that the maximum conversion and selectivity for n-hexane isomerization with Ni-WSZ at the operating temperature of 150 °C was 80.1% and 96 % respectively. While the experimental with light naphtha, the results show that the maximum conversion and selectivity with Ni-WSZ at the operating temperature of 150 °C was 53% and 74% respectively.

Keywords: Light naphtha isomerization, n-hexane, Nickel-tungsten, Sulfated Zirconia, Super acidic catalyst, isomerization process

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1- Introduction

Pollution and climate change have made the world more attentive and concerned about the environment in the last few decades. At the same time, the industrial processes in general and oil refinery, in particular, have touched the growing of fuel demand and quality for the combustion engine efficiency of fuel by the research octane number (RON). The distillation of petroleum fractions in the oil refinery industry cannot meet the required properties of gasoline with RON 92 to 100 as needed by modern engines [1].

In the past, as a result, to increase the octane number, many approaches were adopted like adding some addition, this was achieved using lead compounds, i.e., tetraethyl lead that became restricted and prohibited later due to environmental regulation as they are toxic and poison exhaust gas converters. Another technique was adopted to enhance the RON is by mixing the fuel with benzene and/or other aromatics, also, the legislation of the acceptable degree of these aromatics in fuel is becoming stricter later, on the other hand, Methyl Tetra butyl ether (MTBE) has been related to groundwater pollution, although being less hazardous than lead. Simultaneously, some of the high-octane components found in gasoline, such as benzene, aromatics, and olefins, must be decreased as well. It will be better to use a technique that will improve the octane of gasoline without adding hazardous or ecologically harmful chemicals [2].

So the oil industry has turned to the modern alternative processes that use catalysts to convert the straight chain-alkanes to branched alkanes which have higher octane numbers sufficient to raise the octane rating of gasoline, this is called the isomerization process[3].

Hydroisomerization processes frequently necessitate the use of dual-purpose catalysts. With the help of noble metals like platinum and palladium an acid site, a bifunctional catalyst performs two functions: hydrogenation/dehydrogenation and cracking[4]. Because of the thermodynamics of isomerization, lower reaction temperatures favor the generation of isoparaffins, hence catalysts that operate at low temperatures are often more selective to isomers than those that operate at high temperatures [5,6].

Because of their high acidity and low reaction temperature (about 180°C), platinum-loaded chlorinated alumina catalysts were initially used in industrial isomerization units. However, there are several disadvantages to using this type of catalyst. There are numerous corrosion and environmental issues associated with the use of chlorine in catalyst regeneration [7]. The long life of the Pt/Cl-Al_2O_3 catalyst necessitates the use of feed and make-up gas driers for the removal of moisture. So there's a strong incentive to find a better, less harmful catalyst for n-alkane isomerization to increase the production of isomerate. Zeolites and SZ are examples of potential catalysts for n-alkane isomerization that have been proposed in the literature.

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Low reaction temperature favors n-alkane isomerization since it is a mildly exothermic process. Catalysts that are active between (100-200)^{0}C are thought to be the most appropriate for C_4- C_6 isomerization. Despite numerous tries, zeolite catalysts are no longer thermodynamically advantageous for n-alkane isomerization from this point on. zeolite catalysts must be run at a higher temperature, typically 200°C to 300°C. Finally, compared to the Pt/Cl-Al_2O_3 catalyst, the SZ-based catalysts exhibit satisfactory catalytic performance in n-alkane isomerization [8]. Because of their high activity, simplicity of handling, and absence of corrosiveness, these catalysts are considered promising industrial catalysts. [9].

The addition of several transition metals to sulfated zirconia, such as Pt, Pd [10], Fe, and Mn [8], has been shown to increase the catalytic activity and stability against rapid deactivation. However, Ma et al. [11] demonstrated that Ni impairs the catalytic efficiency of sulfated zirconia. Ni significantly altered the total acidity and concentration of strong acid sites; Ni was utilized in place of Pt as the active metal phase of various acid solids, and the resulting catalysts were evaluated in hydrocarbon processes. Ni is less expensive than noble metals such as Pt or Pd, thus its use would be cost-effective [11]. Additionally, modification of SZ with additional anions, such as WO_3 might result in the formation of strong acid sites on the zirconia surface that are extremely stable[12].

The investigation aims to develop more efficient catalysts consists sulfated zirconia as a based catalyst supported with WO_3, Ni to improve the isomerization of N-Hexane and Iraqi Light Naphtha and to examine in detail the effect of the reaction condition on catalytic activity.

2- Experimental Work

2.1 Feedstock

Midland Refineries Company/Al-Dura refinery terminal supplied Light naphtha utilized as feed to isomerization unit for activity test. Physical Properties and composition of the light naphtha listed in Table **1**

Table 1. Physical Properties and composition of. light.naphtha

Physical properties	Value
Density	0.664 g/cm^3
Initial boiling point	36 ℃
End boiling point	84 ℃
Sulfur content	1.6 ppm
Octane number	60
n-Paraffin	56.33 wt.%
i-Paraffin	30 wt.%
Naphthene	6.78 wt.%
Aromatic	4 wt.%

2.2. Chemicals Used

Table **2** shows the chemicals used with its specifications:

Table 2. chemical compounds Specifications

Chemicals	Formula	Density	Molecular weight (g /gmol)	Purity
Zirconum oxychloride octahydrate	$ZrOCl_2.8H_2O$	1.910 g/ml	322.25	99 %
Ammonia solution	NH_3 aq.	0.91 g/ml	17.03	25%
Sulfuric acid	H_2SO_4	1.83 g/ml	98.08	98%
Nickel (II) nitrate hexahydrate	$Ni(NO3)_2.6H_2O$	2.05 g/ml	290.81	98%
ammonium meta tungsten	$(NH4)_6H_2W_{12}O_{40}.xH_2O$	4.6 g/ml	2956.2	91% w
nanoalumina	Al_2O_3	3.95 g/ml	101.96	99.99 %
Poly Vinyl Alcohol	(CH2CHOH)n	1.19 g/ml	1750	99%
n-hexane	C_6H_{14}	0.655 g/ml	86.18	99%
Bentonite	$AL_2O_3.4(SiO_2).H_2O$	2~3 g/cm^3	360.31	98%

2.3. Preparation of Catalyst

150 g of Zirconium Oxy-chloride salt ($ZrOCl_2.8H_2O$) was dissolved in 2000 ml of deionized water and ammonia solution of about 25% concentration added drop by drop above the solution above under vigorous stirring until the Ph of the slurry reached (8), keeping the slurry for extra time of about 0.5 hr and aged it at room temperature for 16 hr to allow zirconium hydroxide $Zr(OH)_4$ enough time to precipitate. Then, the precipitate of zirconium hydroxide was filtered under vacuum condition, washed with the access of deionized water to remove chlorine ions and get acidity of about 7, drying the sample at 100 °C for 15 hr. Thereafter, hydrous zirconia was grounded to a fine powder and the Sulfation process was carried out by wet-impregnating the sample with H_2SO_4 of 1 mol/l at 2 ml/g for 1hr. , then, submit the sulfated zirconia produced to dried at 100 °C for 15 hr by the digital dryer and calcined at 600 °C for 3 hr [13].

The Wet-impregnation method was adopted to add nickel and tungsten promoters. Firstly, SZ was impregnated with an aqueous solution of nickel nitrate ($(Ni(NO_3)_2.6H_2O)$) as shown in Fig. **1**, to prepare 1% Ni - SZ catalyst which was dried at 110° C and calcined at 450°C in the air for 3 hr. thereafter, an aqueous solution of ammonium metatungstate ($(NH_4)_6(H_2W_{12}O_{40}.nH_2O)$) was used to impregnate Ni/SZ catalyst by dropwise mechanism to load 25% WO_3 on it. Then, the produced catalyst was left for 24 hr at room temperature and then dried overnight at 110 °C and calcined in air at 700 °C for 3 hr. Finally was extruded the catalyst by mixed with 20% Nano alumina, 10% bentonite, and 7% polyvinyl alcohol solution (PVA) as binders with (0.65 cm length and 0.12 cm diameter) as shown in Fig. **2**, a by Formulating machine of catalyst as shown in Fig. **2**, b.

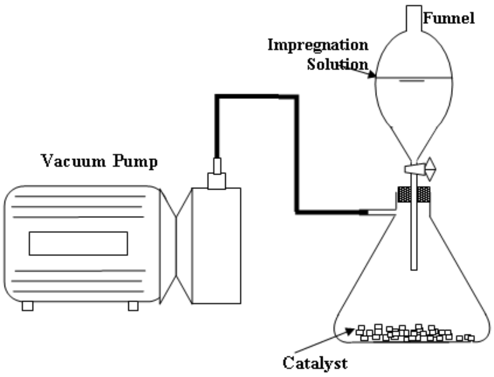


Fig. 1. Scheme of impregnation apparatus

(a)

(b)

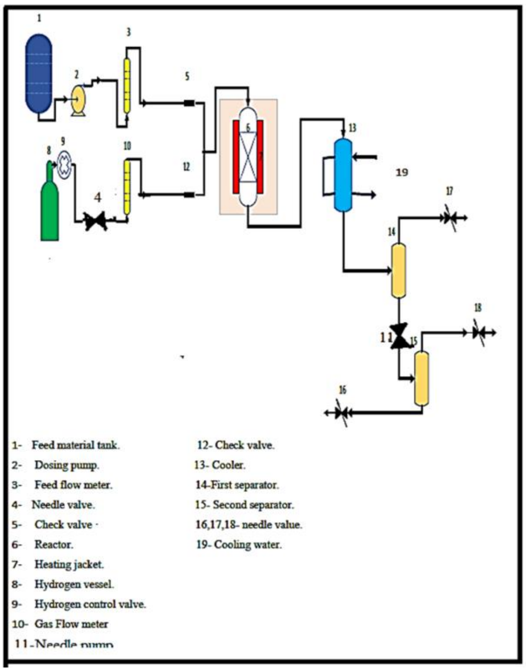
Fig. 2. a. Catalyst formation extruded of powder Ni-WO_3/ SZ, b. Formulating machine of catalyst

2.4. Catalytic Activity Test

7 g of (Ni-WO_3/SZ) catalyst was used in a fixed bed reactor in its designated area of the reactor between two layers of inert ceramic balls material of about 5 mm diameter to ensure a uniform flow and an effective surface area for the catalysts. In the beginning, the nitrogen is passed into the reactor to release the air from the system. At the same time, the reactor is heated to the temperature required for that experiment. And at this moment, the nitrogen passage valve is closed and the reactor is feeding with n-hexane model fuel (or light naphtha) through dosing pump and hydrogen through the control valve, which they mixed in the zone ahead of the experimental reactor. The mixture will pass over the catalyst in the reactor and the reaction will occur. The product of the reactor will be cooled by a refrigerant system and the hydrogen will be separated by a high-pressure separator. At the steady-state operation, the product of the reactor will be sent to the Gas Chromatography Analyzer (GC). The isomerization unit is represented in Fig 3 The reaction conditions for isomerization of n-hexane (or light naphtha) are shown in Table **3** below:

Table 3. Operating condition of n-hexane isomerization process

feed	n-hexane or light Naphtha
Catalysts used are	Ni-WO_3/SZ or Pd-WO_3/SZ
Reaction temperature	120 C – 250 C
Operating pressure	6 bar
Mole ratio of H2/HC	4
Liquid hour space velocity (LHSV)	1 hr.$^{-1}$



(a)

(b)

Fig. 3. . Isomerization process, a. schematic representation of isomerization unit, b. Isomerization Unit

3- Characterization of Synthesized Catalysts

The first part of this study is represented by preparing Ni/WO_3-SZ catalyst by two steps (precipitation-impregnation method) and characterizing it for isomerization of Iraqi light naphtha and n-hexane. This characterization includes; X-ray diffraction (XRD), Fourier Transform Infrared FTIR spectroscopic, atomic force microscope (AFM).

3.1. X-ray Diffraction (XRD)

Sulfated zirconia modified with WO_3 and Ni as promoters improve the catalytic activity of the isomerization process and support the catalyst stability against the rapid deactivation. The promotion of sulfated zirconia with promoters causes the change in the crystal structure accompanied by changes in the textural properties of the synthesized catalyst. Figure 4 showed the XRD pattern of the Ni-WO3/ SZ catalyst. The results showed that the presence of WO_3 stabilizes zirconia, i.e., supports the tetragonal modification even at low calcination temperature. According to the obtained results, the tetragonal zirconia was about 80% and monoclinic was about 20%. More stabilized tetragonal crystallite phase was obtained with Ni loaded as promoters to modify WO_3-SZ. Nickel oxide (NiO) particle inhibited the transformation of tetragonal phase to monoclinic phase at calcination stage, also, it can be seen decreasing crystallite size due to dispersed NiO along with modified sulfated zirconia can restrain the agglomeration of tetragonal SZ grains, besides that, there is a strong interaction between NiO partials and Sulfated Zirconia.

On the other hand, no diffraction peaks assigned to NiO can be detected, meaning the metal promoters are well dispersed in the base and have a very small crystal size [14, 15].

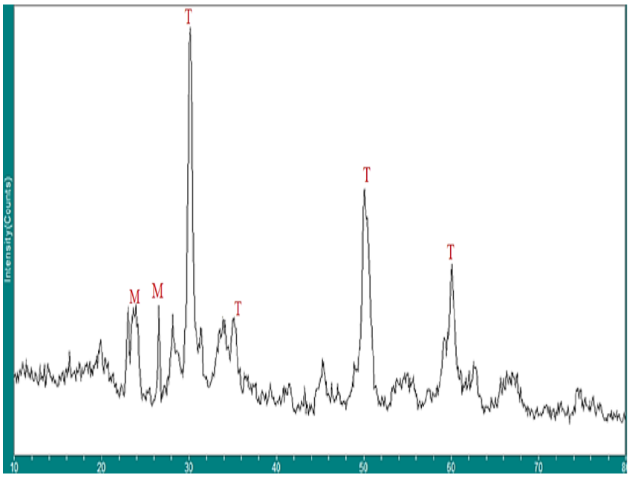


Fig. 4. XRD patterns of Ni-WO_3 / SZ catalyst

3.2 Fourier – Transform Infrared Spectroscopy (FTIR) Characterization

Fig. **5** illustrates the FTIR analysis for prepared sulfated zirconia catalyst, Ni-WSZ catalyst. This technique measured the chemistry of the catalyst surface included the acidity of the active sites.

FTIR results of the study illustrated the absorption bands along the wavenumber 500-4000 Cm^{-1}, in which, the wavenumber of 500-600 Cm^{-1} corresponded to presence (Zr─O─Zr) bond, the wavenumber of (3300-3750) Cm^{-1} was corresponded to the presence the vibration of (O-H) bond, while, the absorption bond of SO_4^{-2} appears at wavenumber of 100-1500 Cm^{-1}.

This observation indicated the appearance of a covalent (S═O) double bond on the surface of sulfated groups at the catalyst which strongly affects the acidity and meets the requirement of the isomerization process.

These results were in very good agreement with other authors. Hauli et al., [16], had studied the preparation and characterization of the Sulfated Zirconia catalyst from Zirconia Nano-powder.

Their results confirm that the characterization of catalyst is highly dependent on sulfonation mechanism and calcination temperature, the results ensure that the SO_4^{-2} peak would appear at a higher concentration of H_2SO_4 in sulfonating step and gradually disappear as the calcination temperature increase.

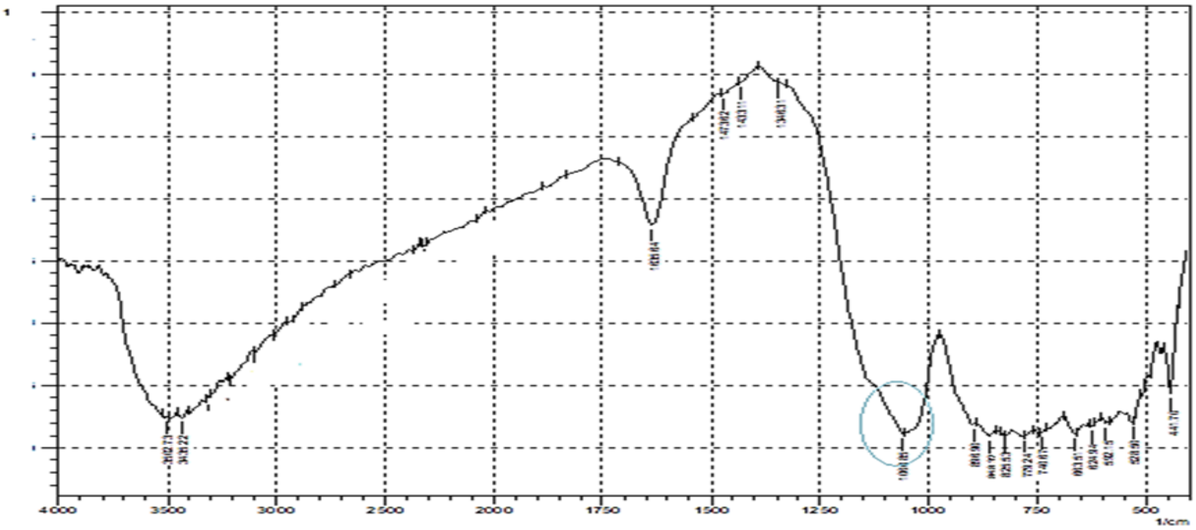


Fig. 5. FT-IR spectra of Ni-WO3/ SZ

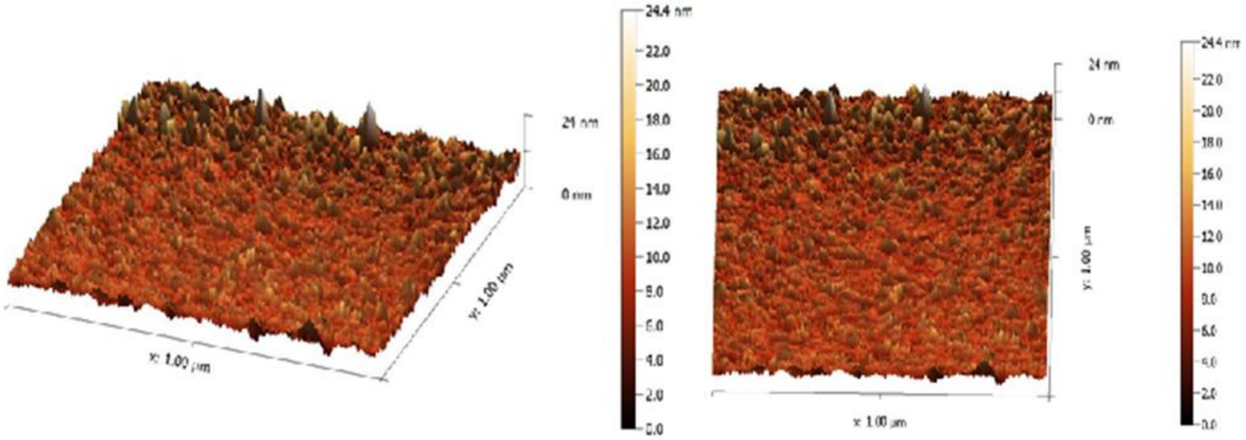


Fig. 6. 3 -D and 2-D surface profiles of Ni-WO_3/modified SZ

3.3. Atomic Force Microscope (AFM) Characterization

Atomic force microscopy is a powerful technique that can image almost any type of surface, it is used to measure the particle size distribution of the catalyst.

The average particle distribution after loaded metal on the catalyst, such as Ni-WO_3 /modified SZ catalyst was 9.27nm with partial size dimeter range not exceeding 24.36 nm. 2 and 3 dimension of surface profiles of Ni-WO_3/ SZ as shown in Fig. **6**.

The preparation mechanism affects the partial size distribution of Sulfated Zirconia catalyst, in particular, the sulfonating mechanism. Sulfate anions increase the surface area, support the stability of the tetragonal phase and minimize the crystallite size. Seen decreasing crystallite size due to dispersed NiO along with modified sulfated zirconia can restrain the agglomeration of tetragonal SZ grains, besides that, there is a strong interaction between NiO partials and Sulfated Zirconia.

4- Catalysts Activity

The experimental runs were carried out for isomerization of refinery light naphtha and n-hexane model to improve the octane number using prepared novel catalysts consisting of sulfated zirconia, as the base with its promoters Ni/WO_3SZ.

The effect of reaction temperature (130-250 °C) was studied, keeping other variable content, LHSV of 1 hr^{-1}, mole ration of H_2/HC of 4, and constant operation pressure of 6 bar.

4.1. Ni/WO_3SZ Activity for Isomerization of N-Hexane Model Fuel

Table **4** shows the chemical composition of the isomerization product by using PONA analysis to evaluate the catalyst performance.

Table 4. PONA analysis for isomerization of n-Hexane at LHSV = 1 hr-1 and different Temperature

	n-hexane	130°C	150°C	170°C	200°C	250°C
n.paraffine	99	35	20	27	36.4	42
i-paraffine	1	62	77	68.7	59	53
Naphthene	0	1.7	2	2.8	3	3
Aromatic	0	1.3	1	1.5	1.6	2

a. n-paraffin Conversion

The results are illustrated in figure 7, which represents the n-paraffin conversion as a function of operating temperature. The conversion of n-paraffin to i-paraffin, naphthene, and aromatic compounds was started at 130 °C in many different proportions toward i-paraffin. Thereafter, it keeps up from 65% to 80% at 150 °C, which represents the maximum conversion obtained in this set of research. Then, it decreases to 73%, 63.6%, and 58% at 170°C, 200°C, and 250 °C respectively.

The results of this research are good and encouraging start in the field of petroleum research that uses a significant acid-grade catalyst that matches the requirement of the process at mild conditions as discussed later with other accompanying conditions.

The maximum conversion achieved was 80% that represents one of the highest degrees as compared with other researchers that used Zirconia-based catalyst.

M. Busto et. al. [18] discovered new paraffin isomerization catalysts based on Pt/SZ, maximum conversion achieved of about 95% at 230 °C. Torres et.al. [19], studied modification of WO_3-ZrO_2 catalyst by metal addition, maximum conversion achieved was about 70%. Ma et.al.[11], studied Pd-Ni doped Sulfated Zirconia for isomerization of n-Hexane, maximum conversion achieved was about 70%.

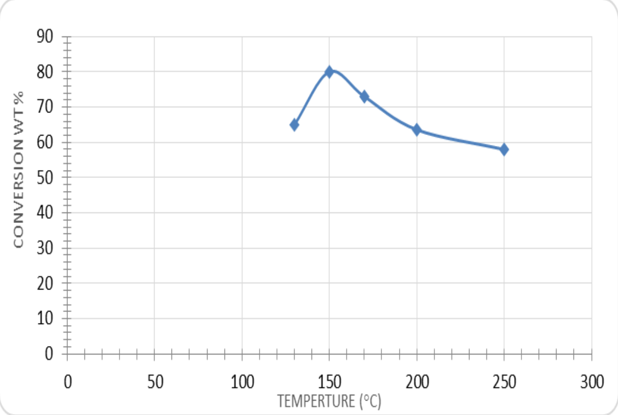


Fig. 7. Effect of temperature on isomerize conversion of n-hexane over Ni-WO_3/ SZ

b. i-paraffins, naphthenes, and aromatic Selectivity and Yield

Operation temperature has a major impact on the isomerization process, in particular, on the conversion of the feed to isomer product and its accompanied naphthenes and aromatic and others when the temperature exceeds the limits of isomerization process. Fig. **8** and Fig. **9** illustrate the effect of temperature on isomer compounds, naphthenes, and aromatic selectivity and yields. The results indicate that the isomer's selectivity begins with a maximum degree of 96% at 150 °C and went on with a slight decrease to meet 90% at 250 °C. At the same time, naphthenes were detected at 130 °C with a 2.6% with a slight increase of only 5.1% at 250 °C. Also, aromatic compounds were detected with 2% at 130 °C and a slight increase reaching 3.4% at 250 °C. Also, the results indicate that the isomers yield begins with a maximum degree of 77% at 150 °C and went on with decreased to reach 53% at 250 °C. At the same time, naphthenes were detected at 130 °C with 1.7% with a slight increase of only 3% at 250 °C. Also, aromatic compounds were detected with 1.3% at 130 °C and a slight increase reaching 2% at 250 °C. These results with mild conditions accompanied the operation refers to the suitable catalyst used and isomerization operation conditions.

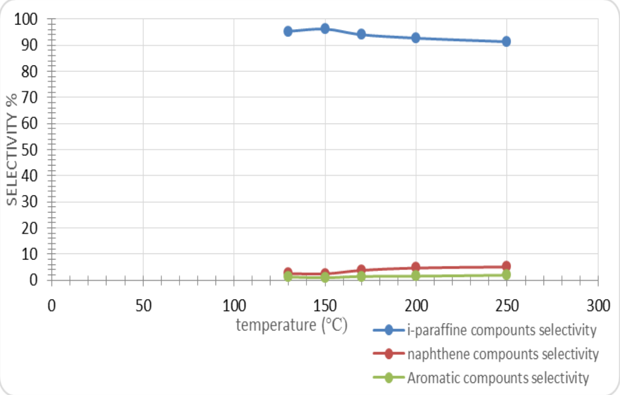


Fig. 8. Effect f temperature on the selectivity of i-paraffins, naphthenes, and aromatic compounds over Ni-WO_3/ SZ catalyst

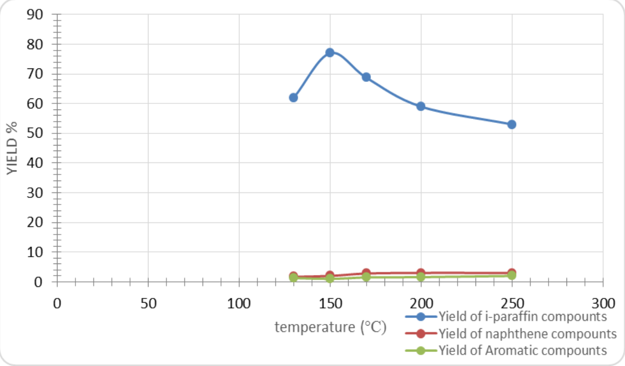


Fig. 9. Effect of temperature on yield of i-paraffins, naphthenes, and aromatic compounds over Ni-WO_3/ SZ catalyst from n-hexane feed

4.2 Ni-WO_3/SZ Activity for Isomerization of Light Naphtha

Table **5** shows the chemical composition of the isomerization product by using PONA analysis to evaluate the catalyst performance.

Table 5. PONA analysis for isomerization of Iraqi light naphtha at LHSV = 1 hr-1 and constant pressure 6 bar

	L.N	130°C	150°C	170°C	200°C	250°C
n.paraffine	56.33	43	26.4	37.7	40.7	42.5
i-paraffine	33	41	49.5	45.2	41.5	37.2
Naphthene	6.78	9	13.9	11.4	9.6	10.8
Aromatic	4	7	10.1	5.9	9	10

a. Light Naphtha (n-paraffin) Conversions

The results obtained here indicate that the conversion of n-paraffin started at 130 °C with 23.7% and reached its maximum value at 150 °C with 53%. Hereafter, the conversion was slightly reduced to meet 24.5% at 250 °C as shown in Fig. **10**. These expected results are in agreement with other authors, due to all the conditions related to the preparation of the catalyst on one side, and to the operational conditions on the other side, as well as, the massive competition of the molecules included the light naphtha composition, i.e., i-paraffines, naphthenes, and aromatics, besides, the intermediate compounds formed during the reactions which largely affected the acidity active sites of the catalysts.

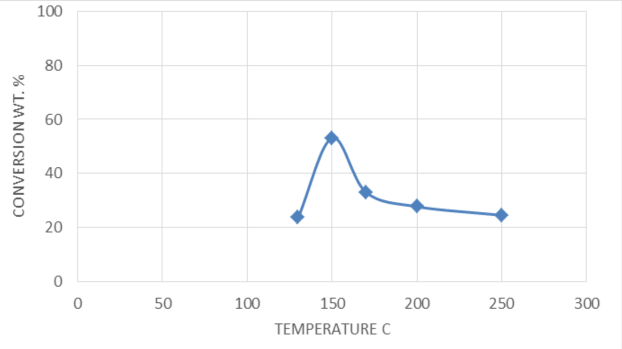


Fig. 10. Effect of temperature on isomerization conversion of light naphtha over Ni-WO_3/ SZ catalyst

b. i-paraffins, naphthenes, and aromatic Selectivity and Yield

In general, catalytic operations are so complex it depends on many variables, catalyst characterization, petroleum fractions, and their compositions, and the operating conditions the results of this set of experiments observed the presence of naphthenes, and aromatics compounds besides the isomers compounds.

The selectivity to isomers started to increase at 130 °C with the value of 72% and reach the maximum at 150 C with 74%, hereafter; the selectivity began to reduce and had 72%, 68%, and 64% at 170 °C, 200 °C, and 250 °C respectively. This behavior was in agreement with other anthers due to the presence of many intermediate compounds that affect the acidic active sites of the catalyst.

Also, the results showed that the presence of naphthenes during the reaction, the selectivity 15%, 19%, 18%, 16 %, and 18% was at 130°C, 150°C, 170 °C, 200°C, 250°C respectively, and the aromatic compounds with the selectivity of 12 %, 14%, 9%, 15%, and 17% at the above operating temperature respectively. This appearance was due to the conversion of n-paraffin to i-paraffin, naphthene, aromatics besides the various behaviors expected by the specialist authors in this field.

Fig. **11** and Fig. **12** illustrate the effect of temperature on isomer compounds, naphthenes, and aromatic selectivity and yields.

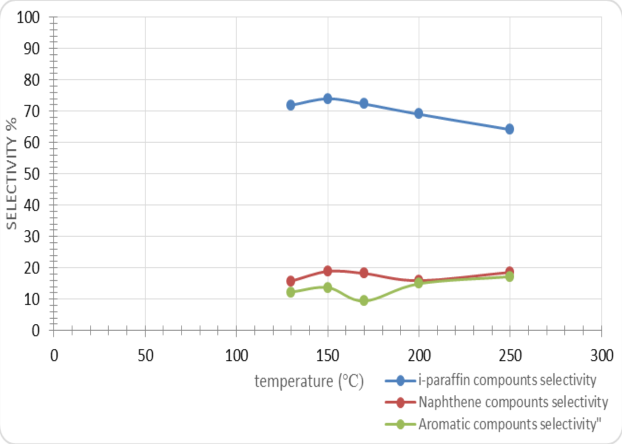


Fig. 11. Effect of temperature on selectivity of i-paraffins, naphthenes, and aromatic compounds over Ni-WO_3/modified SZ catalyst from light naphtha

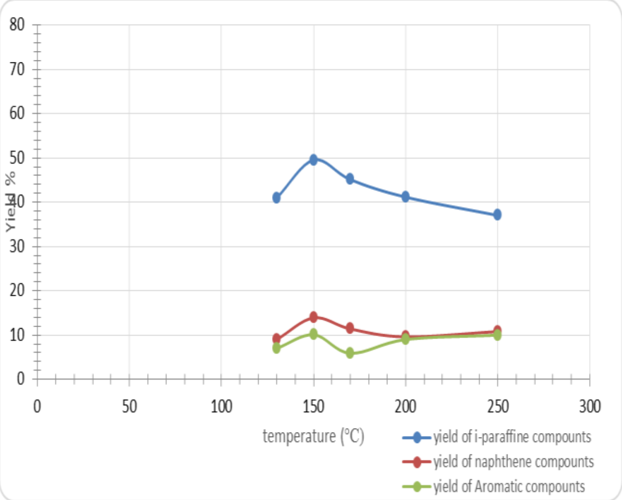


Fig. 12. Effect of temperature on Yield of i-paraffins, naphthenes, and aromatic compounds over Ni-WO_3/modified SZ catalyst from light naphtha

Many studies have tried to determine the nature of the acidity active sites (Bronsted and/or lewis) on the catalyst surface and the mechanism to obtain them. They found that this matter depends on water content, which depends strongly on the preparation method and its conditions [20].

On the other side, the presence of promoters was found to have a great effect in improving the performance of the catalyst. Sulfated Zirconia likes another solid acidic catalyst suffers rapid deactivation during hydrocarbon reactions due to the formation of other side reaction production, in particular, coke formation. The addition of some transition metals, i.e., Ni to the SZ catalyst resulted in a great improvement to the catalyst performance. This was observed from the results of the isomerization process to n-hexane and the refinery light naphtha under mild conditions, which have shown high activity towards isomer compounds.

The addition of Ni and WO_3 to sulfated zirconia improved the performance of the catalyst towards high n-paraffins conversion, isomer compound formation, and diminish coke appearance as a cracking reaction. Many authors studied and discussed this behavior; they related the phenomena to the dependence of chemical reaction activation energy on the enthalpy of transition state complex formation on the catalyst surface, so the activity of such catalyst depends on the lower value of enthalpy [21].

The effect of hydrogen in the isomerization reaction over the SZ catalyst depends on the mechanism of the n-paraffin reactions. For the n-paraffins of light naphtha, the hydrocarbon reaction, i.e., isomerization reaction and/or cracking follow a monomolecular mechanism. So the effect of hydrogen will be positive[22].

5- Conclusion

It is found that Sulfated zirconia is considered to be a very important base catalyst throughout its acidic actives that match the requirement of the isomerization process of n-hexane and light naphtha. Isomerization of alkanes in the presence of sulfated zirconia catalysts needs mild conditions of operating temperature of about 150°C and pressure of about 6 bar. Ni-WSZ gives a high conversion at these conditions of about 80.1%, while the selectivity of isomers of about 96 %.

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تصنيع وتشخيص العامل المساعد النانوي الزركونيا المكبرتة المحملة بالنيكل واوكسيد التنكستن لازمرة الهكسان والنفثا العراقية الخفيفة

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الخلاصة

تم تحضيرمحفز الزركونيا المكبرتة **(SZ)** لازمرة الهكسان والنفثا الخفيفة و تطويرهما , بالاضافة الى التدعيم ببعض المعادن للحصول على الظروف المعتدلة والاستقرارية ومنع تكون الفحم على المواقع الحامضية في العامل المساعد. تم توصيف جميع محفزات التقليدية والمعدلة بواسطة التحليل الطيفي للاشعة تحت الحمراء **FTIR** , الاشعة السينية **XRD** , **Brunauer –Emmett–Teller (BET)** تحليل المساحة السطحية , التحلل الحراري الوزني **TGA** , تحليل الذري المجهري **AFM**. اظهرت النتائج أن الحد الأقصى للتحويل والإنتاجية لأزمرة الهكسان على **Ni–WSZ** بدرجة حرارة 150°م هي 80,1 % و 96% على التوالي. اما باقي التجارب مع النفثا الخفيفة فقد اظهرت ان اعلى نسبة تحول والانتاجية على الالعامل المساعد **Ni–WSZ** وفي درجة حرارة 150°م هي **53** % و 74% على التوالي.

الكلمات الدالة : النفثا الخفيفة, الهكسان, نيكل–تنكستن, الازمرة , الزركونيا المكبرتة