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**Role of Hydrogen in n-Hexane Hydroisomerisation as a Model Reaction
 for Gasoline Quality Valorization**

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ABSTRACT

Consequent to the current global environmental legislations that enforced the phase-out of dangerous fuel additives with associated pollution problems, other research alternatives for improving fuels quality are investigated. Previously, lead and oxygenates have posed emission dangers that accounted for their complete phase-out in many regions. The emergence of hydroisomerisation as an option presents an opportunity for improving gasoline octane features while eliminating the environmental dangers. We prepared and characterized a noble and cheap catalyst based on β -Mo₂C/sulfated zirconia that completely upgraded n-hexane into mono- and di-branched isomers at milder reaction conditions (1 atm, 400°C). The catalyst was 100% selective to n-hexanes at high hydrogen flow rates and recyclable and stable. This way, cheap opportunity for gasoline feed valorization via the hydroisomerisation process became possible.

Keywords: Environment; gasoline; quality; hydroisomerisation; n-hexane.

1.0 INTRODUCTION

The current environmental parameters considered globally during fuels extraction, refining and utilization are directly centered on limiting the emissions of pollutants with harmful consequences. These parameters covered climate change and global warming considerations, humans and animals' health and agricultural land protection (Cavagnaro et al., 2006; Mbow et al., 2014; Mozell et al., 2014). Since decades before now gasoline provides a key fuel for applications in automobiles and household usage. Its escalated demand over the years triggered the search for different methods that are related to fuel-quality enhancement. Gasoline fuels with high octane numbers are also preferred for all applications due to a number of advantages that include energy efficiency, catalytic converter protection and economic sustainability (Myers et al., 1975; Anderson et al., 2015; Demirbas et al., 2015).

Initially, the incorporation of tetraethyl lead (TEL), its related derivatives and oxygenate compounds was prioritized as an important method for bursting the octane properties of

gasoline fuels (Pasadakis et al., 2006; Anderson et al., 2012). However, the emissions of lead and carcinogens forced with dangerous consequences for human and animal health forced the total phase-out of these additives in most global regions (Hilton et al., 1998; Von et al., 2003; Cgen et al., 2005). In the last few decades, the focus was later shifted to the incorporation of BTEX aromatics (i.e. benzene, toluene, ethylbenzenes and xylenes) as replacement candidates due to their higher octane properties than the n-alkanes in gasoline cuts. Unfortunately, combustion of aromatics is similarly associated with emissions of polyaromatic hydrocarbons (PAHs) that are not only carcinogenic but also destructive to the catalytic converters (Giger et al., 1974; Leyval et al., 1998; Kanzari et al., 2014). Accordingly, the PAHs can pollute water systems and exert destruction to marine species (Hawthorne et al., 1994; Wang et al., 2006; Zaghden et al., 2007).

Considering all of the above environmental dangers, the petroleum refineries shifted the scope towards the hydroisomerisation of the linear alkanes in the gasoline fuel. It is a well-known fact

that the branched alkanes (i.e. isomers) exhibit much higher octane properties than the linear counterparts. For example, n-octane has an octane number of 100 but its isomer (2,2,4-trimethylpentane) exhibits an octane number of 90. By this classification, the isomers shall exhibit better combustion properties. Therefore, the hydroisomerisation process which requires no addition of any environmentally-dangerous material provides the best alternative for gasoline quality upgrading. During the process, n-alkane is isomerized into its corresponding isomers under hydrogen pressures (Galadima et al., 2009; Galadima et al., 2012a; Galadima et al., 2012b; Galadima et al., 2015a; Galadima et al., 2015b). Thus, the amount of hydrogen gas supplied can have a tremendous effect in attaining high conversion versus isomers selectivity. Therefore, in the current work, n-hexane (a key constituent of the gasoline cut) was upgraded into its constituent isomers at 1 atm and 400°C using a designed cheap and environmentally-benign catalyst (i.e. carburized 25 wt% MoO₃/SO₄²⁻-ZrO₂). The catalyst can be recovered and reused without difficulties. The role of hydrogen concentration on the process efficiency was evaluated accordingly.

2.0 EXPERIMENTS

2.1 Preparation and Carburization of the Catalyst

4.60 g of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), Fisher Scientific, Laboratory grade reagent) which gives 25 wt% MoO₃/SO₄²⁻-ZrO₂ (calculated based on Mo content) was completely dissolved in 100 mL of distilled water with aid of stirring, after which 7.5 g of sulphated zirconia (MEL chemicals, Analar grade), previously calcined at 550°C for 3 h was added. The excess water was removed by means of rotary evaporation at 80°C and the resulted solids dried in oven at 120°C overnight. The sample was later calcined in an air flow of 50 mL/min at 550°C for 3 h and stored in a pre-cleaned sample bottle under laboratory conditions. This catalyst is henceforth defined as 25MoO₃/SO₄²⁻-ZrO₂. The catalyst was later carburized at 650°C under 1:4 atmosphere of methane to hydrogen.

2.2 Catalyst Characterization

As usual the catalyst was characterized using N₂ adsorption and X-ray photoelectron spectroscopic (XPS) methods. The former analytical method was performed under liquid nitrogen atmosphere to establish the BET surface area and pore volume properties of the catalyst. The results were employed to determine the surface density of molybdenum species over the sulfated zirconia support. The XPS method on the other hand, provided binding energies consistent with complete catalyst carburization at 650°C to the active carbide phase.

2.3 Catalytic Evaluations

Catalyst testing reactions with n-hexane were carried out at the temperature 400°C. In each case, 0.2 g of the catalyst (25MoO₃/SO₄²⁻-ZrO₂) was treated with 0.50 g of an inert phase (i.e. SiC) and loaded to the quartz reactor (1 cm internal diameter and 25 cm long) between quartz wool plugs, giving a total catalyst bed height of 2 cm. The diluted catalyst was carburized in a 1:4 volumetric flow of CH₄:H₂ (i.e. 20% v/v methane) at 650°C for a period of 1 h 15 min. The reactor temperature was later lowered to the desired reaction temperature (400°C) in a 20 ml/min H₂ flow. Reactions were monitored with 15.0 µL/min of the n-hexane (GHSV = 3.23 h⁻¹) into the flowing hydrogen atmosphere for 2 h 15 min. A total of nine samples were trapped, one after every 15 min. The reactions were repeated under different hydrogen flow rates and the products analyzed using standard GC-FID procedure.

3.0 RESULTS AND DISCUSSION

3.1 Characterization Results

Figure 1 and Table 1 reported the results of nitrogen adsorption studies from the characterization of the catalyst and its precursor materials. It could be established that the incorporation of molybdenum species (Mo) raised the active surface area of sulfated zirconia. Before the impregnation process, the surface area was 120 m²/g but increased slightly to 124 m²/g following the addition of 25 wt.% of Mo species to the sulfated zirconia surfaces. However, carburization of the latter phase into β-Mo₂C/SO₄²⁻-ZrO₂ exerted a concomitant reduction in the surface area. This trend is similar to the observations found in previous studies (Galadima, 2012; Galadima et al., 2012c). On the other hand, both the pore volume

and apparent density of surface molybdenum species increased following the carburization reaction. It was therefore beneficial in creating a high surface accessibility of the Mo particles by the reacting n-hexane molecules. Accessibility to

the active sites by reactants/intermediates is a necessary requirement in catalysis for any reaction to be positively favored (Girgis et al., 1996; Topsoe et al., 1983; Martens et al., 2013; Guo et al., 2016).

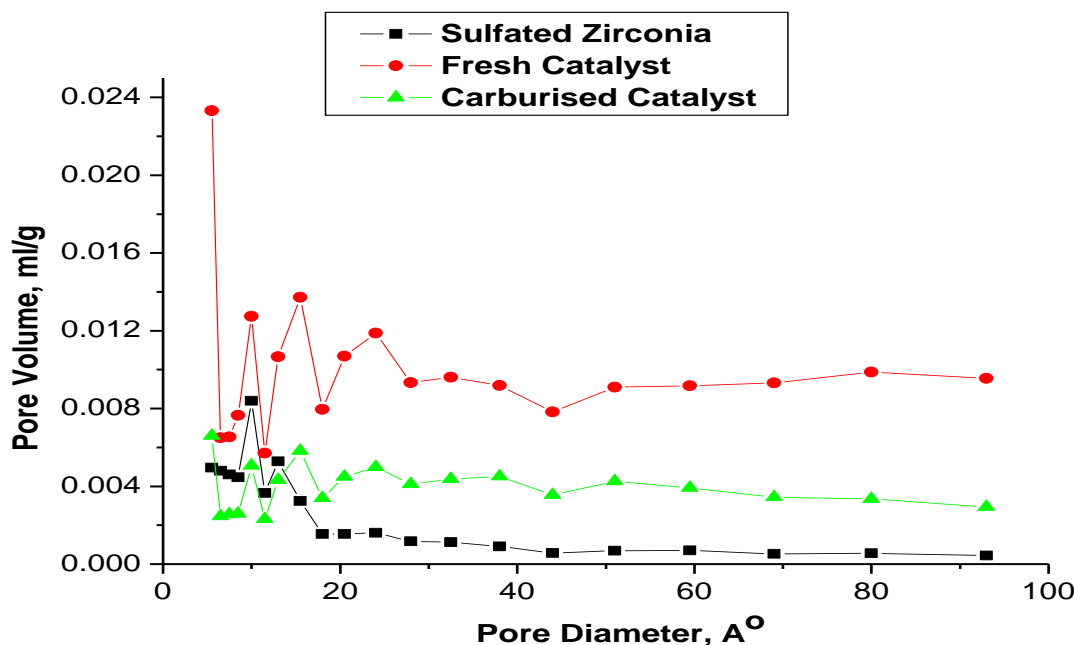


Figure 1: Pore volume distribution of $\text{SO}_4^{2-}\text{-ZrO}_2$ (■), $25\text{MoO}_3/\text{SO}_4^{2-}\text{-ZrO}_2$ (◆) and $\beta\text{-Mo}_2\text{C}/\text{SO}_4^{2-}\text{-ZrO}_2$ (▲) as measured in the micropore and mesopore range.

Table 1. Results of N_2 adsorption experiments for the catalyst employed during the reaction.

Sample	BET, m^2/g	Pore Volume cm^3/g	Apparent Surface Density of Mo Species, atoms nm^{-2}
$\text{SO}_4^{2-}\text{-ZrO}_2$	120	0.0143	-
$25\text{MoO}_3/\text{SO}_4^{2-}\text{-ZrO}_2$	124	0.0149	8.2
$\beta\text{-Mo}_2\text{C}/\text{SO}_4^{2-}\text{-ZrO}_2$	98	0.1726	11.0

Figures 2 and 3 provided the x-ray photoelectron spectra (i.e. XPS spectra) for the carburized catalyst prior to the hydroisomerisation testing. While Figure 2 is for the Mo 3p electronic process, Figure 3 was a consequence of the

electrons ejection from C 1s. According to Roy et al. (2015), the existence of Mo 3p XPS peaks at 400-420 eV is an indication of the formation of a carbide phase in the catalyst. When the XPS peaks were analyzed for the C 1s (Figure 3), it could be

observed that both carbidic and oxycarbide species were detected (284-288 eV). Therefore, coupling the spectra from the two Figures (i.e. Figures 2 and 3), the resulted catalyst after carburization composed of both β - Mo_2C and MoO_xC phases that

participated in the hydroisomerisation reaction. Earlier, Goguet et al. (2008), showed both the two phases as capable of isomerizing n-butane into isobutane at reaction conditions comparable to those employed in this investigation.

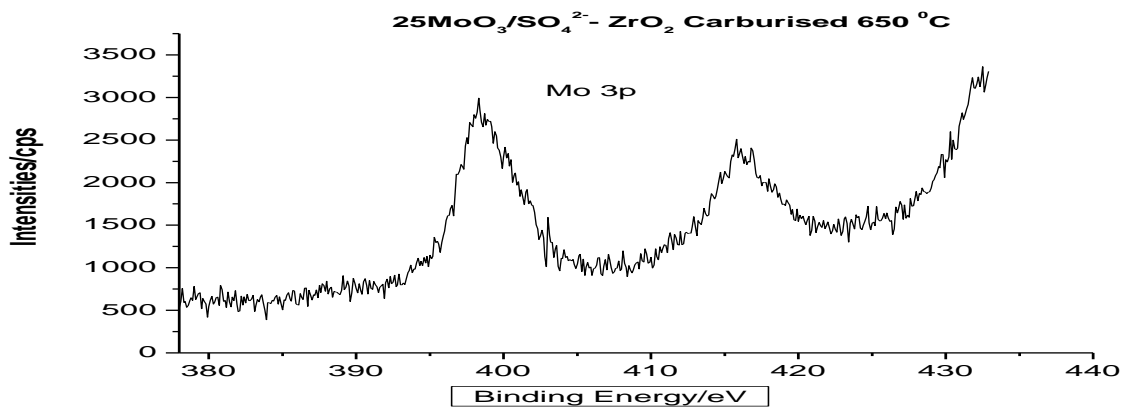


Figure 2: Mo 3p XP spectra for catalyst employed.

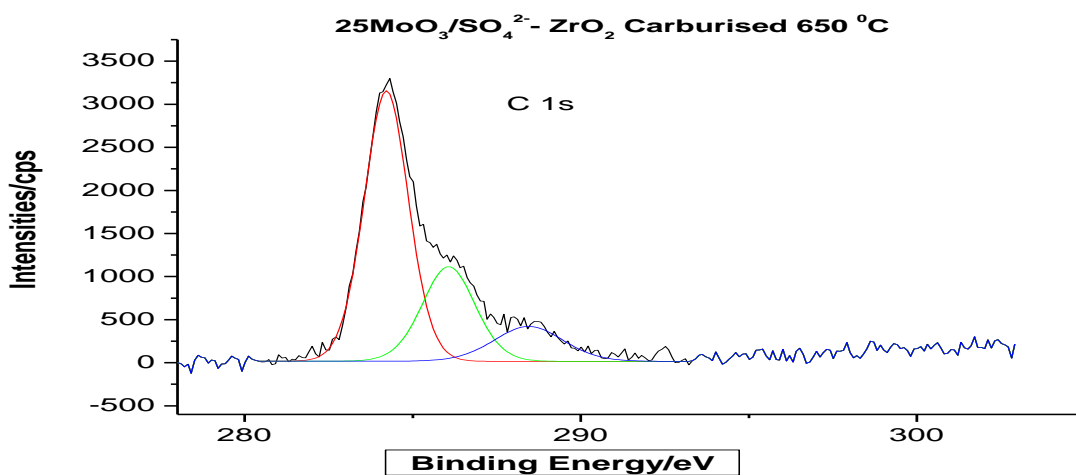


Figure 3: C 1s XP spectra for the catalyst employed.

3.2 Reaction Results

The results of catalytic n-hexane conversion and isomers distribution over the carbided catalyst are illustrated as Figure 1 and Table 2, respectively. Based on these details, low hydrogen concentrations were beneficial for favoring catalytic activity. At the hydrogen flow rate of 20 mL/min, the n-hexane conversion hits 45.2% but declined linearly to 12.3% when the flow rate was raised reaching 50 mL/min. Some earlier investigations postulated that when the flow rates of hydrogen gas are low the chance of accessibility of the reactants to the catalyst active sites became promoted (Dhar et al., 2017; Huyen

et al., 2018; Jaroszewska et al., 2019). This phenomenon in turn ensured higher conversion of the reactants per unit time, whereas a negative effect could be observed at high flow rates of hydrogen. Regarding the isomer distribution, n-hexane has the potentials to undergo hydroisomerisation into a range of isomers (Sanchez et al., 2006; Sazama et al., 2018; Lu et al., 2019). In the current study both mono-branched and multiple branched-hexanes were detected. The low hydrogen flow rate of 20 mL/min produced the highest selectivity to 2,2- and 2,3-dimethylbutanes (i.e. 81.3% selectivity). At higher flow rates of 40 and 50 mL/min, the

mono-branched compounds dominated the reaction. Clearly, the sulfated zirconia supported β -Mo₂C catalyst can provide an opportunity for

improving the octane rating of gasoline fuels without environmental dangers

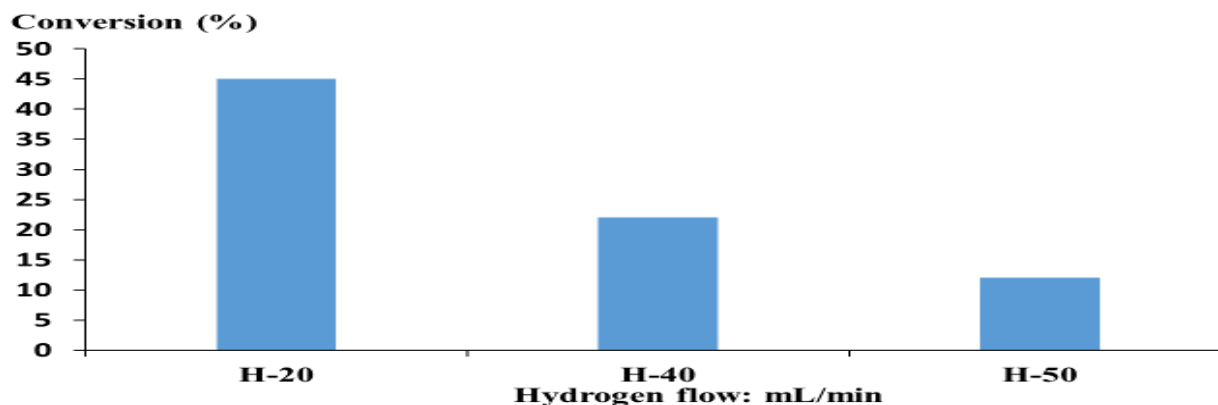


Figure 4. Role of hydrogen concentration (mL/min) of the conversion of n-hexane to isomers. H = hydrogen, the attaching number represents the actual flow rate used

Table 2: Product distribution from n-hexane hydroconversion at various hydrogen flows at 400°C

Hydrogen flow, cm ³ min ⁻¹	C ₁ to C ₅ , %	2-MP, %	3-MP, %	2,2-DMB, %	2,3-DMB, %
20	3.2	08.9	06.6	16.4	64.9
40	0.0	58.6	15.4	26.0	-
50	0.0	63.4	27.2	09.4	-

4.0 CONCLUSION

In attempt to devise a good catalyst with dual advantages of environmental protection and hydroisomerisation capabilities, β -Mo₂C/SO₄²⁻-ZrO₂ was formulated via precursor impregnation, calcination and carburization in a methane/hydrogen atmosphere at 650°C. The characterization results showed the active catalyst to composed of both carbidic and oxycarbide phases. The two phases successfully transformed n-hexane into both mono- and di-dibranched isomers with selectivity of ~ 100%. Accordingly, low hydrogen flow rates were required to establish high n-hexane conversion. Overall, the design catalyst has good potentials for gasoline feed upgrading without posing economic and environmental dangers.

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