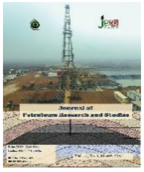
Journal of Petroleum Research and Studies

journal homepage: https://jprs.gov.iq/index.php/jprs/

Print ISSN 2220-5381, Online ISSN 2710-1096



Preparation and Characterization of Sulfated Zirconia-HY Zeolite Catalyst Supported with Pt Metal for Light Naphtha Isomerization

Sura K. Al-Taweel[1], Haider A. Al-Jendeel[1*], Ban A. Al-Tabbakh[2]

[1]Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq.

[2]Petroleum Research and Development Center, Ministry of Oil, Baghdad, Iraq.

[*]Corresponding Author E-mail: haider.aljendeel@coeng.uobaghdad.edu.iq

Article Info

Received 12/11/2024
Revised 25/01/2025
Accepted 28/01/2025
Published 19/03/2026

DOI: http://doi.org/10.52716/jprs.v16i1.1039

Abstract

Platinum (Pt) supported on sulfated zirconia (SZ) and HY-zeolite as a solid acid catalyst was synthesized successfully for isomerization reaction using precipitation and impregnation method. The physicochemical properties of the catalyst were characterized using various techniques including X-ray diffraction (XRD), Fourier transformation infra-red spectroscopy (FTIR), BET Surface area and pore volume, and Field Emission Scanning Electron Microscopy (FESEM). The prepared composite catalyst Pt/SZ-HY consisted of high Bronsted acidic sites and Lewis acidic sites. The addition of multi-walled carbon nanotubes (MWCNTs) to SZ increased the surface area and pore volume, resulting in smaller crystal sizes and a narrower particle size distribution. However, sulfated zirconia without MWCNTs proved more suitable for the isomerization reaction due to its high functional group density. The Pt/SZ-HY composite catalyst exhibited high Bronsted and Lewis acidic sites, with a 1:1 weight ratio of mesoporous SZ and HY zeolite. The catalytic performance of the Pt/SZ-HY composite was evaluated in the isomerization of light Iraqi naphtha, yielding a maximum conversion of 70.76 mol% at 160°C, 15 bar, and 1 hr-1 LHSV.

Keywords: ZrO_2 nanotube, sulfated Zirconia, Multi wall carbon nanotube, Acid treatment, Isomerization, Light naphtha, Pt metal.

تحضير وتوصيف محفز الزركونيا المكبرتة –زيولايت HY المدعوم بمعدن البلاتين لعملية ازمرة النفثا الخفيفة

الخلاصة

يتناول هذا البحث تصنيع الزركونيا المكبرتة باعتبارها كعامل مساعد حامضي ناجح بطريقة الترسيب و التشريب, العامل المساعد المصنع تم توصيفه بواسطة التحليل الطيفي للاشعة تحت الحمراء XRD، الاشعة السينية FTIR، تحليل المساحة السطحية BET، المسح الالكتروني المجهري FESEM. يتم ترسيب الانابيب النانوية الكاربونية على سطح الزركونيا المكبرتة اثناء التصنيع وتظهر النتائج ان اضافته تزيد من المساحة السطحية للزركونيا المكبرتة من 80.2 م2\غم الى 87.74 م2\غم، اظهرت زيادة معقولة بحجم المسامة وصل الى 0.0936

سم^3\غم، اعطى توزيع اضيق مع تقليل لقطر المسامة ليصل الى 3.2417 نم، واعطى حجم كرستالي اقل 10.5 نم، بينما الزركونيا المكبرتة اعطت حجم كرستالي 11.06 نم، حجم بور 0.0789 سم3\غم ومعدل قطر المسامة كان 3.9682 نم. بينما اظهرت النتائج ان الزركونيا المكبرتة بدون اضافة الانابيب النانوية الكاربونية هي اكثر ملائمة لعملية الازمرة لان المجاميع الفعالة فيها اعلى كما ظهر في تحليل الاشعة السينية ال FTIR. ان العامل المساعد المحضر بكميات وزنية متساوية من الزركونيا المكبرتة و الزيولايت نوع HY اعطى اعلى قيمة لتحول النفثا الخفيفة بعملية الازمرة هي 70,76 مول % عند حرارة 160 درجة سيليزية و ضغط 15 بار و 1 ساعة$^{-1}$.

1. Introduction

The isomerization process produce high-quality gasoline with high octane number, minimizing harmful gas emissions and includes low level of benzene and sulfur in the isomerized of light naphtha, which makes it an suitable mixture component for a gasoline blending process[1], [2].

Isomerization reactions produce high octane number branched alkanes from low octane number linear alkanes, which can be used to generate light gasoline[3], by rearranging the structure of hydrocarbon molecules without changing the molecular weight or chemical formula. For instance, the octane number for n-hexane (RON) is 25 while for iso-hexane (2,3-dimethyl butane) is 106.

An efficient highly acidic bifunctional catalyst is required for the isomerization reaction, active metal particles such as platinum, palladium, etc. are loaded to provide a metal site supported on a matrix which provides the acid site such as zeolite, sulfated zirconia and chloride alumina. The catalyst activity and selectivity cannot be optimum unless loaded with a precious metal. Isomerization catalyst loaded with platinum metal is one of the most successful industrial eco-friendly catalytic processes to produce high-octane branched products [4].

Loaded metals provide the hydrogenation /dehydrogenation function. Furthermore, metals can preventing coke deposition to protect the surface of the catalyst from deactivation with the help of hydrogen and keep the catalyst surface clean of heavy hydrocarbons, activate H-H, C-C, and C-H bonds, prolong the catalyst lifespan and increase activity and selectivity of catalyst [5],[6]. Platinum noble metal while being costly but it is a necessary catalyst material as an active metal component because of its activity and stability[6].

Sulfated metal oxides such as sulfated zirconium S-ZrO_2 is a very common acidic heterogeneous catalysts in the chemical and refining industries spatially for isomerization process and furthermore in technologies that use highly hazardous, corrosive, and polluting materials[7], [8].

Zirconia amphoteric surface properties make it an excellent catalyst support. Because of unique properties like strong chemical resistance, high corrosion resistance, mechanical properties, low thermal conductivity, high thermal stability and high adsorbent, have made zirconium oxide popular to use and more attention to develop [9], [10].

Three different crystalline phases for Zirconia can be found, monoclinic phase in the temperature range (400–1170 °C), tetragonal phase in the temperature range of (1170–2370 °C) while cubic phase at temperature range (2370–2680 °C). However, at temperature above 2680 °C zirconia becomes in the liquid phase [11]. The best calcination temperature for sulfated zirconia is around 550 and 650 °C to produce the active tetragonal zirconia phase for isomerization and cracking applications [12].

Zirconium oxide is modified with sulfates to improve the catalytic activity by providing acid sites for an active dual-functional catalyst, with the help of noble metals like platinum and palladium as a metal site. Such a catalyst is suitable for the isomerization or cracking process which performs two functions: hydrogenation/dehydrogenation on metal sites and isomerization or cracking on acid sites [13], [14].

Zeolites are common catalysts utilized in the petroleum and chemical industries. Has a crystalline aluminosilicates microporous structure with large surface area, single pore topologies, excellent acidity, and thermal strength [15], [16].

Unlike other catalysts like zeolites, in which carbon deposition is leading for the deactivation of the catalyst [16,17], the S-ZrO_2 deactivation mechanism is more complex. Deactivation in S-ZrO_2 catalyst can be caused by many reasons besides coke deposition such: leakage of sulfate species at the surface, sulfate species reduction, and zirconia crystal transformation from tetragonal phase to monoclinic phase [19].

Modification of metal oxides such as ZrO_2, TiO_2 and CeO_2 by making the multi-wall carbon nanotube MWCNT as a support is a promising strategy because the structure and the morphology of the support have a significant influence on the catalytic performance. MWCNT can improve the performance of the catalyst by increasing the activity due to its large specific surface area and large volume in addition to the tubular structures which can be utilized as nanoreactors.

After modification by MWCNT, metal oxides have smaller nanoparticles and higher surface area at the same time no change in textural properties of sulfonation of catalyst [20].

MWCNT stability nature at temperatures higher than 750 °C and the good characteristics nature of carbon make it good catalyst support, this stability is back to Zr–O–C bonding with S-ZrO_2 catalyst. Furthermore, the structure of carbon resists the basic media and acidic media, in addition, hydrophilicity can be modified chemically by carbon hydrophobic surface, this is a basic function in stabling the catalysts active phase [21]. The manufacturing method and the precursor used can affect the acidity of zirconia catalysts in addition to several parameters like the calcination temperature, zirconia crystalline phase, the amount of water on the surface and sulphur species present, all these make a significant impact on the final texture of catalysts and the performance. Strong acidity is achieved by sulfating the $Zr(OH)_4$ amorphous crystalline and it is impossible to achieve with ZrO_2 as the starting point for sulfation. Both Bronsted acidic sites and Lewis acidic sites are found in sulfated zirconia, but there is some disagreement about whether the sulfated zirconia acidity is a product of one acid type or a mixture of two acid types [22].

The performance of (Pt/SZ-HY) and (Pt/SZ-mHY) catalyst composites in the conversion of n-hexane and n-heptane was investigated. The results showed that the maximum conversion was achieved with (Pt/SZ-mHY) catalyst which has a higher Si/Al ratio. The conversion was 73.05 mol% for n-heptane and 57.91% for n-hexane at 160 °C and 15 bar [23]. A promoted sulfated zirconia catalyst (Ni–WO_3/SZ) was prepared for the isomerization of refinery light naphtha. The results showed that the maximum conversion was 53% and selectivity was 74% for the light naphtha at temperature of 150 °C, 6 bar, mole ration of H_2/HC of 4 and 1 hr^{-1} liquid hour space velocity[13]. Sulfated zirconia catalysts loaded with tungstophosphoric acid were examined for the isomerization of n-hexane. The results show that loaded the zirconia with 55% WPA gives the best results of 30% conversion and 60% selectivity at 225 °C and LHSV of 1 hr^{-1} [11]. The hydroisomerization of n-heptane over Pt–Zr/HY zeolite catalysts was investigated. The results showed that the bimetallic catalyst Pt-Zr/HY achieved the highest yield and conversion than that of the monometallic (Pt or Zr)/HY catalysts of 70.2 mol% and 82.61 respectively, at 250°C and 1 MPa [5]. The isomerization of Iraqi light naphtha using a Pt/HY–H-Mordenite catalyst was investigated. The results showed that the conversion and the yield increased with increasing the temperature and decreasing the LHSV. Reach the highest yield and conversion of 76.36% and 89.38% respectively at 250 °C and LHSV of 2.46 hr-1 [3].

The current study firstly focuses on preparing Sulfated zirconia and studying the effect of adding MWCNTs to sulfated zirconia on surface area, crystalline structure, Lewis acid sites, particle size and pore volume. Illustrates which are more suitable for isomerization according to the characterization, using; X-ray diffraction (XRD), Fourier transformation infra-red spectroscopy (FTIR), BET Surface Area and Pore Volume, Field Emission Scanning Electron Microscopy (FESEM). Secondly, examine the novel prepared composite sulfated zirconia-HY zeolite catalysts doped by platinum metal to improve the light naphtha isomerization at a temperature range of (140- 200)°C.

2. Material and Methods

2.1. Materials

Iraqi light naphtha was utilized as a feedstock in hydroisomerization experiments. Physical properties and composition analysis of Iraqi light naphtha are listed in Table (1).

Table (1): Physical properties and composition analysis of light naphtha

Physical properties	Value
Initial boiling point	34 °C
End boiling point	120 °C
Sulfur content	1.6 ppm
Density	0.664 g/cm3
Octane number	65
n-Paraffin	44.91 wt%
i-Paraffin	45.42 wt%
Naphthene	3.4 wt%
Aromatic	6.27 wt%

Table (2) shows the used chemicals and their specifications:

Table (2): Chemical compounds specifications

Chemicals	Formula	Molecular weight (g/gmol)	Purity(%)
Zirconium oxychloride octahydrate	$ZrOCl_2.8H_2O$	322.25	99
Multi wall carbon nanotube	C	12.01	90
Ammonia solution	NH_3 aq.	17.03	25
Sulfuric acid	H_2SO_4	98.08	98
Chloro Platinic Acid	$H_2PtCl_6.XH_2O$	---	40% Pt
Bentonite	$AL_2O_3.4(SiO_2).H_2O$	360.31	98
ɤ-nanoalumina	Al_2O_3	101.96	99.99

2.2. Methods

2.2.1. Preparation of Sulfated Zirconia

Sulfated zirconia catalyst was synthesis by precipitating and impregnation method. 150 g of Zirconium Oxy-chloride salt ($ZrOCl_2.8H_2O$) was dissolved in 3750 ml of deionized water.

Ammonia solution with 20% ammonia concentration was added dropwise to the solution with well stirring until the slurry acidity reached pH 8 [7]. The slurry was maintained impregnated at room temperature for about 20 hr, giving extra time for zirconium hydroxide $Zr(OH)_4$ to precipitate. The precipitate of hydroxide was washed with deionized water until reached 7 pH to remove chlorine ions and then filtered. The filtered sample was dried at 100 °C for 18 hr., following, treated with 1M of H_2SO_4 solution by wet impregnating method with 15 ml/g for 1hr. The produced cake was dried at 100 °C for 6 hr and calcined for 3 hr at 650°C at a rate of 10 °C/min to reach a high tetragonal phase and high acidity as studied in [10]. After calcination, zirconium hydroxide S-$Zr(OH)_4$ turned to zirconium oxide S-ZrO_2 as illustrated in Figure (1).

2.2.2. Preparation of Sulfated Zirconia Precipitating with MWCNT

S-ZrO_2/MWCNT catalyst prepared for better catalyst specification with higher tetragonal phase formation and more crystallite. The starting material was $ZrOCl_2.8H_2O$ solution with appropriate amounts of MWCNT (10–30 nm and lengths of 10–30 µm). NH_3.aq. with 20% concentration was gradually dropped in the solution as a precipitating agent until the mixture adjusted to (8) pH, a further time about half an hour on stirring required. After 20 hr of impregnation at room temperature, the obtained $ZrO_2.nH_2O$ solution was washed until pH reached (7), a highly dispersed black colloidal solution dried for 18 h at 100 °C and grounded. 1 M of H_2SO_4 was added to the produced $ZrO_2.nH_2O$/MWCNT as sulfating agent at 15 ml/g with vigorously stirring for 1hr. At last, the powder was calcinated for 3 hr at 650 °C at 10 °C /min rate to obtain S-ZrO_2/MWCNT.

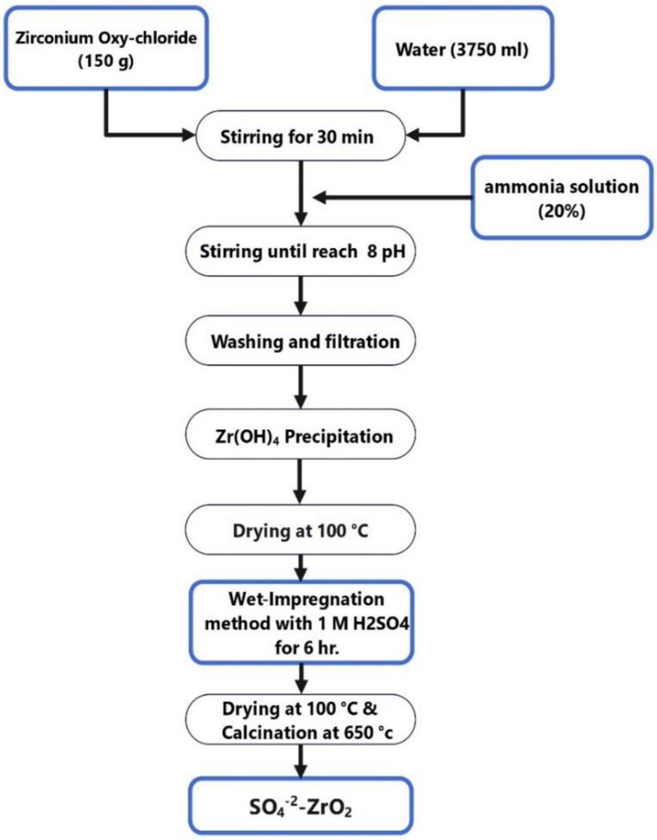


Fig. (1): Block diagram of S-ZrO_2 preparation

2.2.3. Pt/SZ-HY Catalysts Preparation

Novel mesoporous SZ-HY composite catalysts were prepared. It has been characterized the prepared SZ with and without MWCNT and it found that SZ without MWCNT has the best functional group according to the FTIR test and more suitable for isomerization process. HY-zeolite commercial powder with 250 m^2/g surface area and 2.8 Si/Al mole ratio, supplied by KOMPASS was composited with prepared SZ by physical mix at equal wt% ratio. Pt noble metal loaded by wet impregnation method with an aqueous solution of Hexa-chloro-platinic acid, 0.25 g of Pt source was added to 20 g of catalyst composite to load 0.4% of Pt, then 24 hr impregnated, then dried at 100°C for 24 hr and calcined at 550°C for 3 hr. Finally, formation an extrudates catalyst by added 20% bentonite and 5% nano alumina, as binders, then dried and calcined at 100°C and 550 °C respectively.

2.3. Isomerization Process

The catalytic conversion of light naphtha was carried out over Pt/SZ-HY zeolite composite catalysts. 8 g of the extruded composite catalyst particles charged in the stainless steel fixed-bed reactor (68.9 mm inner diameter) between two layers of ceramic balls.

Before the operation process, the catalyst reduction process was performed at 350°C, 10 L/h of hydrogen flow rate and under atmospheric pressure for 3 hr [24]. The light naphtha flow rate was mixed with the hydrogen gas at specified flow rate to achieve 4 H_2/HC molar flow ratio. pre-heater located before the reactor to ensure the feed evaporated. Feed-Hydrogen mixture entered the top of the reactor, distributed uniformly by the ceramic ball, and reacted on the catalyst surface. The product passes through the high-pressure separator and a low-pressure superstore to flash off hydrogen gas, separate liquid and remove most non-condensable gases [25], [26]. The initial products were discarded while the final condensates were collected and sent to the Gas Chromatography Analyzer (GC) when the system stabilized at the desired conditions of temperature (140-200) ºC, pressure of 15 bar, liquid hourly space velocity LHSV of 1 h^{-1} and H2/HC (Hydrogen / light naphtha) mole ratio of 4.

3. Results and Discussions

3.1. X-ray Diffraction (XRD)

XRD patterns of sulfated zirconia show non crystalline structure after drying at 100°C due to the amorphous nature of sulphate content. After calcination at 650 °C the groups of sulfates bind to the surface show more crystallinity and obtain active tetragonal phase for isomerization reaction, this agreed with Liu et al [7] and illustrates in Figure (2) which shows the XRD of sulfate zirconia before and after calcination. Where the zirconia tetragonal phase obtained at the peaks 2θ = 30.2°, 35.3°, 50.2°, 60.2°, and 62.8°, which correspond to (101), (110), (112), (200), and (211) planes. Generally, sulfated tetragonal zirconia has a super acidity however sulfated monoclinic zirconia is about 25% lower than that in the tetragonal phase [26]. The zirconia monoclinic phase obtained at peaks, 2θ = 28.2°, 31.5°, 54.1°, 55.54°, and 65.75° [11], [28], the results clearly show that the tetragonal intensity is higher than the monoclinic intensity which gives a tetragonal SZ catalyst. while Figure (3) illustrates the XRD of sulfate zirconia prepared with MWCNTs at the same conditions. The results showed that the presence of MWCNTs as support for sulfated zirconia catalyst stabilizes the zirconia as the tetragonal phase is modified and gives higher intensities. Also, the results show that sulfated zirconia with MWCNTs achieved a smaller Crystallite Size of 10.5 nm while prepared S-ZrO_2 has a Crystallite Size of 11.06 nm.

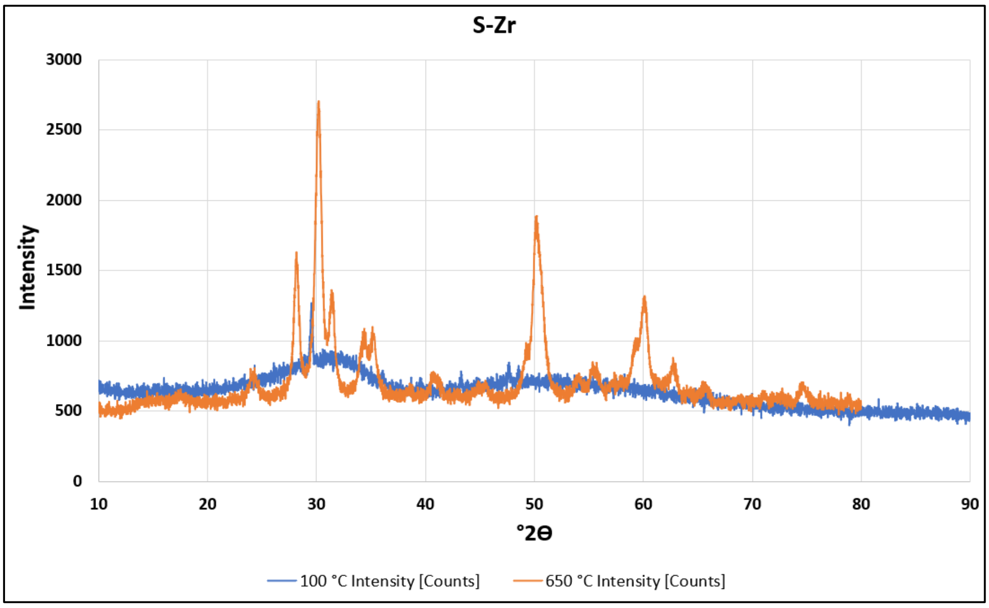


Fig. (2): XRD patterns of Sulfated Zirconia

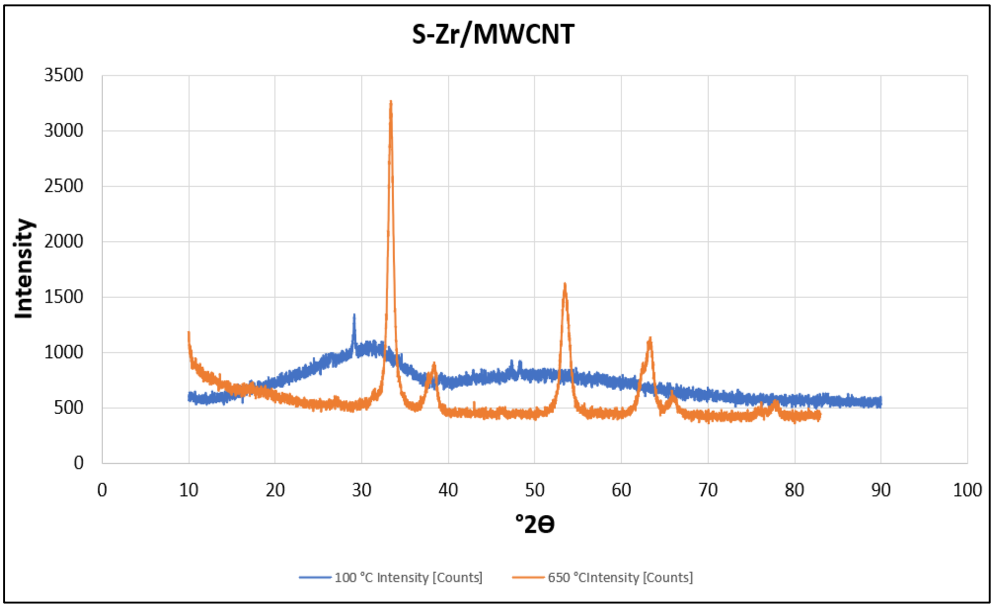


Fig. (3): XRD pattern of Sulfated Zirconia with CNT

3.2. Fourier Transformation Infra-Red (FTIR) Spectroscopy

Figures (4) and (5) show the FT-IR spectra of S-ZrO_2 and S-ZrO_2 /MWCNT. All catalysts exhibited spectral vibration peaks 660–425, 1630, 3400 and 1200 cm^{-1}. According to references[29], a light band 3400 cm^{-1} is consigned to physically adsorbed water, while the band 1630 cm^{-1} corresponds to the existence of the hydroxyl H-O-H vibration peaks of the water molecules[30].

while the vibration peaks that appear at 660–425 cm^{-1} are attributed to the existence of (Zr─O─Zr) bond and the SO_4^{-2} absorption band was attributed to 1200 cm^{-1}, this peak indicated the (S═O) double bond of the sulfated groups at the catalyst [28].

The changes in the peaks at 1200, and 3400 cm^{-1} were attributed to the presence of MWCNT, these peaks were decreased by the use of MWCNTs as support of sulfated zirconia by weakening the acidic bonds and making proton easily release [31]. Based on these results, the S-ZrO_2 is the most suitable catalyst for applications which need high acid catalysts.

The composite characterization bands in Figure (6) show an additional peak at 1065 cm^{-1} assigned to the (Si-O-Si) band and absorption bands peak at 832 cm^{-1} belong to (Si–O–Si) and (Si-O-Al) primary structural units [32], [33].

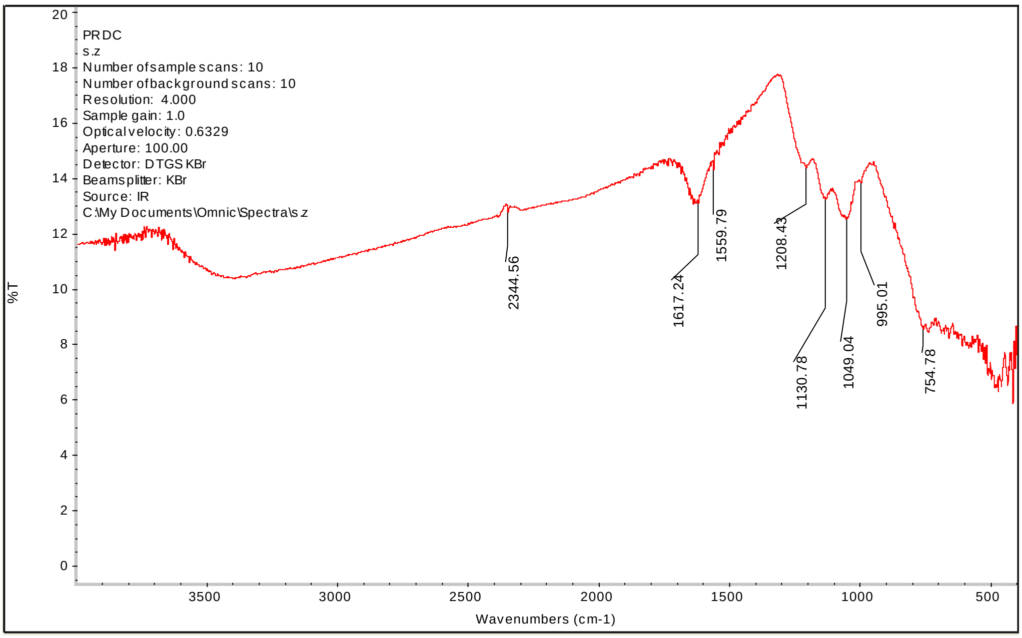


Fig. (4): FTIR pattern of 1 M S-ZrO_2

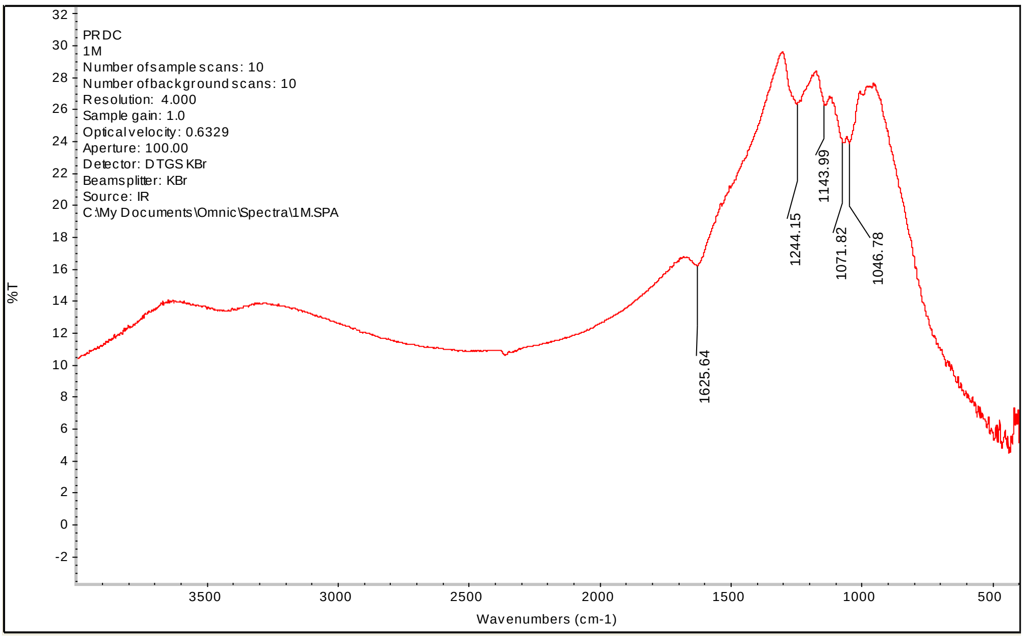


Fig. (5): FTIR pattern of 1 M S-ZrO_2 with MWCNT.

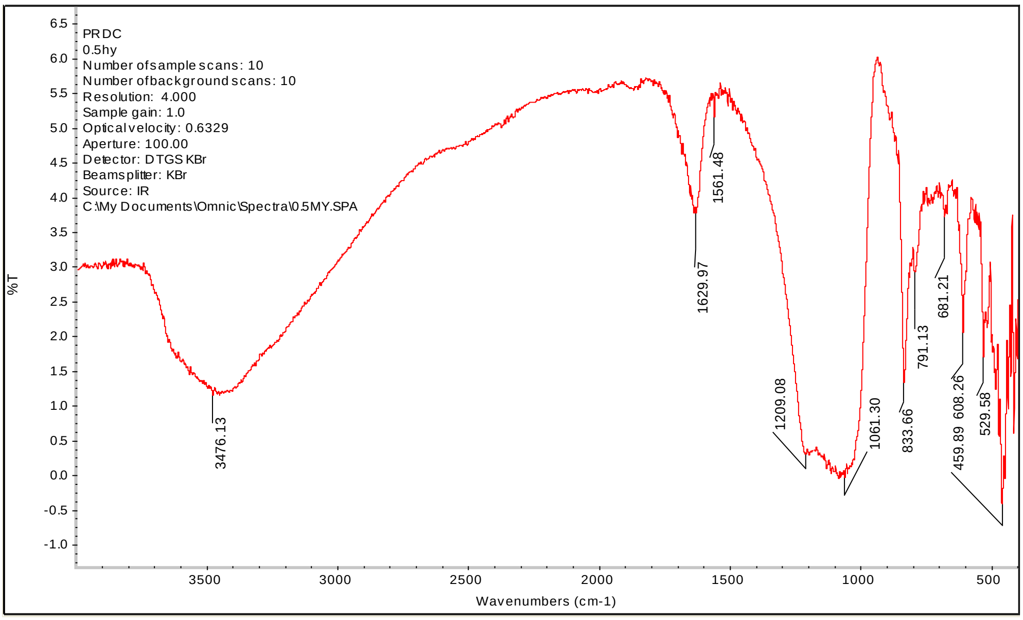


Fig. (6) FTIR pattern of SZ/HY zeolite catalyst composite.

3.3. Surface Area Pore Volume

The effect of MWCNTs on the textural properties of the sulfated zirconia, BET surface area and pore volume was studied using N_2 adsorption-desorption isotherms at −196 °C. According to Table (3), the surface area of the 1 molarity H_2SO_4 prepared catalysts represents the best surface area than zirconia sulfated with (0.1, 0.5 and 2)M of 80.2 m^2/g. The pore volume and surface area of sulfated zirconia are increased with the increase of the sulfuric acid solution molarity and then decreased when the molarity is over 1M.

Added MWCNT during $S\text{-}ZrO_2$ preparation led to an increase in the surface area and also showed a considerable increase in pore volume reaching 87.74 m^2/g and 0.094 cm^3/g respectively, this was achieved because of the use of MWCNTs which led to a high particle distribution, which indicates a big difference in the porosity and surface morphology [20]. Table (4) showed the pore volume and surface area of HY zeolite, 1M sulfated zirconia prepared without added MWCNT which used at preparing the composite catalyst and the composite catalyst.

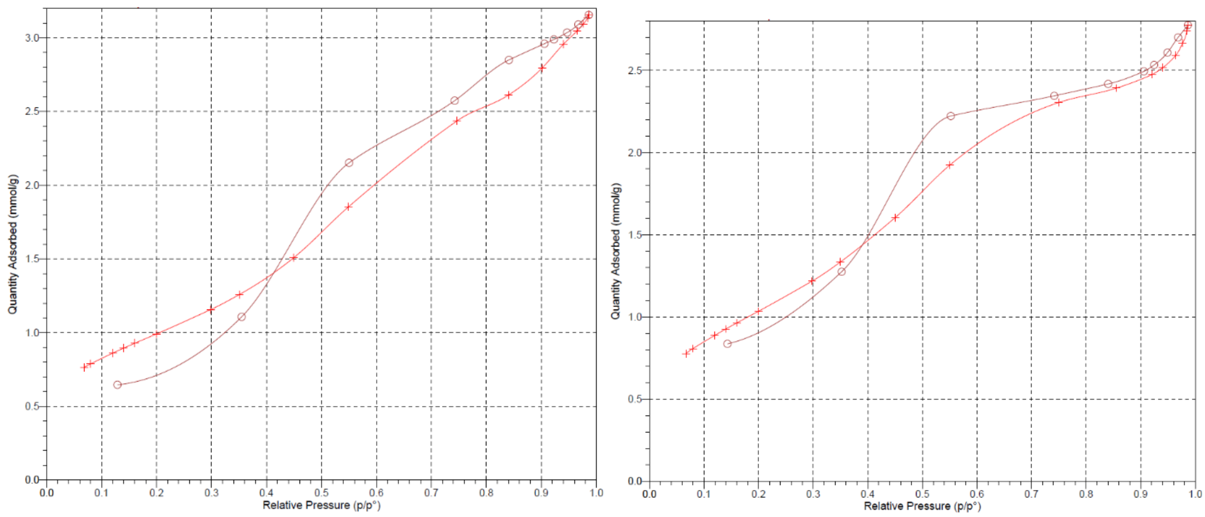
Table (3): Surface area and pore volume of sulfated zirconia catalysts.

Test	Surface area(m^2/g)		Pore volume(cm^3/g)	
Sulfating Molarity	$S\text{-}ZrO_2$	$S\text{-}ZrO_2$/MWCNT	$S\text{-}ZrO_2$	$S\text{-}ZrO_2$/MWCNT
0.1M	61.4	65.98	0.0721	0.0882
0.5M	78.18	84.4	0.079	0.0945
1M	80.2	87.74	0.0789	0.094
2M	59.24	65.63	0.069	0.087

Table (4) Surface area and pore volume of catalysts.

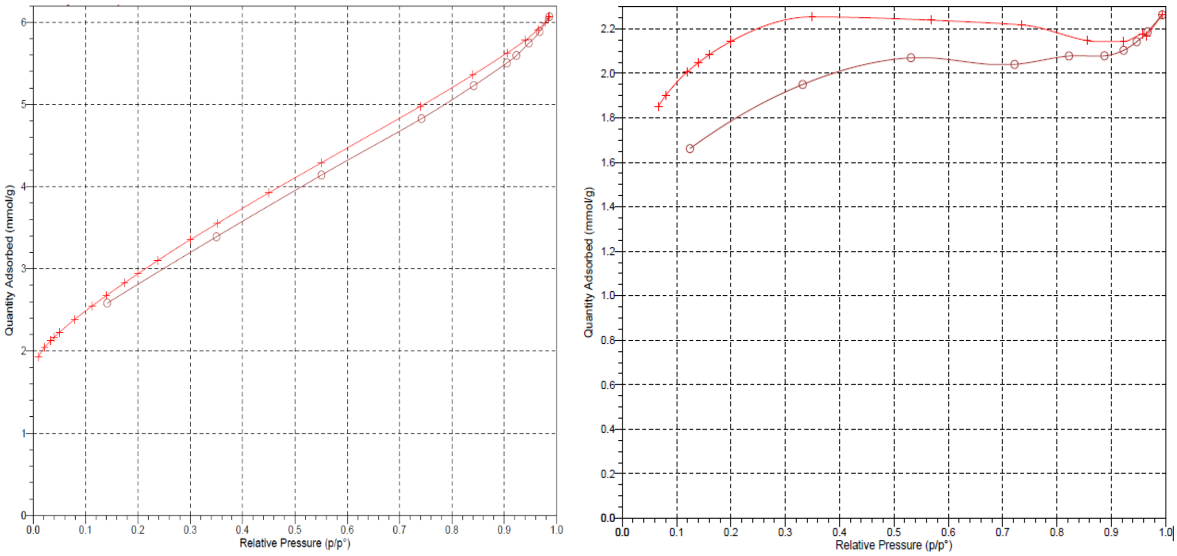
Catalyst	surface area(m^2/g)	Pore volume(cm^3/g)
SZ	80.2	0.0789
HY zeolite	232.52	0.201
SZ/HY	167.64	0.141

On the other hand, Figures (7) and (8) show that according to the IUPAC classification, the adsorption branch of all catalysts is type IV isotherm with a hysteresis loop, which is typical for mesoporous catalysts and indicates the existence of ink-bottle pore formed by non-rigid aggregates of particles[31], [34]. Figure (7) Illustrate A hysteresis loop for S-ZrO_2 is observed at relative pressure of 0.4. This arises from aggregates, which is due to the capillary condensation associated with mesopores, this agrees with[31], [34]. While S-ZrO_2 /MWCNT catalyst showing a wide hysteresis at low relative pressure of 0.4 and a narrow hysteresis loops over higher relative pressure values, this is due to the narrower pore size distribution for S-ZrO_2 /MWCNT. Figure (8) shows a hysteresis loop started at low relative pressure for HY zeolite and a narrow hysteresis loop over higher relative pressure values which agrees with [35]. While SZ-HY composite shows a wide hysteresis loop started at a low relative pressure. While Figure (9) illustrates the BJH (Barrett-Joyner-Halena) pore diameter distribution for S-ZrO_2 is wide and gives a mean value of 3.9682 nm, while S-ZrO_2 /MWCNT gives a narrowed distribution with a lower average pore diameter value of 3.2416 nm.



A. **B.**

Fig. (7): N_2 Adsorption-desorption thermal Analysis of A. S-ZrO_2, B. S-ZrO_2 /MWCNT.



A. **B.**

Fig. (8): N2 Adsorption-desorption thermal Analysis of A. HY zeolite, B. SZ-HY composite.

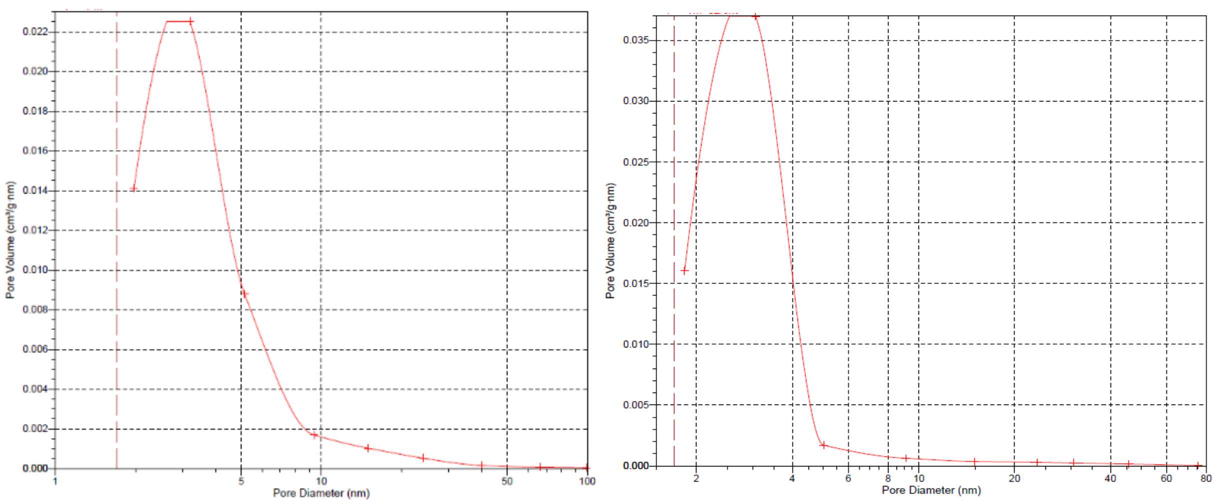
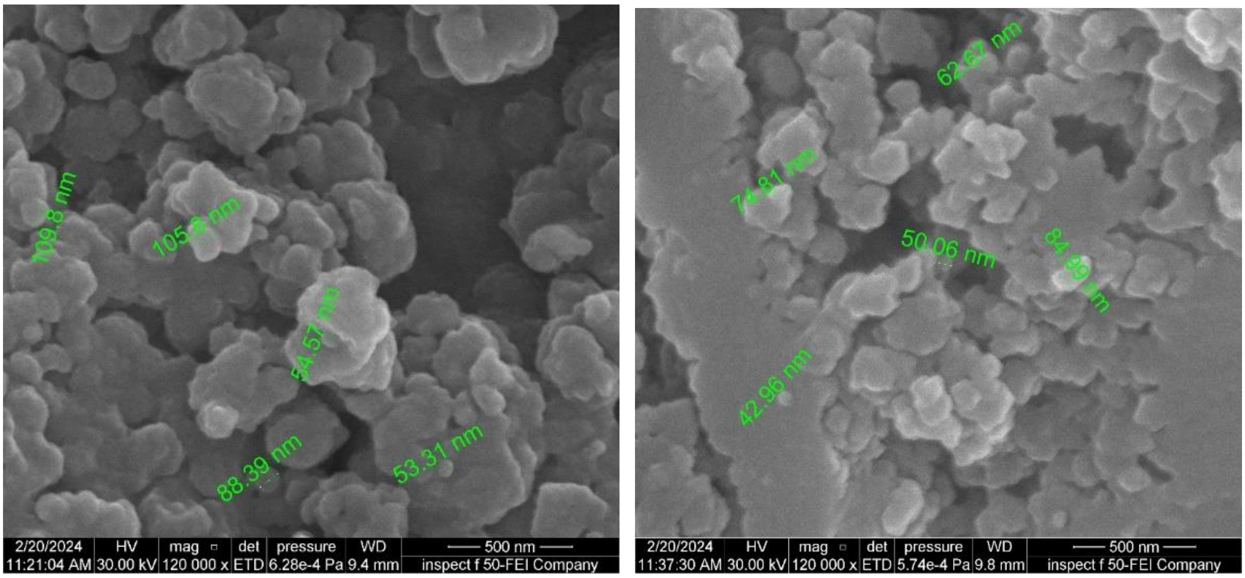


Fig. (9): Pore size distribution of A- S-ZrO_2, B- S-ZrO_2 /MWCNT

3.4. Field Emission Scanning Electron Microscopy (FESEM) and the Energy-Dispersive X-ray Spectroscope (EDX)

The SEM images of both catalysts are presented in Figure (10) Images show a uniform and homogeneous distribution of catalysts with comparatively equal spherical shape sizes. The slight change in shape and size is due to the sulfate ions. It is evident that S-ZrO2 produced with MWCNTs shows slight morphology change in the size of particles this matches with [21]. The catalyst prepared with MWCNTs shows higher particles distributed at the surface and smaller particle sizes range and this agreed with Li [36]. Figure (11) shows the elemental analysis of the catalyst composite by EDX test.



A.S-ZrO_2 **B.S-ZrO_2/MWCNT**

Fig. (10): FSEM images of A. S-ZrO2 and B. S-ZrO2 /MWCNT

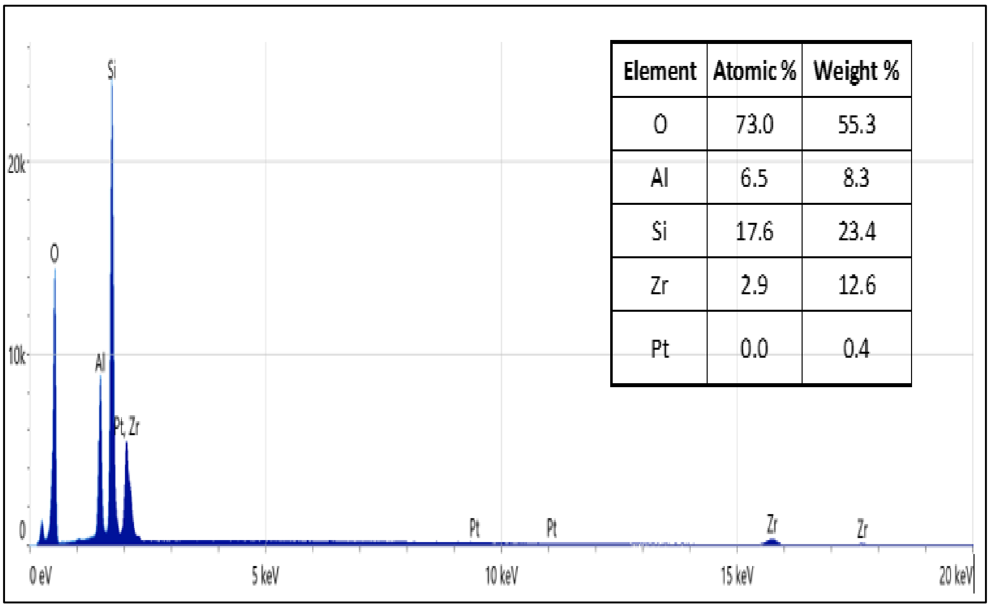


Fig. (11): EDX elemental analysis of Pt/SZ-HY composite catalyst.

3.5. Catalytic Activity Testing

It has been characterized the prepared S-ZrO_2 catalyst with and without MWCNT, it found that S-ZrO_2 without MWCNT has the best functional group according to the FTIR test so it is used in catalyst composited with HY zeolite. SZ-HY loaded with Pt were applied for light naphtha isomerizations at a temperature range of (140-200) °C and under 15 bar. The results in Figure (12) and Table (5) showed that the conversion of light naphtha at 140 °C was 33.7 mol % and reached its maximum value at 160 °C with 45.6 mol% conversion while it slightly reduced to meet 43.3

mol % at 180 °C and reduced to 40.3 mol % at 200°C at a constant LHSV, the isomer decreases with increase temperature due to cracking behavior at a higher temperature, these results are in agreement with Kamel et al. which examined the light naphtha and n-hexane isomerization on Ni-WO_3/Sulfated Zirconia catalyst. The results showed that the maximum conversion was 74% for the light naphtha and 80.1% for n-hexane, at 150 °C, 6 bar, mole ration of H_2/HC of 4 and LHSV of 1 hr^{-1} [13]. Where the conversion to isomer was tested by a GC test. Also, M. Hussain and A.K. Mohammed investigated Iraqi light naphtha isomerization on Ni-Pt/H-mordenite catalyst. The result shows a maximum conversion of 57 wt% at 270 °C and 1hr^{-1} LHSV. However, the reaction shifted towards the hydrocracking above 270 °C [37].

Table (5) PONA analysis for isomerization at 15 bar and LHSV = 1 hr^{-1}.

Temp.	N-paraffine	Isoparaffin	Naphthene	Aromatic
140	37.7	60.58	1.72	3.8
160	24.4	70.76	1.27	3.57
180	25.75	69.32	1.33	3.6
200	26.68	68.13	1.4	3.79

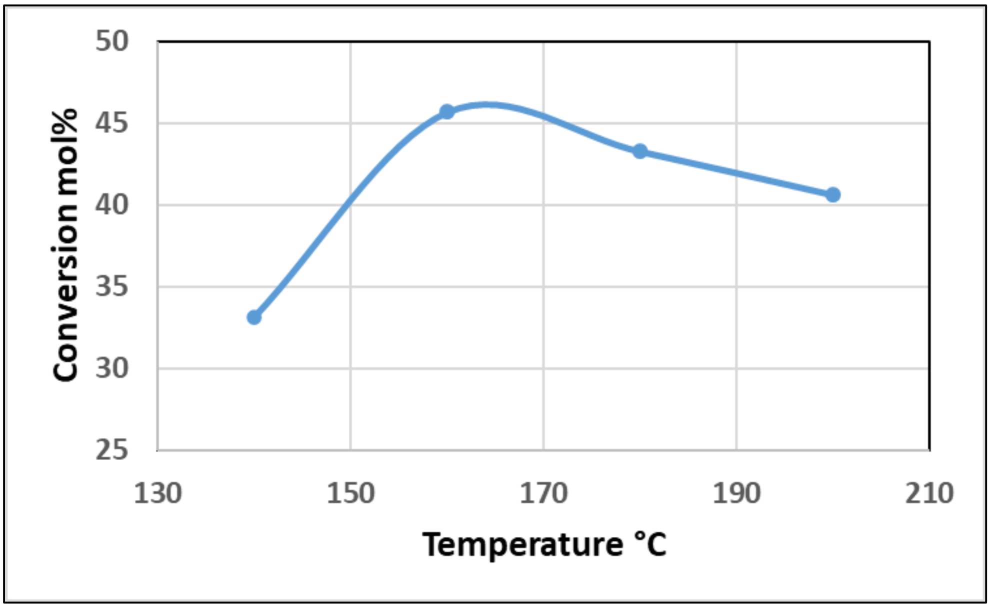


Fig. (12): Temperature effect on conversion to isomer over Pt/SZ-HY catalyst.

4. Conclusions

This study focuses on the synthesize a novel active composite Pt/SZ-HY catalyst for hydroisomerization of light naphtha, that consisted of equal wt% of mesoopore S-ZrO2 and HY zeolite, achieving conversion values of 70.76 mol% at 160°C, 15 bar and 1 hr-LHSV. The results show the effect of adding MWCNTs to the catalysts, the results demonstrate that adding MWCNTs to the acidic catalyst gave catalysts with smaller average diameter, higher surface area and pore volume, lower average pore diameter value, smaller crystal size and decreased Lewis acid sites. Sulfated zirconia without MWCNT is more suitable for isomerization reaction because of the higher functional group. Also confirmed that adding HY zeolite with S-ZrO2 as support can enhance the Bronsted functional group and increased the isomers.

Author Contributions Statement: Sura K. Al-Taweel contributed to the Investigation/ Experiments; Data Curation and Analysis; Writing Original Draft. Haider A. Al-Jendeel contributed to the Methodology; Writing – Review & Editing. Ban A. Al-Tabbakh contributed to the Conception; Methodology; Investigation/ Experiments; Data Analysis and Interpretation. All authors have read and approved the final version of the manuscript.

References

[1] R. S. Hamied, Z. M. Shakor, A. H. Sadeiq, A. A. A. Razak, and A. T. Khadim, "Kinetic Modeling of Light Naphtha Hydroisomerization in an Industrial Universal Oil Products Penex TM Unit", *Energy Engineering*, vol. 120, no. 6, pp. 1371-1386, 2023. https://doi.org/10.32604/ee.2023.028441.

[2] S. A. Al, N. Haider, and A. Al Jendeel, "Hydroisomerization of n - hexane over Pt / TiO 2 catalysts", *Chemical Papers*, vol. 78, pp. 9069–9076, 2024. https://doi.org/10.1007/s11696-024-03727-5.

[3] A. T. Jarullah, A. M. Ahmed, H. M. Hussein, A. N. Ahmed, and H. J. Mohammed, "Evaluation of Synthesized Pt/HY-H-Mordenite Composite Catalyst for Isomerization of Light Naphtha", *Tikrit J. Eng. Sci.*, vol. 30, no. 1, pp. 94–103, 2023. https://doi.org/10.25130/tjes.30.1.9.

[4] Z. Ghaderi, M. H. Peyrovi, and N. Parsafard, "Catalytic study of the n-heptane isomerization over hybrid catalysts", *3ed International Conference on the: New Technologies in the Oil, Gas & Petrochemical Industries*, December, 2021.

[5] Y. H. Khalaf, B. Y. Sherhan Al-Zaidi, and Z. M. Shakour, "Experimental and Kinetic Study of the Effect of using Zr-and Pt-loaded Metals on Y-zeolite-based Catalyst to Improve the Products of n-heptane Hydroisomerization Reactions", *Orbital: The Electronic Journal of Chemistry*, vol. 14, no. 3, pp. 153–167, 2022. http://dx.doi.org/10.17807/orbital.v14i3.17429.

[6] A. N. Ahmed, A. T. Jarulah, B. A. A. Altabakh, A. M. Ahmed, and H. J. Mohammed, "Preparation and Characterization of Metal Carbide Zeolite Composite Catalyst", *Journal of Petroleum Research and Studies*, vol. 13, no. 4, pp. 115–130, 2023. https://doi.org/10.52716/jprs.v13i4.737.

[7] D. B. A. A. Al-Tabbakh and M. M. Dawood, "Synthesis and Characterization of Sulfated Zirconia Catalyst for Light Naphtha Isomerization Process", *Journal of Petroleum Research and Studies*, vol.

12, no. 1(Suppl.), pp. 186–198, 2022. https://doi.org/10.52716/jprs.v12i1(Suppl.).630.

[8] Y. Shao, Y. Li, K. Sun, Z. Zhang, H. Tian, G. Gao, Q. Li, Q. Liu, Q. Liu, and X. Hu, "Sulfated Zirconia with Different Crystal Phases for the Production of Ethyl Levulinate and 5-Hydroxymethylfurfural", *Energy Technology*, vol. 8, no. 3 p. 1900951, 2020. https://doi.org/10.1002/ente.201900951.

[9] J. Liu, Z. Zhao, C. Xu, and J. Liu, "Structure , synthesis , and catalytic properties of nanosize cerium-zirconium-based solid solutions in environmental catalysis", *Chinese J. Catal.*, vol. 40, no. 10, pp. 1438–1487, 2019. https://doi.org/10.1016/S1872-2067(19)63400-5.

[10] S. J. Sekewael, R. A. Pratika, L. Hauli, A. K. Amin, M. Utami, and K. Wijaya, "Recent Progress on Sulfated Nanozirconia as a Solid Acid Catalyst in the Hydrocracking Reaction", *Catalysts*, vol. 12, no. 2, p. 191, 2022. https://doi.org/10.3390/catal12020191.

[11] A. Kumar, Priyanka, J. Mangalam, V. Yadav, and T. Goswami, "Synthesis of sulfated zirconia catalyst using sol–gel technique for alkane isomerization", *Reaction Kinetics, Mechanisms and Catalysis*, vol. 135, pp. 1929–1944, 2022. https://doi.org/10.1007/s11144-022-02254-2.

[12] M. D. Smolikov, V. A. Shkurenok, D. I. Kir'yanov, and A. S. Belyi, "Active surface formation of tungstated zirconia catalysts for n-heptane isomerization", *Catalysis Today*, vol. 329, June 2018, pp. 63–70, 2019. https://doi.org/10.1016/j.cattod.2019.01.036.

[13] S. A. S. Kamel, W. T. Mohammed, and H. Aljendeel, "Synthesis and Characterization of Ni-WO3/Sulfated Zirconia Nano catalyst for Isomerization of N-Hexane and Iraqi Light Naphtha", *Iraqi J. Chem. Pet. Eng.*, vol. 22, no. 4, pp. 1–10, 2021. https://doi.org/10.31699/IJCPE.2021.4.1.

[14] Z. Ma, X. Meng, N. Liu, and L. Shi, "Pd-Ni doped sulfated zirconia: Study of hydrogen spillover and isomerization of N-hexane", *Mol. Catal.*, vol. 449, November 2017, pp. 114–121, 2018. https://doi.org/10.1016/j.mcat.2018.02.003.

[15] A. M. Ahmed, A. T. Jarullah, H. M. Hussein, and A. N. Ahmed, "Mordenite-Type Zeolite from Iraq Sand: Synthesis and Characterization", *Journal of Petroleum Research and Studies*, vol. 13, no. 3, pp. 126-142, Sep. 2023. https://doi.org/10.52716/jprs.v13i3.709.

[16] N. S. A. Zeki, Y. M. Jaeed, and M. N. Abass, "(JPR & S) The Effect of Surfactant on Zeolite Preparation from Iraqi Kaolin", *Journal of Petroleum Research and Studies*, vol. 8, no. 4, pp. 71–86, 2021. https://doi.org/10.52716/jprs.v8i4.263.

[17] K. Yang, H. Li, S. Zhao, S. Lai, W. Lai, Y. Lian, and W. Fang, "Improvement of Activity and Stability of CuGa Promoted Sulfated Zirconia Catalyst for n-Butane Isomerization", *Industrial & Engineering Chemistry Research*, vol. 57, no. 11, pp. 3855–3865, 2018. https://doi.org/10.1021/acs.iecr.7b04590.

[18] P. Wang, W. Zhang, Q. Zhang, Z. Xu, C. Yang, and C. Li, "Comparative study of n -butane isomerization over SO_4^{2-} / Al_2O_3 -ZrO_2 and HZSM-5 zeolites at low reaction temperatures", *Applied Catalysis A: General*, vol. 550, pp. 98–104, 2018. https://doi.org/10.1016/j.apcata.2017.11.006.

[19] N. Liu, Z. Ma, S. Wang, L. Shi, X. Hu, and X. Meng, "Palladium-doped sulfated zirconia: Deactivation behavior in isomerization of n-hexane", *Fuel*, vol. 262, p. 116566, 2020.

https://doi.org/10.1016/j.fuel.2019.116566.

[20] M. Malekkiani, A. Heshmati, J. Magham, F. Ravari, and M. Dadmehr, "One Pot Synthesis of Ternary MWCNTs/ZnO/Chitosan Nanocomposite for Enhanced Photocatalytic Degradation of Organic Dyes and Antibacterial Activity", *Research Square*, 2021. https://doi.org/10.21203/rs.3.rs-882501/v1.

[21] J. Wang, X. Duan, and L. Gong, "Interfacial and Filler Size Effects on Mechanical/ Thermal/ Electrical Properties of CNTs-Reinforced Nanocomposites", *Polymers*, vol. 16, no. 6, p. 808, 2024. https://doi.org/10.3390/polym16060808.

[22] R. Rajwanti and D. Tyagi, "Nano sulfated zirconia over silica for highly effective nano sulfated zirconia", *International Journal of Health Sciences*, vol. 6, no. S3, pp. 8492–8500, May 2022. https://doi.org/10.53730/ijhs.v6nS3.8007.

[23] S. K. Al-Taweel, H. A. Al-jendeel, and B. A. Al-tabbakh, "Synthesis of sulfated zirconia-HY zeolite catalysts doped by platinum metal for hydroisomerization reaction", *Journal of Ecological Engineering*, vol. 26, no. 3, pp. 147–158, 2025. https://doi.org/10.12911/22998993/199586.

[24] Y. Khalaf, B. Sherhan, and Z. Shakour, "Hydroisomerization of n-Heptane in a Fixed-Bed Reactor Using a Synthesized Bimetallic Type-HY Zeolite Catalyst", *Engineering and Technology Journal*, vol. 40, no. 9, pp. 1–13, 2022. https://doi.org/10.30684/etj.2022.132491.1124.

[25] N. M. Al-Mhanna, "Simulation of high pressure separator used in crude oil processing", *Processes*, vol. 6, no. 11, p. 219, 2018. https://doi.org/10.3390/pr6110219.

[26] N. Johnson, U. C. Sunday, and N. H. Andrew, "Harnessing the Power of Pressurized Separation : Revolutionizing Crude Oil Processing and Storage for Optimal Performance", *Research Square*, 2024. https://doi.org/10.21203/rs.3.rs-4169880/v1.

[27] D. Huang, W. Feng, L. Zhang, B. Yue, and H. He, "Insight into the Acidity and Catalytic Performance on Butane Isomerization of Thermal Stable Sulfated Monoclinic Zirconia", *Processes*, vol. 10, no. 12, 2022. https://doi.org/10.3390/pr10122693.

[28] D. S. El-Desouki, A. H. Ibrahim, S. M. Abdelazim, N. A. K. Aboul-Gheit, and D. R. Abdel-Hafizar, "The optimum conditions for methanol conversion to dimethyl ether over modified sulfated zirconia catalysts prepared by different methods", *Journal of Fuel Chemistry and Technology*, vol. 49, no. 1, pp. 63–71, 2021. https://doi.org/10.1016/S1872-5813(21)60009-9.

[29] Y. Cui, X. Dong, Z. Jiang, Y. Suo, W. Zhang, and Y. Wang, "RSC Advances Study on the preparation and n -heptane", *RSC advances*, vol. 14, pp. 4105–4115, 2024. https://doi.org/10.1039/D3RA08454J.

[30] A. K. Hussein, B. A. Al-Tabbakh, and A. T. Jarullah, "Oxidative Desulfurization of Kerosene in Batch Reactor using Magnetite Mesoporous Silica Composite Zeolite Catalyst", *Journal of Petroleum Research and Studies*, vol. 14, no. 3, pp. 75-88, Sep. 2024. https://doi.org/10.52716/jprs.v14i3.804.

[31] Y. Gao, R. Gao, G. Zhang, Y. Zheng, and J. Zhao, "Oxidative desulfurization of model fuel in the presence of molecular oxygen over polyoxometalate based catalysts supported on carbon

nanotubes", *Fuel*, vol. 224, pp. 261–270, July 2018. https://doi.org/10.1016/j.fuel.2018.03.034.

[32] Z. Ghaderi, M. H. Peyrovi, and N. Parsafard, "Effects of Zr, Al, and mordenite on Pt-MCM-48 catalyst in n-heptane isomerization: preparation, characterization and catalytic performance", *Journal of Porous Materials*, vol. 30, no. 5, pp. 1789–1795, 2023. https://doi.org/10.1007/s10934-023-01463-x.

[33] P. Zhu, S. Meier, S. Saravanamurugan, and A. Riisager, "Modification of commercial Y zeolites by alkaline-treatment for improved performance in the isomerization of glucose to fructose", *Molecular Catalysis*, vol. 510, p. 111686, June 2021. https://doi.org/10.1016/j.mcat.2021.111686.

[34] A. Rachmat, R. Dwifahmi, N. Yuliasari, A. Mara, and D. Desnelli, "Preparation of Ga2O3-modified sulfated zirconia mesopore and its application on cellobiose hydrolysis", *Journal of Metals, Materials and Minerals*, vol. 33, no. 3, pp. 12–14, 2023. https://doi.org/10.55713/jmmm.v33i3.1702.

[35] L. Patrylak, O. Pertko, Y. Voloshyna, A. Yakovenko, V. Povazhnyi, O. Melnychuk, and K. Zlochevskyi, "Linear hexane isomerization over bimetallic zeolite catalysts", *Chem. Chem. Technol.*, vol. 15, no. 3, pp. 330–335, 2021. https://doi.org/10.23939/chcht15.03.330.

[36] L. Shaolong, L. Yuchen, C. Qiang, G. Fanchuan, W. Yixuan, W. Jingyu, Z. Ye, G. Ruiyu, and G. Jiaru, "Preparation of Pt/ CNT Catalyst with High Dispersion Structure via Plasma Jet", *Diamond and Related Materials*, p. 110674, 2024, https://doi.org/10.1016/j.diamond.2023.110674.

[37] H. M. Hussain and A. A.K. Mohammed, "Experimental Study of Iraqi Light Naphtha Isomerization over Ni-Pt/H-Mordenite", *Iraqi J. Chem. Pet. Eng.*, vol. 20, no. 4, pp. 61–66, 2019. https://doi.org/10.31699/IJCPE.2019.4.10.