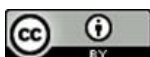


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Synthesis and Characterization of Sulfated Zirconia Catalyst for Light Naphtha Isomerization Process

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Abstract

The platinum-loaded zirconium oxide ($\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2$) catalyst was developed for the light naphtha atoms over the reaction temperature range of 160 to 220 °C, 1 and 3 h⁻¹ LSHV and 10 bar. Platinum improved the stability of the catalyst by preventing the formation of a coke precursor at the strong acid site of sulfur zirconium. The acidity of the catalyst was characterized by of NH_3 -TPD and the effect of sulfur and calcination temperature on the surface area of the final prepared zirconia was studied. The prepared catalyst shows high structural similar activity at temperature between 200 and 210°C for two types of light naphtha feed.

Keywords: Sulfated zirconia, Isomerization, light naphtha.

1. Introduction

The use of acidic catalysts is very common in the chemical and refining industries, as well as those technologies that use highly corrosive, hazardous, and polluting materials. Solid acids and ultra-acid catalysts have been of constant interest due to their numerous applications in many areas of the chemical industry, and the use of acidic catalysts is very prevalent in the chemical and refining industries, and those technologies that use highly corrosive, hazardous, and polluting materials. Solid acids such as clays, zeolites, metropolitan acids, ion exchange resins, and metal oxides are replacing traditional liquid acids and Lewis acids such as H_2SO_4 , HCL , HF , H_3PO_4 , and ZnCl_2 . Some of these solid and super acidic acids have various advantages such as ease of handling, simplicity, versatility in process engineering, and catalyst regeneration. Reducing the problems of corrosion of reactors and factories, and the safe disposal of the environment.[1],[2]

Because of their better catalytic activity for hydrocarbon conversions under mild circumstances, zirconia (ZrO_2)-based acids have gotten a lot of interest among other hard acids. Because of their better catalytic activity for hydrocarbon conversions under mild circumstances, zirconia (ZrO_2)-based hard acids have gotten a lot of attention among other hard acids. SO_4/ZrO_2 catalyst is becoming increasingly popular and active among solid acidic zirconia-based catalysts for various chemical synthesis and conversion, including numerous reactions, isomerization, alkylation, and esterification. Many promoters, including as Fe, Mn, and noble ions, have been utilized to increase catalytic activity and stability during operation. [3].

The hydro isomerization process of n-alkanes (C_4-C_6) – light naphtha- that taking place over noble metals supported on acidic support in the presence of hydrogen, plays an important role in the petroleum industry for the production of gasoline with high octane number. This process reactions needs a strongly acidic solid acid such as chlorinated alumina, zeolites, sulphated zirconia and heteropolyacids. [4]

Hydroconversion of $C_6 - C_9$ n-alkane was investigated over a carbided molybdena on sulfated zirconia support $MoO_3/SO_4^{2-}/ZrO_2$ catalyst in the temperature range 350–4500 C at 1 atm pressure. High selectivities to hydroisomerisation obtained with n-heptane and n-hexane (90%) at all the temperatures. [5].

2. Experimental work

2.1 Preparation of catalyst

The catalyst was prepared by precipitation method to produce 45 g of sulfated zirconium oxide as shown in Figure (1) showing the preparation procedure with zirconium oxychloride. Therefore, after the solution was filtered and washed several times to remove any chlorine ion, the filter paste was dried at 120 °C for 20 h and the remaining shell was ground and impregnated on 1 M H_2SO_4 solution for 1 h 800 rpm with stirring. Since then, the solution was filtered and dried at 120 °C for 5 h and then calcined at 650 °C for 3 h at a rate of 10 °C/min. A rotary vacuum evaporator was used to impregnate 20 g of the support with 0.16 g of hexachloroplatinate hexahydrate.

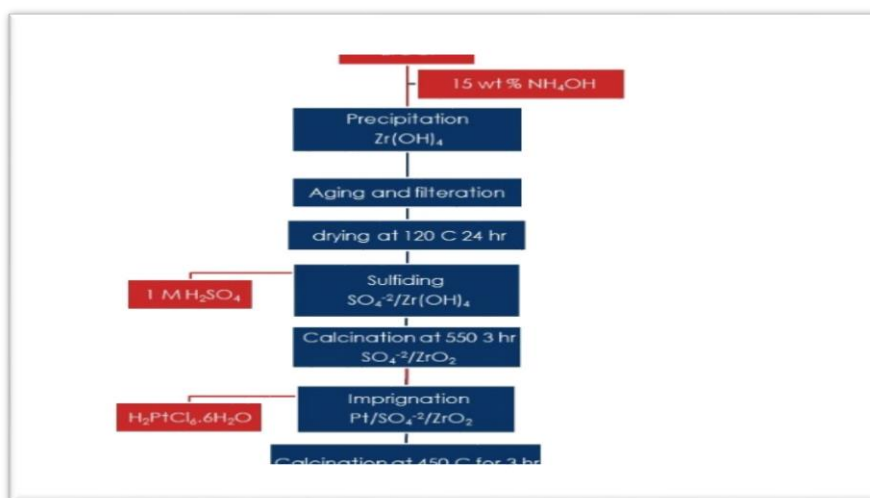


Fig. (1): Schematic flow diagram of Pt /SO₄²⁻/ZrO₂

2.2 Catalyst evaluation

The activity evaluation of prepared catalyst for light naphtha isomerization in micro reactor unit contain two reactors each reactor connects with its own feed system, control board and online Gas Chromatography Analysis system as shown in Figure (2).

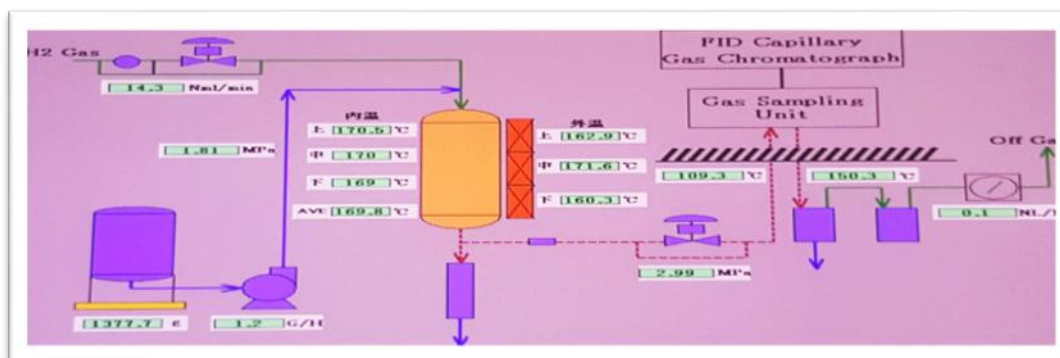


Fig. (2) Flow diagram of micro reactor unit

The properties of light naphtha used in the evaluation experiments were listed in Table (1).

Table (1) Properties of Light naphtha

carbon number	n-paraffin.	i-paraffin.	olefin	naphthene.	aromatics.	TOTAL
5	27.6	18.6	0.0	1.8	****	48.0
6	20.1	19.8	0.0	7.0	1.4	48.2
7	0.1	1.3	0.0	0.3	0.0	1.7
TOTAL	49.9	39.7	0.0	9.1	1.4	100.0

3. Results and discussions

3.1 X-Ray diffraction

The prepared catalyst shows two **zirconia** phases, a monoclinic phase and a tetragonal phase. The peaks of the monoclinic phase appear at $2\theta = 24.2026^\circ$, 28.1736° , 31.5652° , 49.2786° , and 50.2281° while the peaks of the tetragonal phase appear at $2\theta = 30.2191^\circ$, 34.4384° , 35.2085° , and 60.0820° . These values for the grains are almost **an equivalent** as those obtained from sulfuric zirconia used for drying aliphatic alcohols by [6]. The dependence of ZrO_2 crystal structure on calcination temperature has been studied previously; ZrO_2 was amorphous until about $300^\circ C$, tetragonal phase at about $350^\circ C$, a mixture of tetragonal and monoclinic form at about $400\text{--}800^\circ C$ and pure monoclinic phase at about $900^\circ C$.

In addition, ZrO_2 , calcined at about $600^\circ C$, contains mainly the monoclinic phase and partly the tetragonal phase. The monoclinic phase peaks appear at $2\theta = 24.0$, 28.2 , 31.5 , 49.3 and 50.1° . After modification with **vitriol**, the monoclinic phase transforms into a tetragonal phase at $2\theta = 30.6$, 34.0 , 35.2 , 49.5 , and 60.1° **within the S/ ZrO_2 sample that's according to other studies [7]**

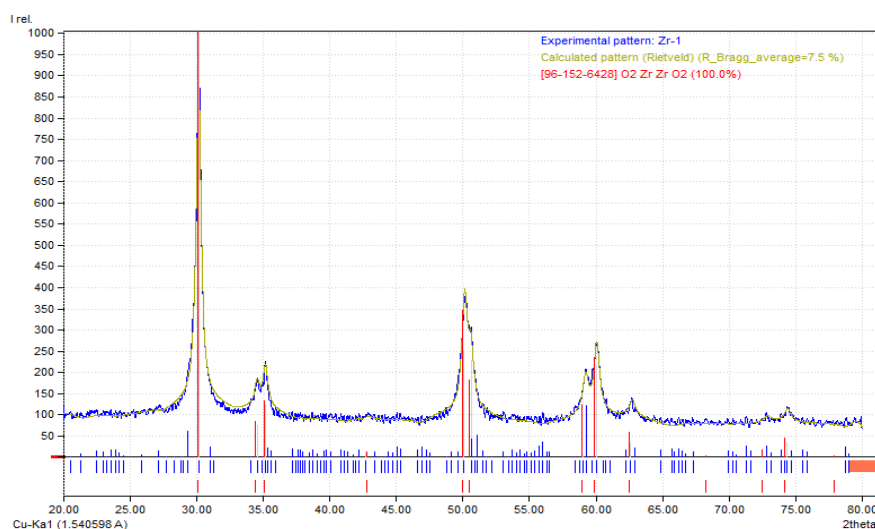


Fig. (3): XRD Patterns of prepared sulfated zirconium

3.2 Thermal Gravimetric Analysis (TGA)

The sulfur content of sulfate-containing zirconia is a crucial parameter for the amount of active sites (acidic sites). generally, a better sulfur content is vital to

possess more acidic sites under an equivalent condition. Thermal analysis of the prepared catalyst was performed to get information about the character of the catalyst and weight loss was measured as a function of temperature.

Figures (4, 5 & 6) shows TGA and DTG curves of prepared sulfated zirconia. This curve indicates thermal stability and a weight loss observed from 50-300°C of about 4 wt.% due to moisture and chemically bonded water for sample which calcined at 550, 650 & 750°C.

At a temperature 400-500°C approximately 6 wt.% weight loss due to free sulfur decomposition while at higher temperature 500-900°C about 2 wt.% weight loss due to bonded sulfur decomposition which leading to ultimate formation of SO₃ [8][9]

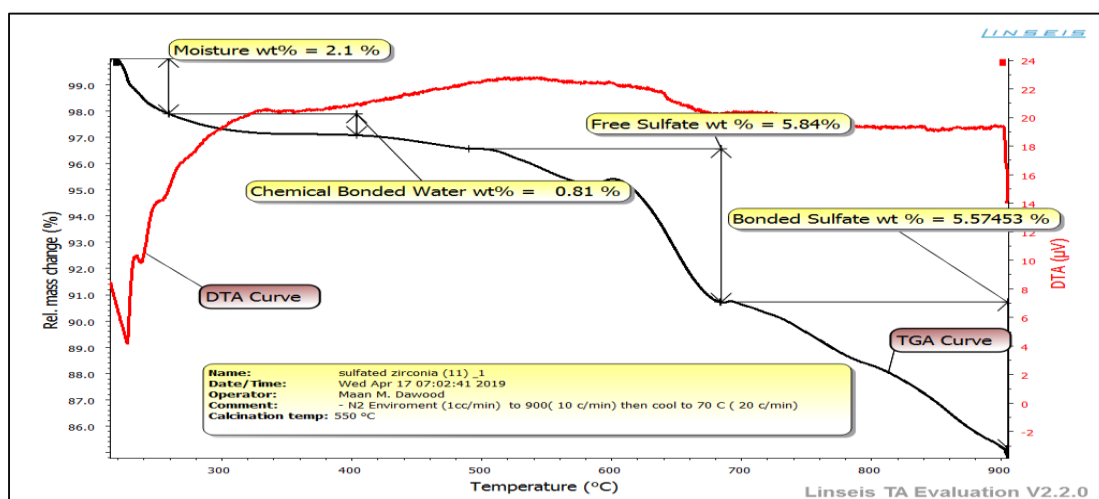


Fig. (4): TGA analysis for prepared sulfated zirconium at 550°C

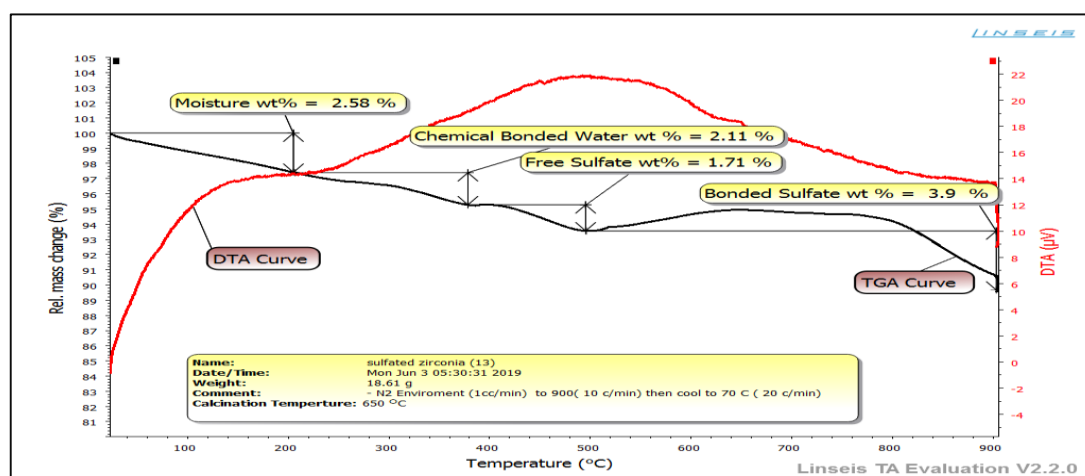


Fig. (5): TGA analysis for prepared sulfated zirconium at 650°C.

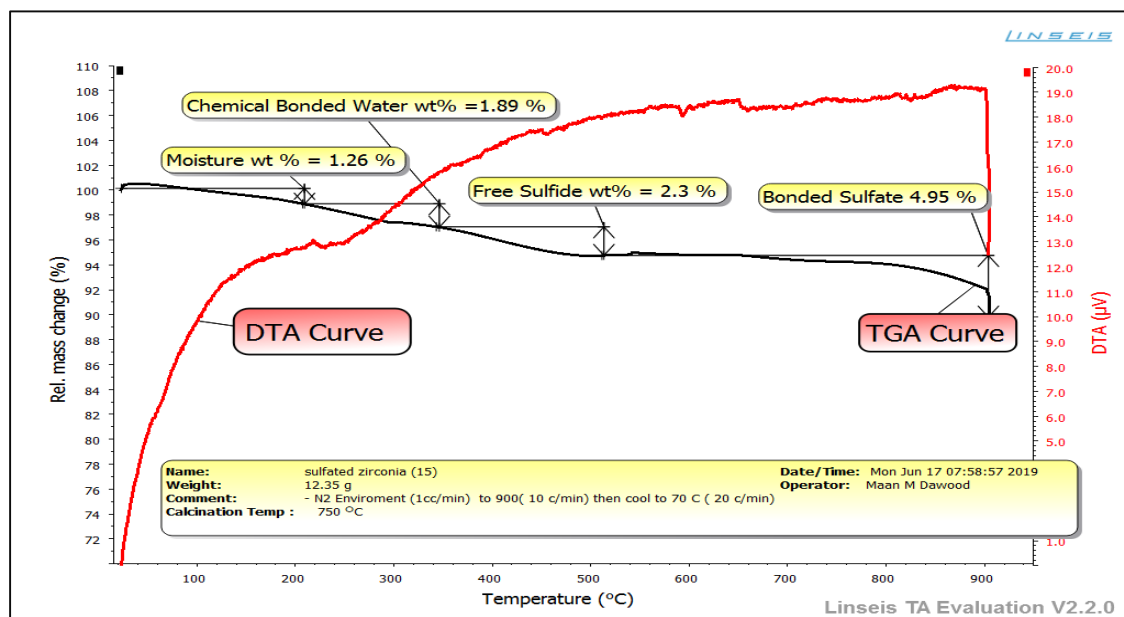


Fig. (6): TGA analysis for prepared sulfated zirconium at 750°C.

3.5 NH₃-TPD Ammonia temperature programmed desorption

Ammonia (NH₃-TPD) has been measured for synthesized sulfated zirconia catalyst the total amount of acidity obtained by calculating the area under the curve. The results showed high acidity of about 1918 µL of NH₃/g catalyst.

Two high acidity peaks were obtained at 500 °C and 650 °C as shown in Figure (8). Bronsted site and Lewis acid site can be attributed to ammonia uptake at high temperature peak while the low temperature peak refers to the number of ammonia molecules adsorbed over a weak acidic site such as Bronsted, Lewis and silanol groups and formation of NH⁺ groups.

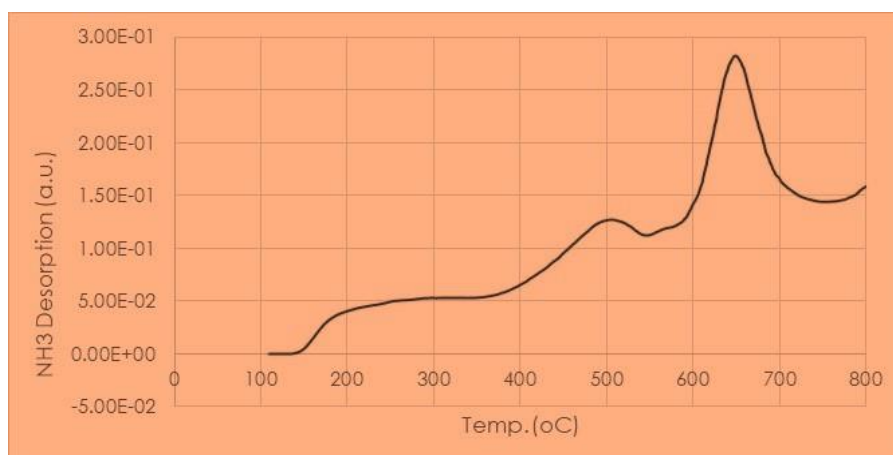


Fig. (7): NH₃- TPD of prepared sulfated zirconium

3.6 Surface Area

The corresponding results of the BET surface area of sulfated zirconia are summarized in Table (2) All surface areas are within values agreed with literature and the effect of concentration of ammonium solution at constant calcination temperature is from (89) to (134) m²/g are agreed with [10] & [11].

The surface area is 104 and 125 m²/g of the final Pt /SO₄-ZrO₂ and Commercial catalyst, respectively. On the other hand, the result of pore volume that show a considerable decreasing from 0.182 cm³/g for commercial catalyst to 0.0853 cm³/g which indicate that there is big difference in the surface morphology and porosity.[12] .

Table (2) BET surface area of prepared sulfated zirconium catalyst at different ammonium solution wt. %, different molarity of H₂SO₄ at 650 °C calcination Temperature

No. of	NH ₄ OH	H ₂ SO ₄	BET surface m ² /g
1	15	0.5	90
2	15	1	95
3	15	2	65
4	20	0.5	133
5	20	1	134
6	20	2	93
7	25	0.5	93
8	25	1	114
9	25	2	89

Results is combatable with previous studies that the materials prepared by soaking in acid of varying concentration followed by filtration showed an equivalent specific area for sulfur contents between 1% and 4 take a while an outsized decrease in area was observed when the sulfur content was 7.2% (21.6% sulfate). This due to the alteration of crystal structure and sulfate migration into the majority phase of the solid. [2]

4. catalyst evaluation

The activity of the prepared and commercial catalyst was studied. The effect of reaction temperatures, pressure and space velocity of the fluid clock was studied. The results showed that the higher the reaction temperature the higher the search octane number at a constant LHSV, this could be attributed to the precedence of the acidic active site and the metallic site Pt which promotes the transfer of the coke precursor from the catalyst surface the rate of isomerization reaction as high as possible as shown in Figures (8 and 9), this result could be due to the different acid type of these catalysts from the acidic sites of the chlorinated alumina catalyst operating at lower temperature, and on the other hand, the active sites of the zeolite catalyst would perform at a higher temperature instinctively [11]

All results indicate that lower LHSV is favorable for isomerization process, while with higher space velocities; Conversions are less, unless the temperature rises. As in Figure (8) at 1 h^{-1} LHSV, RON increases for all reaction temperatures and when LHSV rises to 3 h^{-1} , RON at the same reaction temperature as in Figure (9). This is due to reduced real contact time of gaseous reactants and active sites for the catalyst. These observations agree well with the previous investigation reported [13]

The isoparanic carbenium ion is converted to olfne through the release of a proton on the acid side, then rapidly hydrogenated to the corresponding nisobar on the metal side. pt appears to play an important role in the formation of the primary n intermediate and in the hydrogenation of the primary n branch during this isomerization pathway. in addition to these functions, the hydrogenation function of pt makes a significant contribution to the removal of the coke precursor from the catalyst surface an ion that is converted to an initial n via loss of a proton at the acid site, and, therefore, is rapidly hydrogenated to isobarone. compatible with the metal position. It appears that pt plays an important role in the formation of olefin intermediates and in the hydrogenation of branched olefins during this isomerization pathway. in addition to these functions, the hydrogenation function of pt contributes greatly to the removal of coke precursors from the catalyst surface.[14]

The selectivity of the catalyst towards isomerate iso-C₅ ratio (isopentane/ (pentane + isopentane) · 100, and di branched increases with increasing reaction temperatures as shown in Figures (10, 11, 12, & 13). This may be also attributed to the size of platinum particles in catalyst, the number of platinum particles on the surface of catalyst and the distances of platinum particles are longer which cause only cyclic compounds that adsorb to the neighborhood of the platinum have high probability of contact with the spillover hydrogen, and the others could make the coke because of the much slower desorption.

As shown in the chemical composition of the product, the methylcyclopentane fraction increased while the cyclohexane and benzene fractions decreased. Therefore, methylcyclopentane is formed from cyclohexane or benzene by a bifunctional mechanism with the first step of associative adsorption and when the active site is a metalloprotonic [Pt-H] + mixture. This collapsing bifunctional site should be responsible for the reactivity of the catalyst showing a more pronounced acidic character explaining the behavior of Pt/ZrO₂/SO₄+2. [5].

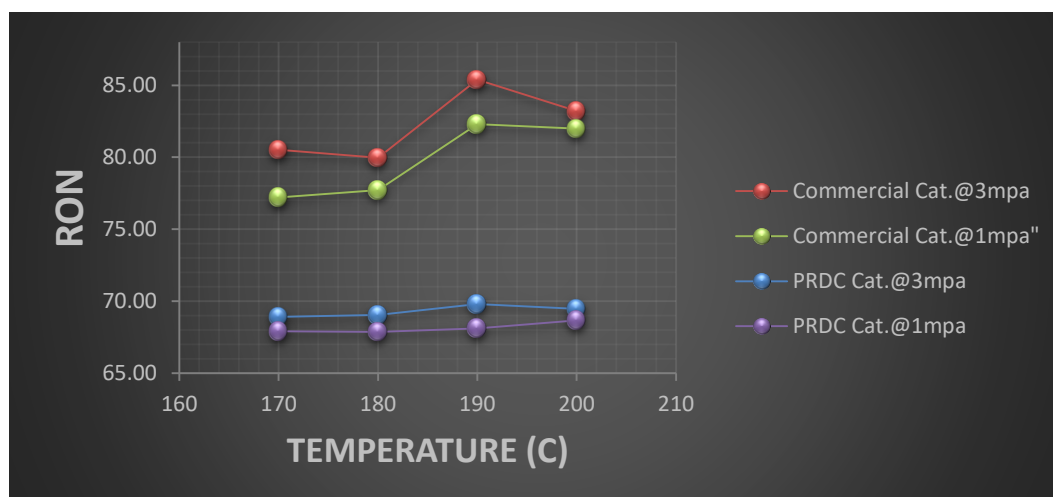


Fig. (8): Temperature and pressure effect on the Isomerate RON at 1 h⁻¹ LHSV

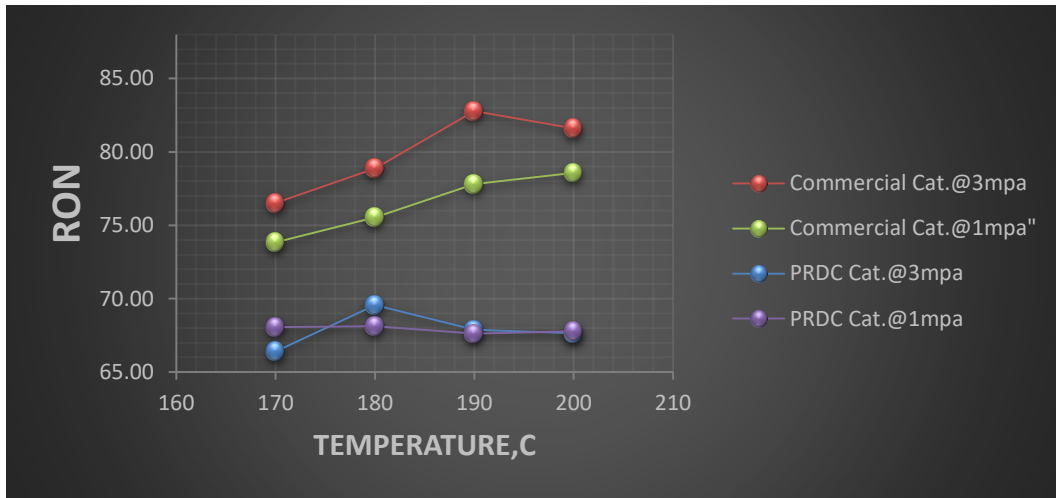


Fig. (9): Temperature and pressure effect on the Isomerate RON at 3 h⁻¹ LHSV.

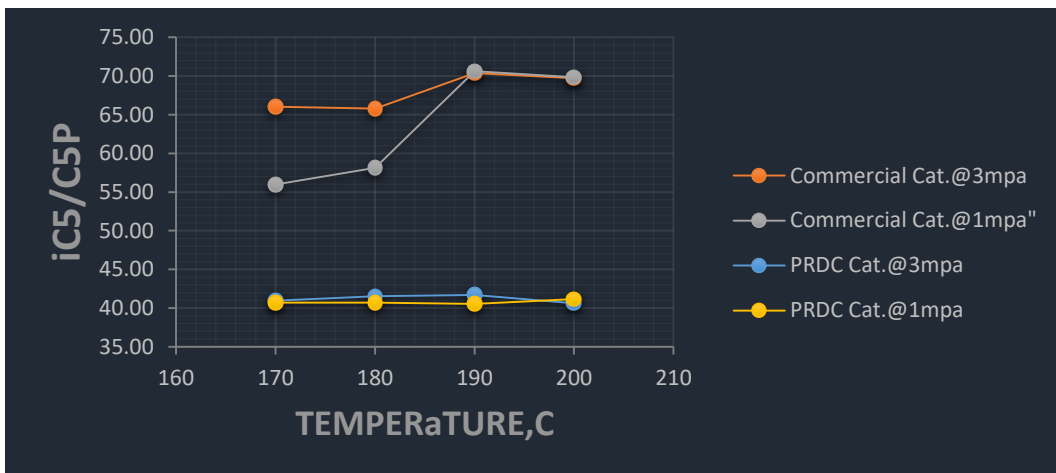


Fig. (10): Temperature and pressure effect on the Isomerate i-C5/C5P at 1 h⁻¹ LHSV.

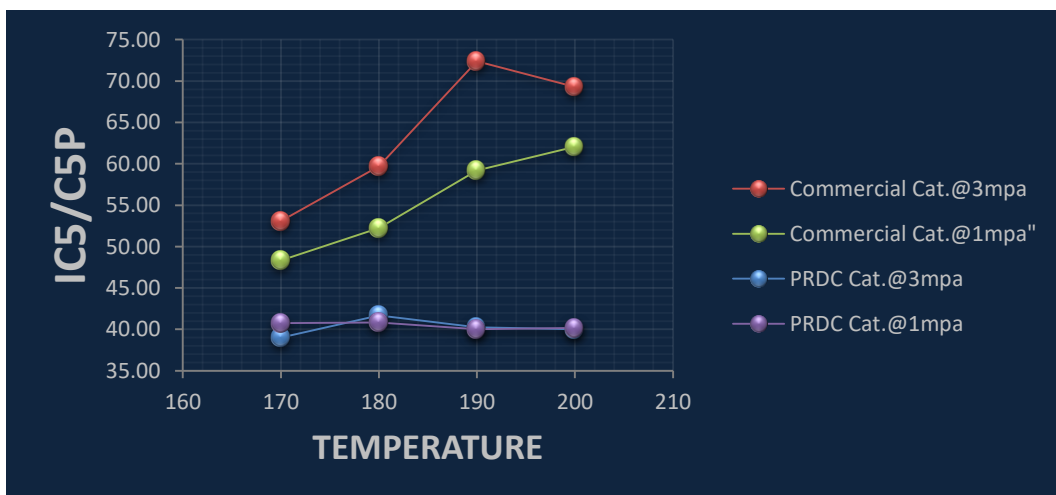


Fig. (11): Temperature and pressure effect on the Isomerate i-C5/C5P at 3 h⁻¹ LHSV.

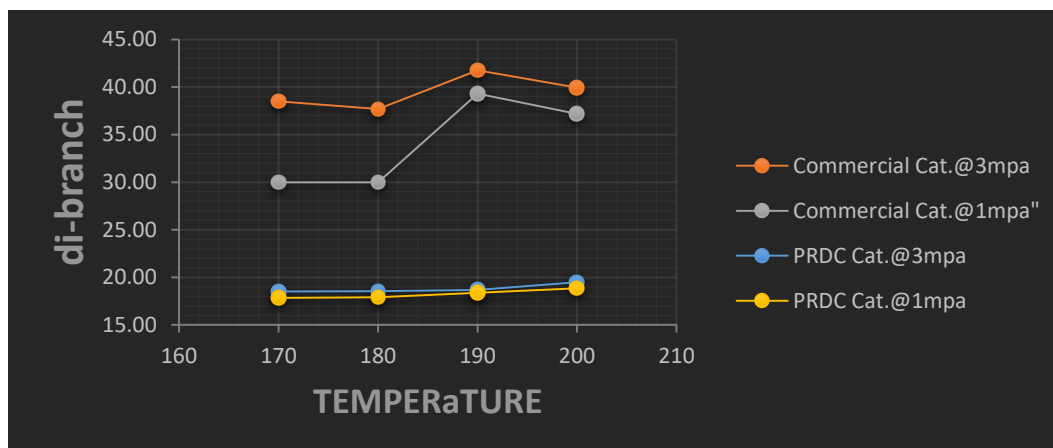


Fig. (12): Temperature and pressure effect on the Isomerate Di-Branch Ratio at 1 h-1 LHSV

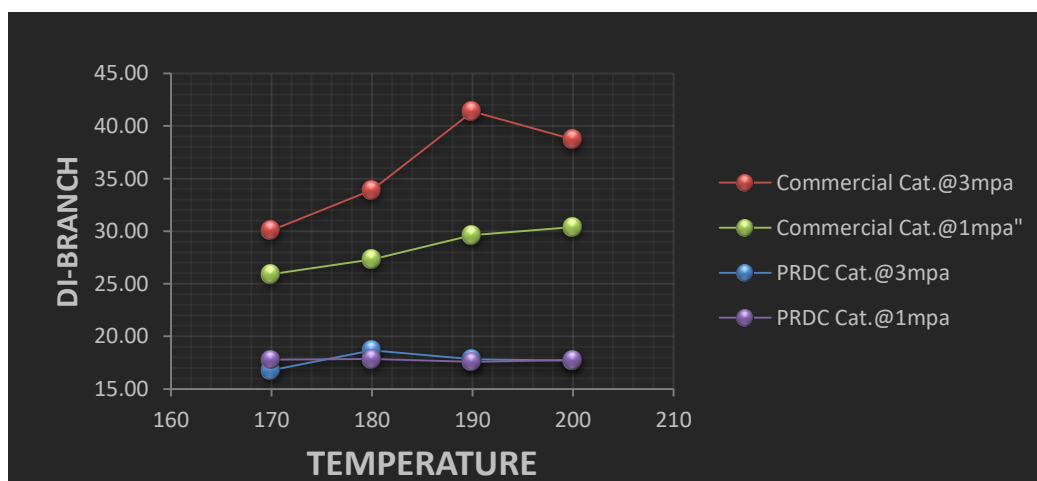


Fig. (13): Temperature and pressure effect on the Isomerate Di-Branch Ratio at 3 h-1 LHSV.

5. Conclusion

Sulfated zirconia catalyst is prepared successfully and investigated for isomerization reaction of light naphtha after Pt loading. Results shows that prepared catalyst has a good activity for skeletal rearrangement for naphtha isomerization over a reaction temperature range from 160 to 220 °C.

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