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FEDERAL UNIVERSITY
GUSAU-NIGERIA

INTERNATIONAL JOURNAL OF SCIENCE FOR GLOBAL SUSTAINABILITY

Catalytic Upgrading of n-Hexane and n-Octane for Light Hydrocarbons Production

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Received: October 2015 Revised and Accepted: November 2015

Abstract

Light hydrocarbon compounds are of great importance for direct usage as gaseous fuels or the production of petrochemicals. Therefore, their synthesis via catalytic upgrading of heavier hydrocarbons in the gasoline or diesel feedstock would be economically relevant. The current research developed a Mo_2C/ZrO_2 catalyst modified with Rh species for n-hexane and n-octane hydroconversion to light hydrocarbons (i.e. C_1 to C_4) at 450^{o}C and 1 atm in a fixed-bed continuous flow reactor system. Both reactants produced similar conversions in the range of 18 to 20%, with more than 88% selectivity to the desired hydrocarbons. Mechanistically, the reaction was assumed to proceed via facile hydrogenolysis, involving the central and end C-C bonds. Overall, the catalyst could be considered industrial suitable but new parameters for improving catalytic conversion must be designed.

Keywords: *Light hydrocarbons; upgrading; n-hexane; n-octane; catalyst.*

1.0 INTRODUCTION

Although the production of biofuels had been significantly emphasized as the most suitable alternative for global sustenance, the fossil fuels would continue to play a key role at least for the medium term. The current proven reserves of oil and gas can provide the global population with energy and petrochemicals for decades to come. Similarly, the proven heavy oil deposits have strong potentials to escalate industrial-dependence on these sources for more decades (Meyer *et al.*, 2007; Muraza and Galadima, 2015). In view of this perspective, further investigations on the alternative routes for deriving light range (i.e. C_1-C_4) hydrocarbon with vital industrial application would be very critical for global sustainability.

In addition to direct utilization as liquefied petroleum gas, polymer production and as refrigerants, some of these compounds can further be upgraded into industrially-based useful chemicals like aromatics, esters and organic acids. Hydrocracking of the long chain alkanes like n-C_9 to n-C_{17} with solid acid catalysts, usually the zeolites and heteropoly acids, represents a common industrial route for light hydrocarbon production (Eswaramoorthi *et al.*, 2004). However, key noticeable difficulties associated with these catalyst systems include acidity decay with time, loss of active sites via solvation, rapid catalyst coking and poor thermal stability (Galadima *et al.*, 2013). Therefore, developing an alternative catalyst or method will upgrade the industrial relevance of the process.

Catalysts based on molybdenum carbide have been incorporated in many reactions, achieving optimal activities with limited or no noticeable difficulties. They have been utilized as hydro treating catalyst for the successful removal of N, S and O species from heterocyclic compounds in petroleum. For example, Celzard *et al.* (2005) employed Mo_2C nano-particles of 1-5 nm sizes supported over monolithic carbon for indole hydrodenitrogenation at 350^{o}C. The catalyst was completely stable and the conversion and selectivity approached 100%. In fact, this catalyst was more active than a commercial activated carbon (NC 100) catalyst. In a related development, Da Costa *et al.* (2003) have demonstrated Mo_2C/Al_2O_3 as more active, stable and selective catalyst for 4,6-dimethyldibenzothiophene hydrodesulphurization than a Pt/SiO_2 at 340^{o}C and 4 MPa pressure.

The current study explored the activity of a 0.5wt %$Rh/Mo_2C/ZrO_2$ catalyst during n-hexane and n-octane upgrading to lighter hydrocarbon species via catalytic hydrogenolysis process.

2.0 EXPERIMENTAL

2.1 Preparation of Catalyst Precursor

The catalyst precursor (i.e. 0.5 wt.% Rh/25wt% MoO_3/ZrO_2) was prepared as follows. An accurately weighed 4.60 g of ammonium molybdate was calcined in 100cm^3 of water with the aid of constant stirring water. 7.45g ZrO_2 (stabilized with 3.5 wt%SiO_2) was added. The mixture was subjected to rotary evaporation at 80^{o}C and the resulting solids dried in an oven at 120^{o}C for 24 h. The developed material was calcined at 550^{o}C for 3 h using a 50cm^3/min air flow. The calcined materials (i.e. 25wt.% MoO_3/ZO_2) was later impregnated with 0.5 wt.% Rh, using Rh $(NO_3)_3$ as the source solution.

2.2 Precursor Conversion to Active Catalyst

The active 0.5wt.%$Rh/Mo_2C/ZrO_2$ catalyst was developed by carburization of the prepared precursor in the reaction set-up. An atmosphere of methane and hydrogen (1:4, v/v) was employed as the carburization source, and the process was achieved at 600^{o}C for a period of 90 minutes.

2.3 Catalyst Characterization

The prepared catalyst was characterized using X-ray diffraction and N_2 adsorption studies. For the X-ray diffraction, measurements were conducted employing a Bruker-AXS model X-ray diffractometer, with Cu Kα monochromatic radiation (0.1542 nm wavelength). The analysis was carried out at 22^{o}C with steps of 0.02^o for 2θ ranges of 5 to 70^o and 2.5s/step.

Samples for N_2 adsorption were initially degassed at 200^{o}C in a vacuum line for a period of 24 h. The degassed samples were quickly transferred into a surface area and pore volume analyzer (i.e. coulter SA3100) and the measurements conducted at liquid N_2 temperature.

2.4 Catalyst Evaluation (Hydroconversion)

Catalyst testing was performed using n-hexane and n- octane as the reactants. The in-situ carburized catalyst diluted with 0.5g of SiC (an inert phase) formed a catalyst bed of 1cm, and was heated to the reaction temperature of 450^{o}C. The GHSV of n-hexane and n-octane, using H_2 as the carrier gas, were 2.95 and 3.16h^{-1}, respectively. GC-FID program (20 cm^3/min N_2 flow, 100^{o}C oven temperature and 200^{o}C injector/detector temperature).

3.0 RESULTS AND DISCUSSION

3.1 Catalyst Preparation

Among the procedures available for the preparation of supported oxide catalysts, the impregnation method was considered the most

suitable for developing the precursor material (i.e 0.5 wt% Rh/25 wt% MoO_3/ZrO_2) due to some important factors. The solubility of ammonium molybdate can be enhanced and consequently the deposition over ZrO_2 support. Although the calcination of the dried procursor material can be achieved at temperatures higher than the 550°C employed, the problem of sintering and polymolybdates formation could be encountered. Therefore, the moderate condition was adopted to ensure phase stability and permit enhanced dispersion of Rh and MoO_3 species over the ZrO_2 support (Cheng *et al.*, 1999). It can similarly favour the synergic interaction between Rh and MoO_3. This factor can in turn promote the reducibility of MoO_3 and its successful transformation into Mo_2C during carburization process.

3.2 Catalyst Characterization.

The results of N_2 adsorption studies were presented in Table 1. As reported in the experimental section, the materials were initially out-gassed at 200°C for 24 h. This action removes physically adsorbed water and any other contaminant that can alter the surface analysis (i.e. lead to wrong BET surface area and pore volume values). From Table 1, the ZrO_2 support and the catalyst stabilizer possessed closer values of BET surface area, indicating the suitability of the SiO_2 as an effective stabilizer.

The introduction of Rh species had a negative effect on the overall BET surface area of the precursor material. However, the pore volume was favoured. Catalytic materials with good pore properties are very good candidates for hydroconversion reactions. They allow both inward and outward diffusion of reactants and products without restriction. Thus, allow enhanced catalytic activiity and selectivity to the desired reaction products. The results in the Table 1 further showed carburization with CH_4 to reduce the active BET surface area (i.e. by 20 m^2g^{-1}), with a slight modification to the pore properties.

Table 1. Results of N_2 adsorption studies.

Material	BET surface area (m^2/g)	Pore volume (cm^3/g)
3.5wt.% SiO_2 stabilizer	100	0.13
ZrO_2 support	120	0.014
0.5wt.% Rh/ 25t.%MoO_3/ZrO_2	90	0.029
0.5wt.%Rh/Mo_2 C/ZrO_2	70	0.032

The results of the X-ray diffraction studies are illustrated in figures 1 and 2. No any peaks can be assigned to Rh species. Therefore, the amount of these species (i.e. 0.5 wt. % Rh) does not form detectable crystallite materials. This can be either due to very high dispersion or low sizes of the crystals (i.e. < 5 nm). In both figures, peaks could be observed at 2θ values of 30.2, 35.4, 50.2 and 60.1° the most intense of which appeared at 30.2. These features are characteristics of tetragonal ZrO_2 (Galadima *et al.*, 2012a; Galadima et al., 2012b; Galadima *et al.*, 2014a; Galadima *et al.*, 2014b), and the phase was therefore very stable under the carburization temperature of 600°C. Figure 2 revealed new features at 2θ values of 34.4, 37.9, 61.5 and 69.4° that are characteristics of Mo_2C (Galadima *et al.*, 2012a; Galadima *et al.*, 2012b; Galadima *et al.*, 2014a; Galadima *et al.*, 2014b). Therefore, the transformation of MoO_3 to Mo_2C could be considered successful.

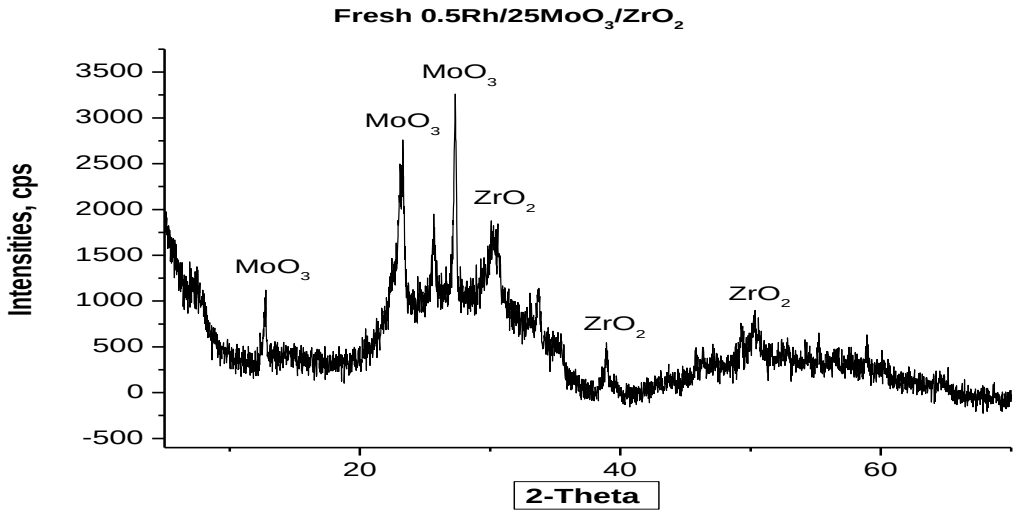


Figure 1: X-ray diffraction patterns of 0.5wt.%Rh/25wt.%MoO_3/ZrO_2 precursor.

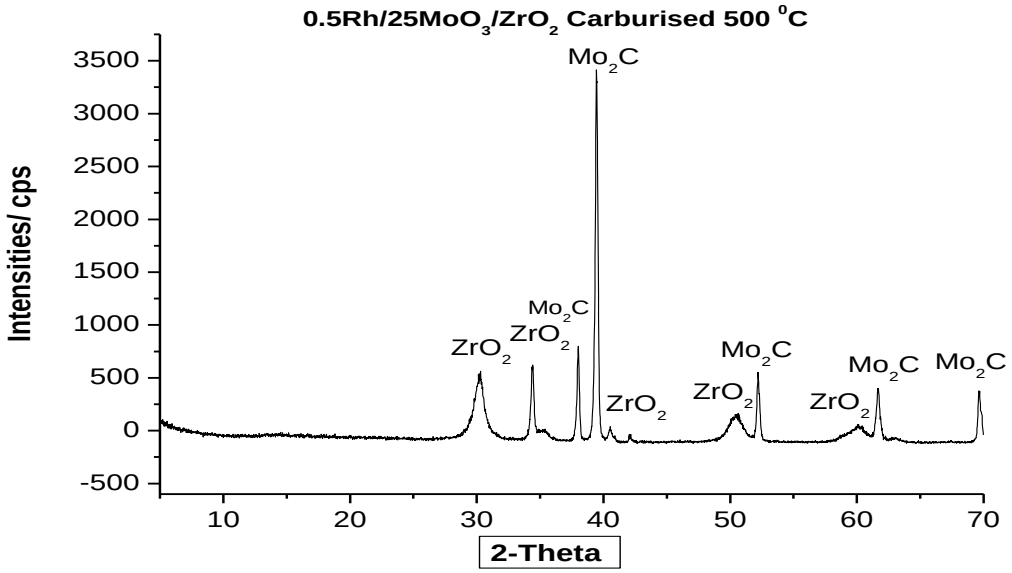


Figure 2: X-ray diffraction patterns of a 0.5wt.%Rh/Mo_2C/ZrO_2 catalyst.

3.3 Catalyst Evaluation

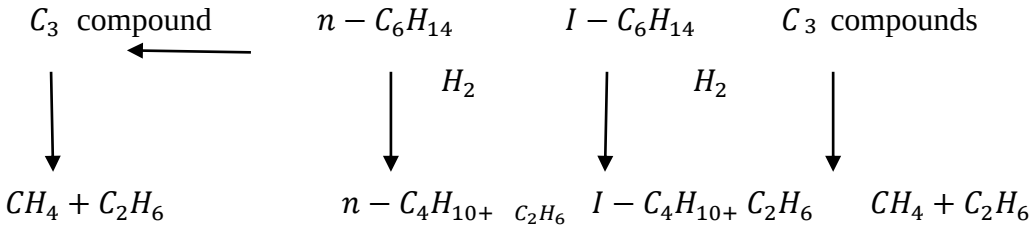
The results of n-hexane and n-octane hydroconversion into light hydrocarbons at 450°C and 1 atm are presented in Table 2. Both reactants produced closer values of conversion, indicating the catalytic activity to only be slight influenced by the nature of the reactant. Similarly, no any alkenes, alkyne or cyclic hydrocarbon was detected with both reactants. Therefore, the hydrogenolysis paths illustrated as schemes 1 and 2 are the most likely mechanistic routes for the reaction. In both cases, methane was produced to the highest selectivity, especially in the case of n-octane (~ 42%).

Therefore, the C-C fission was very rapid. No any butane was detected with n-octane contrary to 6.4% selectivity observed with the n-hexane. Hence, these species were considered to have underwent facile transformation into lighter hydrocarbons. As demonstrated in figure 3, both reactants produced comparative quantities of C_1 to C_4 hydrocarbons, further indicating the hydrogenolysis path as the main reaction route. The detection of very low concentration of butanes and C_5^+ hydrocarbons could be associated with transition state isomerization of some cracked products.

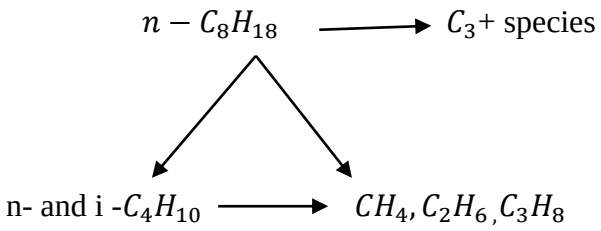
Table 2. Summary of results from catalytic hydroconversion studies.

	n-Hexane	n-Octane
Conversion (%)	20	18
CH_4 (%)	33.20	41.7
C_2H_6 (%)	25.70	24.2
C_3H_8 (%)	23.60	23.7
n- and i-C_4H_{10} (%)	6.40	None
C_5^+ (%)	11.10	10.40

Scheme 1. Hydrogenolysis pathways for n-hexane.



Scheme 2. Hydrogenolysis pathways for n-octane.



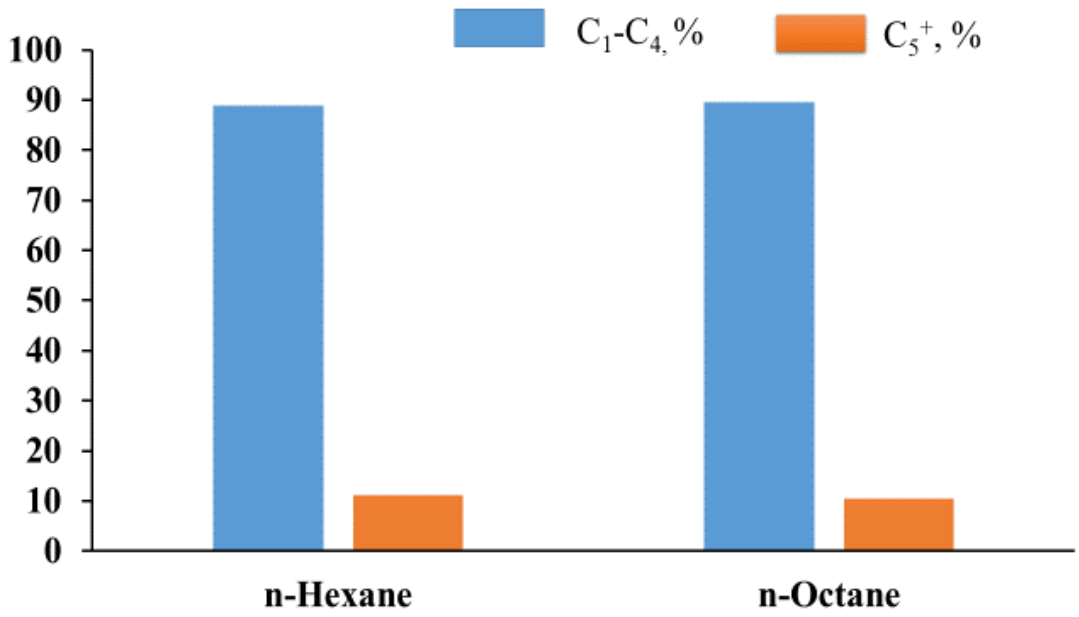


Figure 3: Comparison of the catalyst selectivity to light hydrocarbon species

4.0 CONCLUSIONS

An active 0.5 wt.%Rh/Mo_2C/ZrO_2 was successfully synthesized via simultaneous impregnation and in-situ carburization processes. The X-ray characterization data revealed the Mo_2C as possessing of a hexagonal-closed-pack (i.e. hcp) structure. The catalyst demonstrated comparative activity and light alkanes selectivity during both n-hexane and n-octane conversion at 450^{o}C and 1 atm. Therefore, the activity/selectivity properties of the catalyst were only partly influenced by the chain length of the reacting hydrocarbons. The reaction mechanism was assumed to involve both the end and central C-C facile fissions. Overall, the catalyst can be considered prospective for industrial hydrogenolysis/hydrocracking reaction, but ways of improving n-alkane conversion must be developed.

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