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Synthesis of sulfated zirconia-HY zeolite catalysts doped by platinum metal for hydroisomerization reaction

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ABSTRACT

In this study, active catalysts of platinum supported on sulfated zirconia and HY zeolite (Pt/SZ-HY), and platinum supported on sulfated zirconia – mHY zeolite (Pt/SZ-mHY) were prepared using two different mesopore HY zeolite and sulfated zirconia (SZ). The synthesized catalysts were characterized by X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FTIR), BET surface area and pore volume, field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) analysis. The characterisation results showed that adding sulfated zirconia to HY zeolite as a composite increased the active sites on the catalyst and increased the activity of isomerization. Isomerization experiments were studied using a different range of temperature (140–200 °C), constant pressure and LHSV of 15 bar and 1 hr^{-1}, respectively. The results showed Pt/SZ-HY composite catalyst gives 17.95 mol% conversions for n-hexane and 27.5 mol% for n-heptane at optimum conditions of 160 °C, 15 bar and LHSV of 1 hr^{-1}. On the other hand, the composite catalyst Pt/SZ-mHY with smaller pore size achieved higher conversion to isomers, also proved that the conversion to isomer was more for n-heptane than n-hexane, which achieved 73.05 mol% conversion of n-heptane, while 57.91% for n-hexane at the optimum operation conditions.

Keywords: sulfated zirconia, HY zeolite, iisomerization, catalyst composite, bifunctional.

INTRODUCTION

One of the most important processes to produce gasoline with high quality is isomerization process, which works well for producing unarguably indispensable high-quality gasoline while minimizing environmentally harmful exhausts and maximizing octane number to meet the necessities of high-compression motors [Hamied et al., 2023]. Isomerization process converts low octane number linear alkanes to high octane number branched alkanes [Jarullah et al., 2023] by rearranging the hydrocarbon molecule's structure while keeping the same molecular weight and chemical formula [Mohammed et al., 2009]. For instance, the octane number for n-hexane is 25, while for 2.3-dimethyl butane iso-hexane is 106.

A highly acidic bifunctional catalyst is required for the isomerization process [Mohammed et al., 2008], which consists of an active metallic substance such as platinum, palladium, etc., distributed over an acidic support such as zeolite, sulfated zirconia and chloride alumina [Al-naib and Al-jendeel, 2024]. Platinum is one of the most successful industrial eco-friendly metals for isomerization catalytic processes to produce high-octane branched products [Yakun et al., 2024]. Hydrogenation and dehydrogenation steps were increased by increasing metal sites, while skeletal rearrangement of the acidic structure takes place through the acidic site on the surface of the catalyst. Exposing the reactants to a series of isomerization reactions increases branching [Al-naib and Al-jendeel, 2024].

In current petroleum refining and industrial processes, zeolite catalysts are commonly loaded with platinum (Pt) as a noble metal that produces a highly efficient bifunctional catalyst. The metal loading on zeolite is generally performed via the ion-exchange process [Khalaf et al., 2023].

Noble metals provide the hydrogenation /dehydrogenation function. Furthermore, metals can activate H-H, C-C, and C-H bonds, 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, increase activity and selectivity, and prolong the catalyst lifespan [Khalaf et al.,2022; Liu et al., 2019]. Platinum noble metal (while being costly) is a necessary catalyst material as an active metal component because of its activity and stability [Ahmed et al., 2023; Ahmedzeki and Al-Tabbakh, 2016].

Zeolite is a porous media consisting of crystalline aluminosilicates with the property of molecular sieving and a high surface area [Hammadi and Shakir, 2019]. Zeolite with large pores produces a large yield of cracked products for the n-alkane isomerization process. This could be due to shape selectivity or excessive acid sites that would induce cracking [Al-jendeel and Hussein, 2021], while a smaller pore volume leads to higher isomerization, lower aromatization activity and cracking activity [Aljendeel and Hussein, 2018; Hussain and Mohammed, 2019]. However, zeolite dealumination shows strong Bronsted acid sites, which leads to enhanced activity in yielding the desired products in acid-catalyzed reactions [Pastvova et al., 2017; Ayad et al., 2020]. Sulfated zirconia metal oxides have caught attention because their amphoteric surface makes them excellent catalyst support, and they have unique properties like strong chemical resistance, high corrosion resistance, strong mechanical properties, low thermal conductivity, and high thermal stability [Kumar et al., 2022].

Isomerization process essential variables include catalyst type, promoter type, feed compositions, and operating conditions like pressure, reactor temperature, feed octane number, liquid hourly space velocity (LHSV), benzene content, and a hydrogen /hydrocarbon ratio. Also, it must be noted that the operation temperature should not be too high and controlled in a known range because isomerization is an exothermal reaction, and the isomer formation rate raises the temperature [Fathy and Soliman, 2019; Al-Hassany, 2009].

Pastvova et al. [2017] studied the effect of Si/Al ratio on isomerization, and it was found that dealumination improved the accessibility of the OH groups and the yield of branched isomers. Furthermore, Khalaf et al. [2022] examined that adding SZ as loaded metal to Pt/zeolite catalysts for hydroisomerization reaction of n-heptane improves the acidity and increases the conversion of isomers achieved 82.61% at 250 °C and 1 MPa. Jarullah et al. [2023] examined the isomerization of naphtha on Pt/HY-H-Mordenite catalyst. It was found that the yield and conversion increased with decreasing the LHSV and increasing the temperature, giving 89.38% conversion at 250 °C and LHSV of 2.46 hr^{-1}. Voloshyna et al. [2023] investigated the isomerization of n-hexane on a Ni/mordenite zeolite catalyst. The results showed that the catalyst treated with low-concentration acid increased the micropore, while the higher-concentrated acid increased the mesoporosity of the catalyst. 5 mol/L HCl concentration gives the best isomerization yield of 20%. While Kumar et al. [2022] examined the isomerization of n-hexane on WPA/sulfated zirconia catalyst, loading with 10 to 60 wt% of WPA, The results indicate that modification with 55% WPA gives the best results of 30% conversion and 60% selectivity at 225 °C and LHSV of 1 hr^{-1}. Patrylak et al. [2021] investigated the isomerization of n-hexane on the MFI zeolite catalyst. The results showed an inverse relationship between temperature and yield, and the best content of loaded Ni and Pd was 0.5 wt%, which achieved 44 wt % yield and 93% selectivity.

In this study, sulfated zirconia as an important catalyst with high isomerization performance because of its high activity, selectivity, super acidity, stability, in addition to the absence of a necessity to add chlorogenic compounds during the isomerization reaction. One of the methods for enhancing the isomerization catalyst efficiency is by distributing the active component sulfated zirconia in the porous matrix of the support. Sulfated zirconia was synthesized using precipitation and impregnation method aimed to evaluate the activity of prepared composite of sulfated zirconia-HY zeolite catalysts as support doped by platinum as active metal, which is necessary for hydrogenation and dehydrogenation, examine the activity of the composite catalyst on the isomerization of n-hexane and n-heptane at different operating temperature also investigated the effect of catalyst pore size and Si/Al ratio.

Experimental work

Chemicals

The chemicals used are listed in Table 1

Table 1. Chemicals used with their specifications

Chemicals	Formula	Molecular weigh (g /mol)	Purity %	Supplier
Zirconium oxychloride octahydrate	$ZrOCl_2.8H_2O$	322.25	99.5	(Srlchem) India
Ammoniasolution	NH_3 aq.	17.03	25	CDH (India)
Sulfuric acid	H_2SO_4	98.08	98	HIMEDIA (India)
Chloro Platinic Acid	$H_2PtCl_6.XH_2O$	---	40% Pt	(CDH) India
n-hexane	C_6H_{14}	86.18	99	(Supelco) Germany
n-heptane	C_7H_{16}	100.205	99	(J.T.Baker) Germany
Bentonite	$AL_2O_3.4(SiO_2).H_2O$	360.31	98	(CDH) India
ɤ-nanoalumina	Al_2O_3	101.96	99.99	(CDH) India

Catalyst preparation

An acidic sulfated zirconia solid catalyst was prepared using the precipitating and impregnation method. The first step was the preparation of zirconia hydroxide by dissolving 20 g of zirconium oxy-chloride precursor salt in 500 ml of deionized water. Then, 20 wt% of ammonia solution [Al-Tabbakh and Dawood, 2022] was added dropwise until the pH of the solution will be 8 [Yang et al., 2018]. After aging the suspension for 20 hr at room temperature, the zirconium hydroxide precipitate was filtered, washed with deionized water to remove chlorine ions and impurities, dried at 100 °C for 18 hr and grounded the produced hydrous zirconia $Zr(OH)_4$ to a fine powder. Subsequently, this powder was sulfated using a wet impregnating method at a 15 ml/g ratio [Kumar et al., 2022; Ma et al., 2018] of 1 M H_2SO_4 solution for 1hr. Then, it dried at 100 °C for 6 hr and calcination at 650 °C for 3 hr [Ma et al., 2018] at a 10 °C/min rate to produce zirconium oxide ZrO_2.

SZ-HY composite catalysts preparation

Mesoporous SZ-HY composite catalysts were prepared to improve catalyst performance. Two types of HY zeolite were used. The first one was (CBV600) HY-zeolite commercial powder with a unit cell of 24.35 Å and a surface area of 660 m^2g^{-1}, supplied by Zeolyst International (UWE Ohlrogge (VF)) composited with prepared SZ by physical mix at equal wt% ratios of SZ and HY zeolite. The second zeolite type was HY-zeolite commercial powder (mHY) with a surface area of 250 m^2g^{-1}, supplied by KOMPASS composited with prepared SZ by physical mix at equal wt% ratio.

Loading Pt on catalyst composite

Pt metal was loaded by impregnated with an aqueous solution of hexa-chloro-platinic acid by wet impregnation, 0.25 g of Pt source (40% Pt content) was added to 20 g of catalyst composite to load 0.4% of Pt, then impregnate the solution for 24 hr, dried at 100 °C and calcined at 550 °C for 3 hr. After completing the synthesis process 20 g of loaded bifunctional composite catalyst powder was mixed with 5% nano alumina, and 20% bentonite as binders to achieve an extrudates catalyst. Fine powder cannot be used directly in the reactor because of the back pressure problem [Khalaf et al., 2022]. The final steps were dried and calcined at 100 °C and 550 °C respectively. Prior to the operation process, reduction of the catalyst was performed. Reduction conditions are atmospheric pressure, 350 °C and under hydrogen flow rate for 3 hr [Khalaf et al., 2022].

Isomerization experiments

The catalytic conversion of n-alkane was carried out over sulfated zirconia-HY zeolite composite catalysts loaded with platinum metal. 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 to achieve a uniform flow, an effective catalyst surface area, and to fill the dead volume of the reactor.

Before the reaction, the catalyst reduction process was performed at atmospheric pressure, 350 °C and under 10 L/h of hydrogen flow rate. The feed flow rate of (n-hexane or n-heptane) was set on and mixed with the hydrogen gas at specified flow rates to achieve H_2/HC molar flow ratio of 4. Pre-heater section was located before the reactor to ensure the feed evaporated. Then the feed-H_2 mixture entered from the top of the reactor, distributed uniformly by the ceramic ball, and reacted on the catalyst surface. The out 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 [Al-Mhanna, 2018; Alhassani et al., 2018] as illustrated in Figure 1. The initial products were discarded while the final condensates were collected and sent to the gas chromatography analyzer when the system stabilized at the desired conditions of temperature 140–200°C, pressure of 15 bar, liquid hourly space velocity LHSV of 1 h^{-1} and H_2/HC (Hydrogen/n-hexane or n-heptane) mole ratio of 4.

Catalysts characterization

XRD (Aeris-Malvern, UK) characterized the catalyst crystal structure using Cu radiation operated at 40 kV and 8 mA. Diffraction lines 2Ө range of 5–80° with a scanning speed of 0.01/6 s to determine the crystalline phase of the catalyst.

According to ISO 9277-2010, the BET-specific surface area was determined using adsorption-desorption. Total pore volume, pore size, and surface area were measured on Micrometrics (ASAP2020, USA) after the samples were pretreated for 200 °C in a vacuum.

FT-IR method determined the functional groups of molecules to investigate the acidity properties of samples using (IR-Affinity, Shimadzu, Japan) spectrophotometer. The sample was examined in the range of 400– 4000 cm^{-1}.

The SEM and EDX tests investigate the morphology of the surface and the elemental analysis by scanning the sample with a high-energy beam in a raster scan pattern. The catalyst samples tested by Axia ChemiSEM-Thermo Fisher / USA were conducted through Inspect F50-FEI/USA and Energy-dispersive X-ray spectroscope.

RESULTS AND DISCUSSIONS

Figure 2 shows the XRD patterns of SZ before and after calcination. A crystalline nature is observed after calcination at 650 °C with a diffraction band corresponding to the tetragonal and monoclinic zirconia. In contrast, an amorphous nature is observed before calcination due to the sulphate amorphous nature, which is agreed with [Al-Tabbakh and Dawood, 2022]. The increased in peaks 30.2° and 35.3° indicate strong lewis acidity which increase the hydrogenation reaction [Aljandeel and Hussein, 2018].

The bands obtained at 2Ө are 30.2°, 35.3°, 50.2°, 60.2°, and 62.8° representing the tetragonal phase of zirconia which correspond to (101), (112),

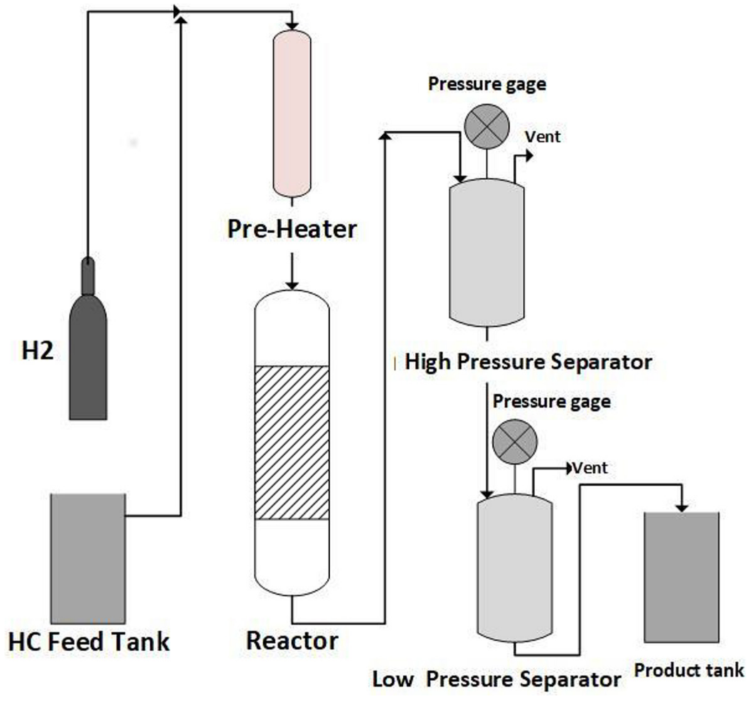


Figure 1. Schematic diagram of isomerization unit

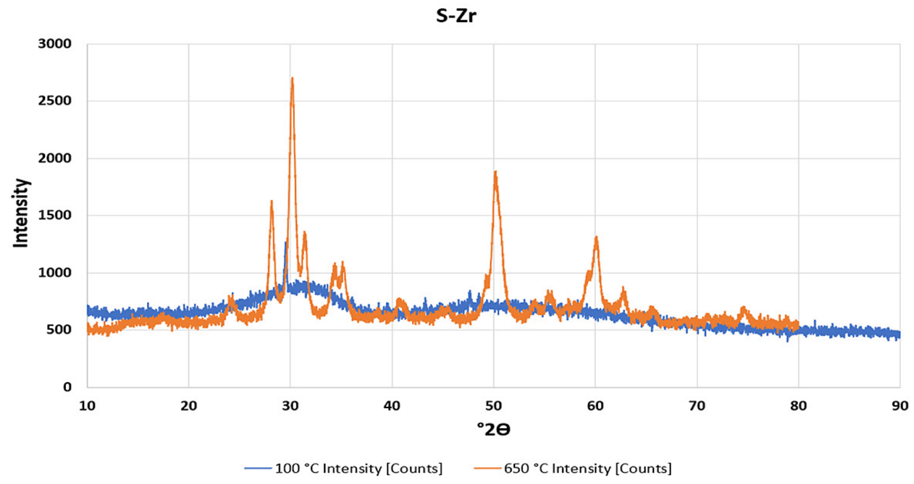


Figure 2. XRD patterns of synthesized SZ

(110), (211) and (200) planes, however, the bands at 28.2°, 31.5°, 54.1°, 55.54°, and 65.75°are consigned to the monoclinic phase [Kumar et al., 2022; El-Desouki et al., 2021]. Figure 3 shows the FTIR spectra of the prepared SZ and composite catalysts. In the sulfated-group stretching region, the peak at 1200 cm^{-1} could be attributed to the SO_4^{-2}, and this peak indicated the double bond (S=O), which represents the super acidity of sulfated zirconia [El-Desouki et al., 2021], and 660–425 cm^{-1} was assigned to the (Zr-O-Zr) bond vibration [Kumar et al., 2022]. A deformation vibration of physically adsorbed water can be observed at 3400 cm^{-1} and also at 1630 cm^{-1}, which corresponds to the existence of the hydroxyl H-O-H vibration peaks of the water molecules [Cui et al., 2024].

The characterization bands of the composite show an additional peak at 1065 cm^{-1} which is assigned to the (Si-O-Si) band. Also, the absorption bands peak at 832 $cm^{-1,}$ which belong to (Si–O–Si) and (Si-O-Al) primary structural units, and these are agreed with [Ghaderi et al., 2023; Zhu et al., 2021]. Figures 4 and 5 show the FT-IR of the synthesized composites. The figures showed that the intensities were significantly higher at Pt/SZ-mHY than Pt/SZ-HY composite. For all composite catalysts, the high functional group is due to the HY-zeolite high acidity (Bronsted type), and the second effect comes from SZ high acidity (Lewis type) [Khalaf et al., 2022]. On the other hand, Table 2 shows the surface area and pore volume of the synthesized SZ and the composite catalysts, in which the surface area of composites showed that the Pt/SZ-HY composite has a higher surface area and pore volume value of 378.45 $m^2 \cdot g^{-1}$ and 0.259 $cm^3 \cdot g^{-1}$ respectively. Correspondingly, Barrett-Joyner-Halena (BJH) distribution of pore diameter was in the

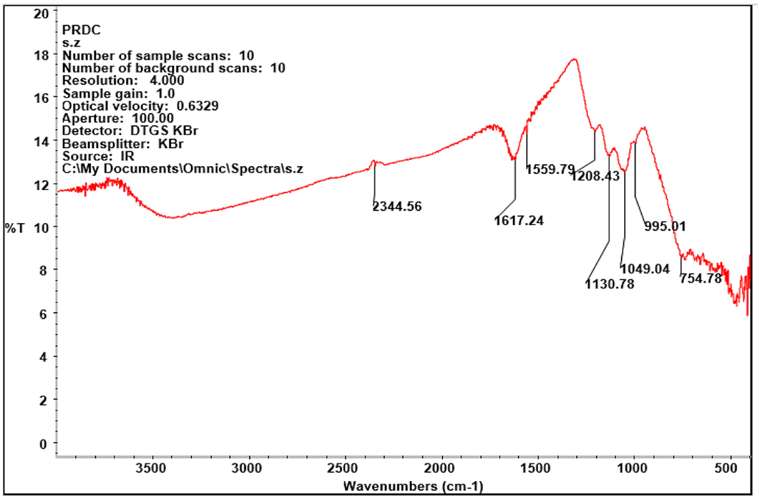


Figure 3. FT-IR pattern of prepared SZ

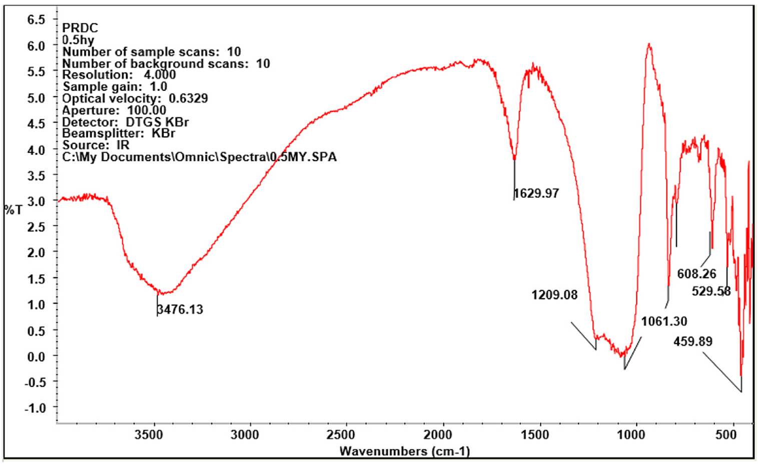


Figure 4. FT-IR pattern of SZ-mHY composite

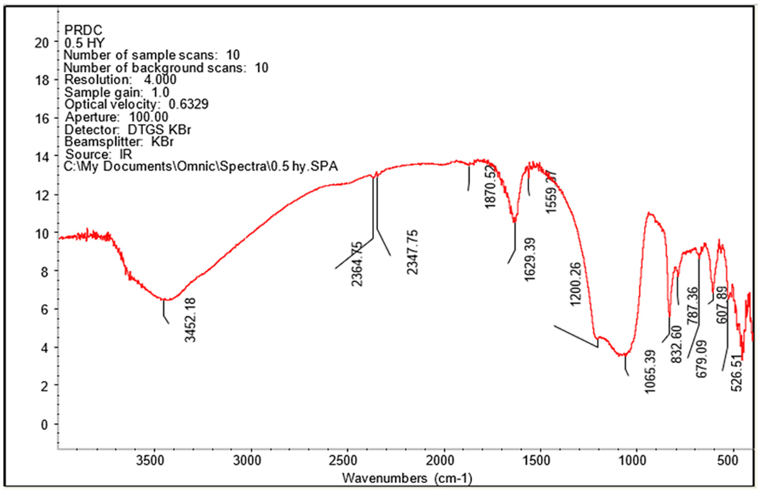


Figure 5. FTIR pattern of SZ-HY composite

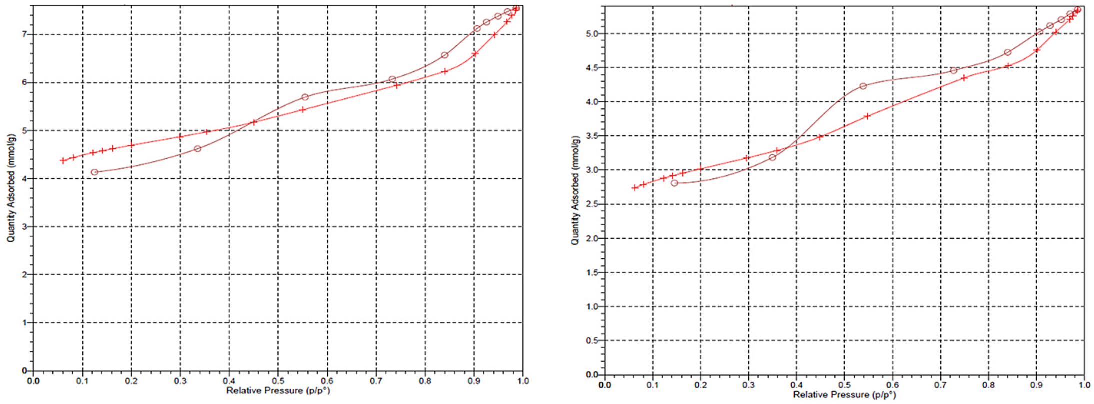
mesoporous range for all catalysts, and this is because the pore diameter lies between 2 and 50 nm, which is in the mesoporous range [Oloye et al., 2018], which means more spaces among particles, increasing the pore volume of the catalyst. Therefore, because of its huge surface area, the synthesized catalyst might serve as a highly chemically active catalyst for the isomerization process [Hammadi and Shakir, 2019]. SZ pore diameter is smaller than that of HY zeolite, which is close to mHY. The smaller pore diameter helps to make the composite more suitable for alkane isomerization.

Figure 6 shows low-temperature N_2 adsorption/desorption isotherm. The hysteresis phenomenon is a low-temperature nitrogen adsorption isotherm that is related to the capillary condensation at the mesoporous structures. Closed and unclosed hysteresis loops are seen in tested samples and assigned to the interconnected pore feature, the actuality of the ink-bottle pore, and the tensile strength effect. The non-rigid structure is the reason for the existence of the ink-bottle pore. IUPAC classification mentioned Six types of adsorption/desorption isotherms to be the relation between the porous material and the adsorption shape, and it turns out that the composite samples present type IV behavior with a hysteresis loop, which is observed in mesoporous materials, and this agrees with [Chen et al., 2018; Lassoued et al., 2023]. The isotherm hysteresis and the pore size between 2 and 50 nm indicate the presence of mesoporous catalyst [Juanjuan, 2010].

Figure 7 shows the FESEM, which shows the high crystallinity, uniform and homogeneous distribution. At the same time, there is some agglomeration in a block for the

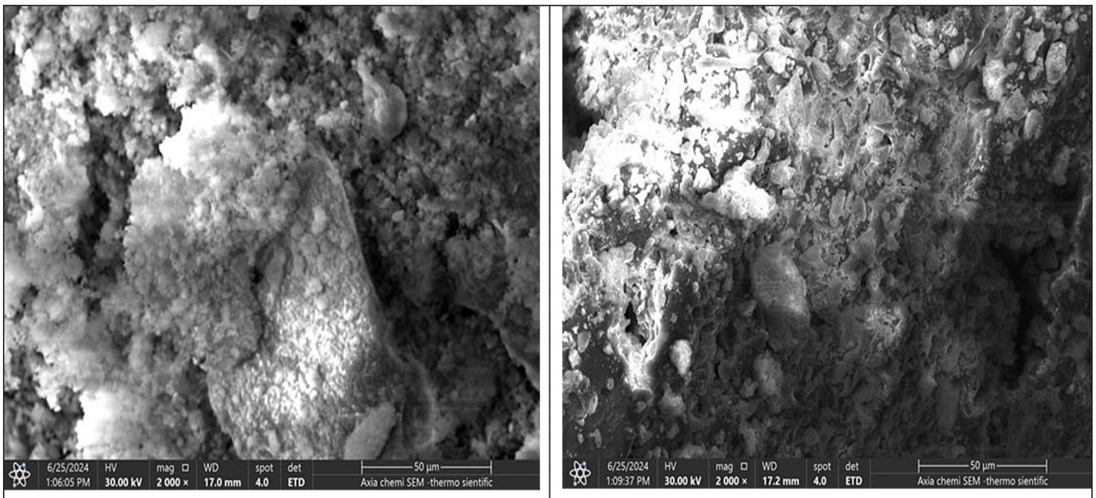
Table 2. Surface area and pore volume of prepares SZ and composite catalyst

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Average pore diameter (nm)
SZ	80.2	0.0789	3.9682
HY Zeolite	648.13	0.399	5.6330
Pt/SZ-HY	378.45	0.259	4.4246
mHY zeolite	232.52	0.201	3.7114
Pt/SZ-mHY	167.64	0.141	3.6182



(a) (b)

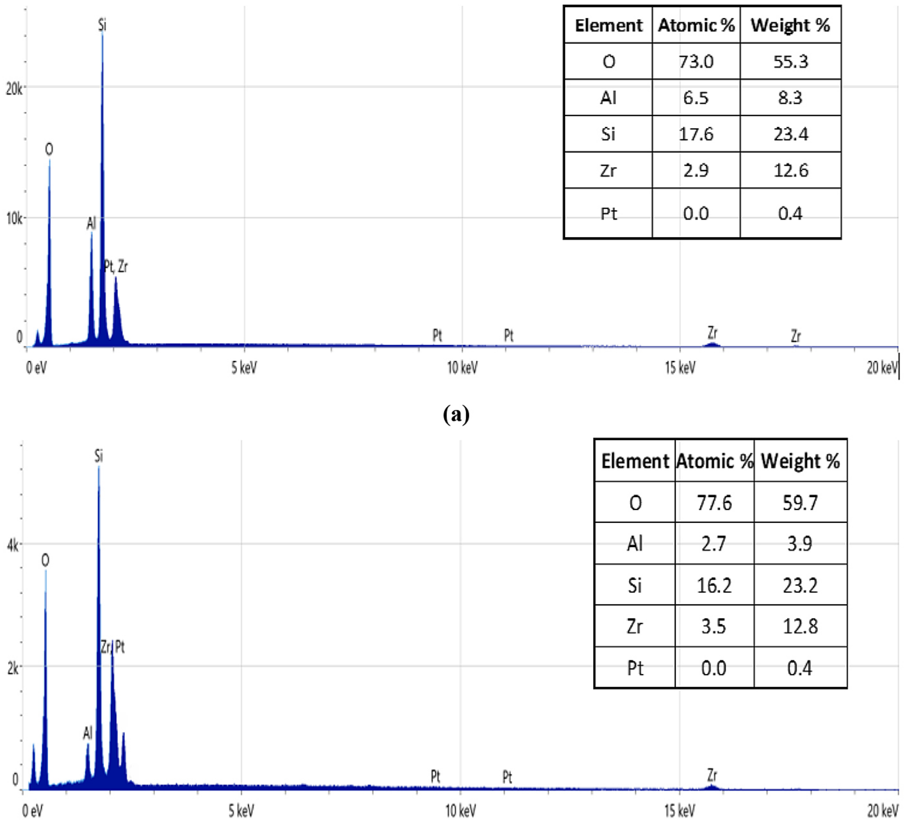
Figure 6. Adsorption-desorption thermal analysis of (a) Pt/SZ-HY and (b) Pt/SZ-mHY



a.Pt/SZ-HY b.Pt/SZ-mHY

Figure 7. FSEM images at 2000× magnifications: (a) Pt/SZ-HY and (b) Pt/SZ-mHY

synthesis Pt/SZ-HY and Pt/SZ-mHY composites catalysts surface. Figure 8 shows the elemental analysis of the catalyst composites by EDX test. The analysis showed that the two composite catalysts had the same element wt% of pt metal loaded onto the surface using the wetness impregnation method, and showed that the difference between the two catalysts was in the silica to alumina ratio. Pt/SZ-mHY catalyst had a higher silica to alumina ratio than Pt/SZ-HY catalyst. Higher Si/Al ratios increase the thermal stability, the solid acidity of the zeolite and give smaller pore width [Ayad et al., 2020]. Zirconia concentration% is approximately the same in the two catalyst composites with 0.4 analysis error %.



Element	Atomic %	Weight %
O	73.0	55.3
Al	6.5	8.3
Si	17.6	23.4
Zr	2.9	12.6
Pt	0.0	0.4

(a)

Element	Atomic %	Weight %
O	77.6	59.7
Al	2.7	3.9
Si	16.2	23.2
Zr	3.5	12.8
Pt	0.0	0.4

(b)

Figure 8. EDX elemental analysis of (a) Pt/SZ-HY and (b) Pt/SZ-mHY catalyst composite

Catalytic activity testing

Sixteen hydroisomerization experiments of n-hexane and n-heptane were conducted using Pt/SZ-mHY and Pt/SZ-HY composite catalysts at a temperature range of 140–200 °C, constant pressure of 15 bar and 1 hr^{-1} LHSV. The products were condensed and by a GC test which explains the conversion to isomer.

Activity for isomerization of n-hexane

Pt/SZ-HY composite catalyst runs with n-hexane. The conversion to i-paraffin was started at 140°C with a low conversion of 9.75 mol% and increased to 17.95 mol% at 160 °C, representing the maximum conversion for n-hexane. Then, it decreases to 10.26 mol% and 7.32 mol% at 180 and 200 °C respectively.

The Pt/SZ-mHY composite catalyst gives higher conversion for n-hexane, achieving 39.82 mol% at 140 °C. At 160 °C, it reached a maximum value of 57.91 mol%, then decreased to 51.36 mol% and 43.45 mol% at 180 and 200 °Crespectively, all results are illustrated in Figure 9.

The conversion of n-hexane increased from 17.95 mol% in Pt/SZ-HY catalyst to 57.91 mol% in Pt/SZ-mHY catalyst at the optimum operation temperature of 160 °C; this occurred for two reasons; first, the higher Si/Al ratio increases the locations of Bronsted acid in the zeolite, leading to increased acidity of catalyst, this is agreed with Pastvova et al. [2017]. The second reason is that a smaller pore size is more suitable for isomerization reactions because smaller pore allow diffusion of smaller molecules, and a larger pore is preferred for cracking reactions, which is agreed with Voloshyna et al. [2023].

Activity for isomerization of n-heptane

Pt/SZ-HY composite catalyst runs with n-heptane; the conversion to isomers at 140 °C was 18.86 mol% and increased to 27.5 mol% at 160 °C, then, it decreased to 24.56 mol% and 17.06 mol% at 180 and 200 °C respectively.

The results obtained indicate that the conversion of Pt/SZ-mHY composite catalyst gives higher conversion for n-heptane which achieved 57.4 mol% at 140 °C. At 160 °C reached its

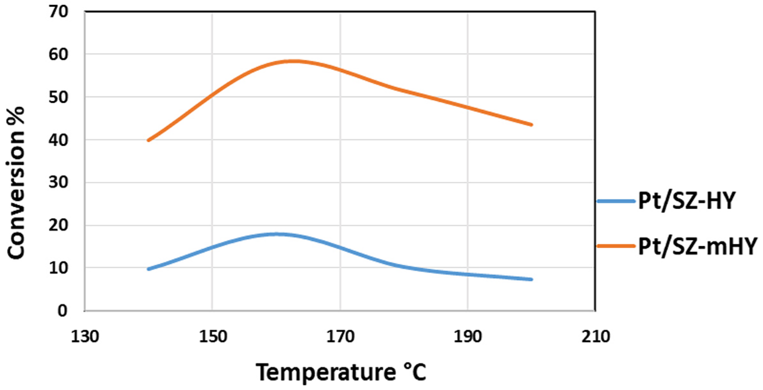


Figure 9. Conversion of n-hexane over different catalysts

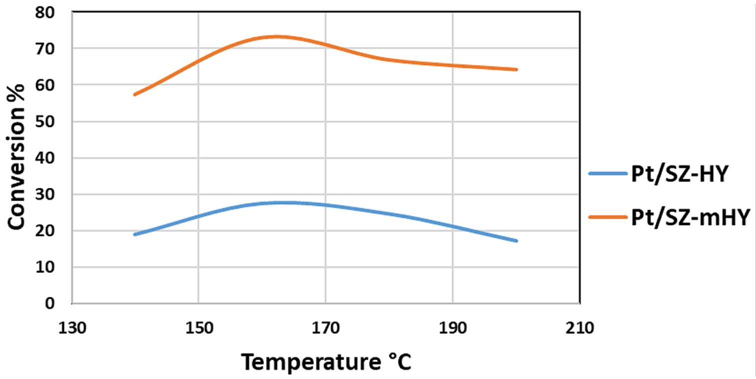


Figure 10. Conversion of n-heptane over different catalysts

maximum value of 73.05 mol%, then decreased to 66.91 mol% at 180 Hereafter, the conversion was slightly reduced to 64.26 mol% at 200°, as shown in Figure 10. Pt/SZ-mHY catalyst gives better performance for n-heptane as well as n-hexane as shown in Figures 9 and 10, where the conversion of n-heptane increased from 27.5 mol% in Pt/SZ-HY catalyst to 73.05 mol% in Pt/SZ-mHY at 160 °C, many research has tried to determine the nature of acid sites (Bronsted and lewis site) at the surface of the catalyst. They found that the mechanism to obtain them depends on water content, which depends strongly on the preparation conditions and method [Kamel et al., 2021]. The two catalysts gave more conversion to isomers for n-heptane than n-hexane as illustrated in Figures 11 and 12, because the mesoporous structure for catalysts composite are more suitable for higher molecular weight.

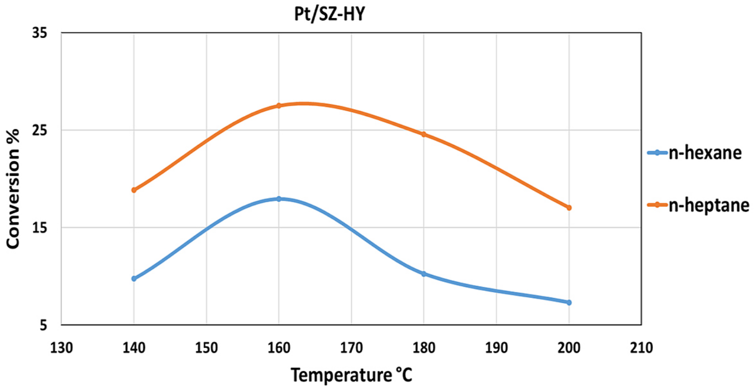


Figure 11. Temperature effect on isomerize conversion over Pt/SZ-HY catalysts

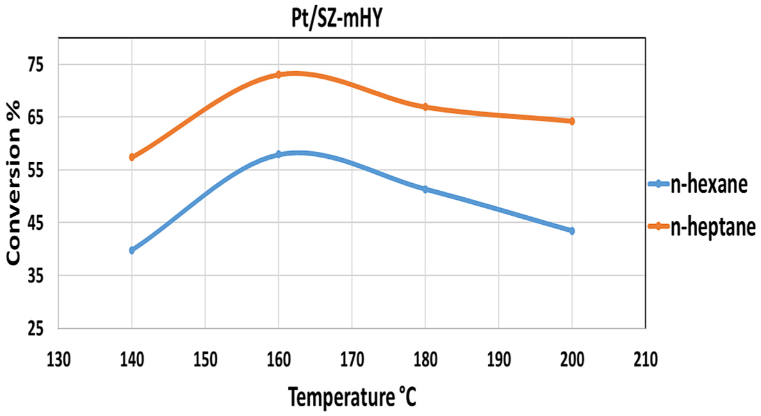


Figure 12. Temperature effect on isomerization over Pt/SZ-mHY catalyst

The results show that increasing the reaction temperature produces a peak at 160 °C. Then a slight drop in the conversion % to isomers with increasing temperature may be caused by the cracking path rather than the isomerization pathway when increasing the reaction temperature is more than 180 °C. These expected results are similar to the behavior of isomerization on Ni-WO_3/sulfated zirconia catalyst. The results showed that the maximum conversion was 80.1% for n-hexane, and 74% for the light naphtha at 150 °C, 6 bar, 1 hr^{-1} LHSV, and mole ration of H_2/HC of 4 [Kamel et al., 2021]. Lower reaction temperatures promote isomers production and make the catalysts more selective toward isomers because the isomerization reaction is exothermic, which is agreed with Mohammed et al. [2008].

CONCLUSIONS

In this study, the hydroisomerization for n-hexane and n-heptane is done using Pt supported sulfated zirconia and HY zeolite. This study consists of the investigation of temperature and different kinds of catalysts for isomerization process. Platinum supported on zeolite catalysts is a basic part of the petroleum refining catalytic industry. It was confirmed in the FTIR test that adding HY zeolite with SZ as support can enhance the acidity of catalysts. The results show that Pt/SZ-mHY catalyst achieved higher conversion values for n-heptane of 73.05 mol% than n-hexane of 27.5 mol% at the optimum operation temperature of 160 °C, 15 bar and low LHSV of 1 hr^{-1}. It was proven that the composite catalyst with a smaller pore size and higher Si/Al ratio could be more suitable for the isomerization of n-hexane and n-heptane.

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