

Production of Liquefied Petroleum Gas (LPG) Range Alkanes from n-Octane *via* Catalytic Hydroconversion

A. Galadima^{**1}, L. Leke³, A. Ismaila², S. Sani¹, Abdullahi, I.⁴, M.U. Okoronkwo³

¹Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, P.M.B. 2346, Sokoto, Nigeria.

^{**}Corresponding author: ahmadgldm@yahoo.com

²Department of Physics, Ahmadu Bello University, P.M.B. 1044, Zaria, Nigeria.

³Surface Chemistry and Catalysis Research Group, Chemistry Department, University of Aberdeen, AB24 3UE, Aberdeen, United Kingdom.

⁴School of Basic and Remedial Studies, Funtua, a Division of Ahmadu Bello University, Zaria, Nigeria.

Abstract

The production of light range alkanes with potentials as LPGs was carried out at 1 atm pressure over a range of reaction temperatures using both *in situ* and *ex situ* prepared molybdenum carbide supported sulphated zirconia catalysts. The *in situ* synthesized material formed the best system in terms of stability, conversion and selectivity to desired reaction products, as well as resistance to thermal treatment. This suggests its prospects as industrial material. Mechanistically, the reaction was believed to involve the participation of both the carbide and the sulphated zirconia surfaces via hydrogenolysis and hydrocracking, respectively. Reactions over the carbide formed mainly methane whereas propane and butanes could significantly be obtained over the sulphated zirconia.

Keywords: n-octane, hydroconversion, light gases, fuel, prospect.

1.0 INTRODUCTION

Over the recent years, international energy organizations like the Department of Energy (DOE), Energy Information Administration (EIA) and International Energy Agency (IEA) of the United States of America have seriously warned on the projected increase in energy demand across the global regions, particularly due to the rapid increase in human population and the development of science and technology coupled with industrialization[1-4].

The currently relied fossil fuels are fast declining in terms of reserves, similarly their exploitation and utilization are associated with great environmental challenges. The emission of carbon dioxide and other greenhouse gases associated with their combustion has thrown this planet into another round of disaster[5, 6]. On the other hand, their release into the sea or on land in liquid forms has increasingly crippled the survival of people around the exploration areas, with additional considerable damages to plants and animals species [7-9].

One of the alternatives being explored for handling some of these challenges is the production of petrol and diesel range hydrocarbon fuels from biomass [10-12]. The technology generally proceeds via two key routes; gasification and pyrolysis of solid biomass to generate gaseous and liquid products followed by subsequent upgrading to the desired hydrocarbon fuels. Primarily, solid or liquid biomass gasification yields synthetic gas (syngas, H₂/CO), which through Fischer-Tropsch reaction is converted to liquid hydrocarbon fuels. On the other hand, the pyrolysis process produces bio-oil consisting both hydrocarbons and oxygenated compounds. These could be upgraded to the affordable fuel grade.

Although this newly explored technology generate low level of LPG range products, the larger hydrocarbons could be treated to the desired fraction *via* catalytic hydroconversion. In the recent work, we have studied the possibility of generating LPG grade n-alkanes from n-octane using both *in situ* and *ex situ* prepared molybdenum carbide supported sulphated zirconia catalyst at atmospheric pressure. Our reason was to evaluate the possibility of extending the biomass-to-petrol technology to include light hydrocarbon fuels production.

2.0 EXPERIMENTAL

2.1 Preparation of Catalyst Precursor

The catalyst precursor was 25 wt% MoO₃/SO₄-ZrO₂ prepared by incipient wetness impregnation of desired weights of ammonium heptamolybdate tetrahydrate (Lab grade, Fisher chemical) and sulphated zirconia (MEL chemical, lab grade, 7 wt% SO₄²⁻). The upper MoO₃ was obtained from the impregnated material after

calcinations in compressed air flow of 50 ml/min at 550°C for 3 h. Precursor material was stored in cleaned plastic sample bottles under laboratory conditions prior to carburization and/or hydroconversion studies.

2.2 *Ex situ* Carburisation

A required weight of the precursor was loaded to quartz tube and placed in heating furnace. The carburization atmosphere composed of 1:4 methane to hydrogen by volume (100 ml/min total flow), the furnace temperature raised slowly to 750°C and maintained for 1h 30 min before cooling to room temperature in a H₂ flow of 20 ml/min.

2.3 *In situ* Carburisation

In situ carburization was carried out in the reaction system using the same carburization atmosphere and time. The maximum temperature was 650°C. The key difference with the *ex situ* case was the chance of catalyst interaction with air prior to hydroconversion with the former case.

2.4 Catalyst Characterisation

Physicochemical properties of the prepared materials were evaluated using BET, BJH and x-ray diffraction measurements. Outgassed sample (200°C overnight) was subjected to BET measurements using a Beckman Coulter SA 3100 surface area and pore volume analyser at liquid nitrogen temperature. The BET surface area of the sample was automatically calculated by the instrument from the N₂ isotherm using the BET method.

Phase identification studies were performed by X-ray diffraction studies, using a Bruker-AXS model x-ray diffractometer with Cu α monochromatic radiation (0.15418 nm wavelength). Measurements were generally carried out at 22°C with steps of 0.02° of 2 θ range of 5 to 70° and 2.5s/step. Phase identifications were performed with the aid of a program developed in Bruker-D8 software stored in a PC connected to the spectrometer.

2.5 Hydroconversion of n-Octane

Generally, 0.2 g of the precursor (in the case of *in situ* carburisation) or the carburized sample (in the case of *ex situ* carburization) was diluted with 0.50 g of SiC and loaded to the quartz reactor between quartz wool, given a total catalyst bed height of 2 cm. Reactions were monitored with 15.0 μ L/min of the n-octane (GHSV = 3.16 h⁻¹) into the flowing hydrogen atmosphere for 2 h 15 min at 450°C and 1 atm. A total of nine samples were trapped at ¼ h intervals. The n-octane reaction products were analysed with the aid of Perkin-Elmer 8410 Gas Chromatograph (GC) with flame ionisation detection (FID).

3.0 RESULTS AND DISCUSSION

3.1 Physicochemical Data

The results of N₂ adsorption studies are presented in Table 1. Carburisation process appeared to have negative effect on the BET surface area of the initial precursor material. Before any treatment, the active surface area was 124 m²/g but significantly decreased to 98 and 92 m²/g for the *ex situ* and *in situ* materials, respectively. It is a known fact that, surface area reduction causes tremendous effect on the overall pore volume of powdered catalysts. This can account for the significant increased in the pore volume of the synthesized materials. The alteration can have positive effect on the diffusion of high hydrocarbons during hydroconversion.

Table 1: Results of BET and BJH measurements.

Material	BET Surface area (m ² /g)	BJH pore volume (ml/g)
MoO ₃ /SO ₄ -ZrO ₂	124	0.0149
β -Mo ₂ C/SO ₄ -ZrO ₂ (<i>ex situ</i>)	98	0.1726
β -Mo ₂ C/SO ₄ -ZrO ₂ (<i>in situ</i>)	92	0.2258

Figures 1 and 2 represent the x-ray diffraction pattern for the two catalytic systems. Each diffractogram possesses weak partly-resolved peaks at 34.5, 37.9, 39.5, 61.5 and 69.6° that are features of the β - Mo₂C[13]. The most intense peaks in Figure 2 are characteristics of the SiC diluant. The diffraction pattern also showed diffraction angles at 30.2, 35.4, 50.2 and 60.1° of 2 θ , with the strongest peak at 30.2°[13]. These peaks are characteristics of tetragonal zirconia. It could be seen that, the influence of the higher temperature conditions produced both zirconia and β - Mo₂C peaks, with out any noticeable structural destruction.

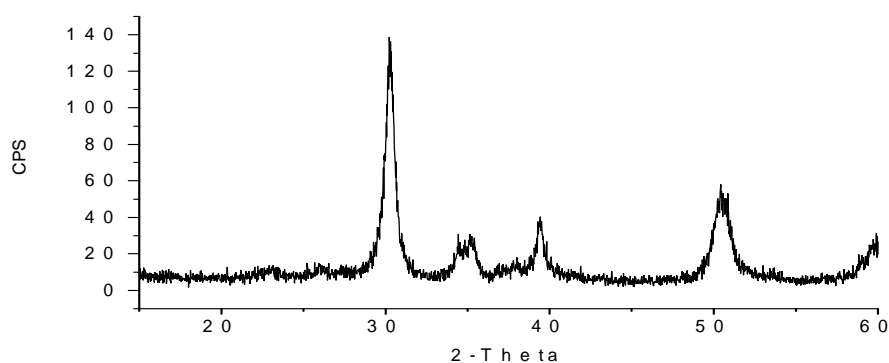


Figure 1: X-ray diffraction patterns of *ex situ* carburized precursor material at 750°C.

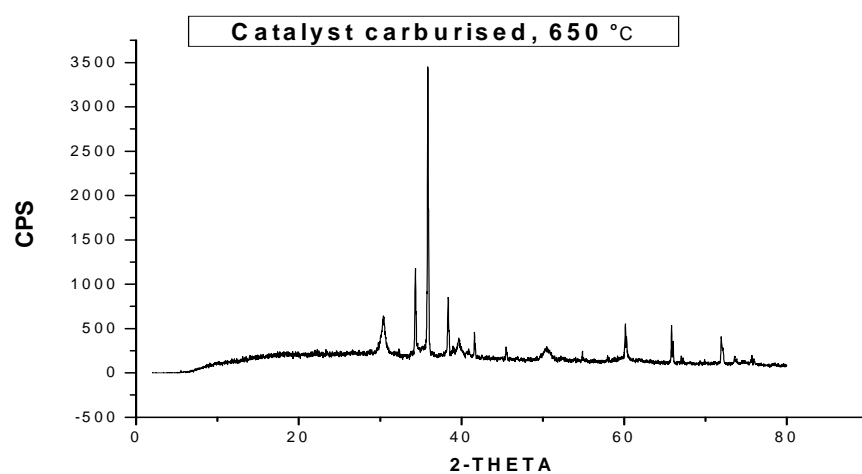
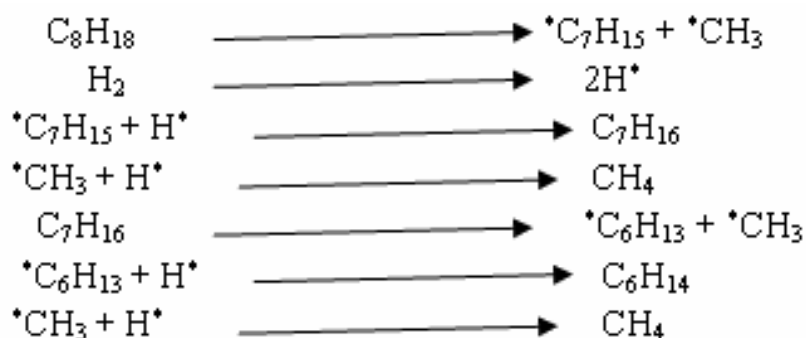


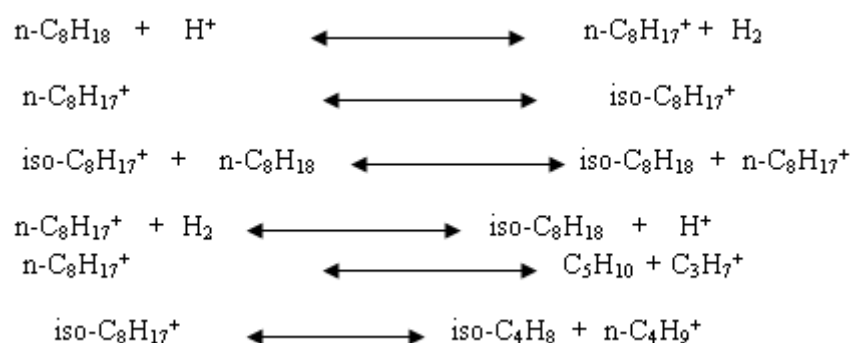
Figure 2: X-ray diffraction patterns of *in situ* carburized precursor material diluted with SiC at 750°C.

3.2 Hydroconversion Studies

The *ex situ* carburized catalyst was employed for the hydroconversion testing without any further treatment. Even though the x-ray diffraction data does not reveal the presence of any oxycarbide phase, exposure of this material to air may have destructive effects on its catalytic performance. It produced a maximum of only 7% conversion that quickly decays after 3 h period. This insignificant activity entails the carburization route to be unsuitable for designing refining grade catalyst. The product distribution indicates a partial production of iso-octanes (< 5%) with overall selectivity to lighter C₁ to C₇ alkanes. Methane, ethane and propane formed the dominant species (> 60%). Both iso- and n- derivatives of butane to heptane were obtained. Absent of lighter alkenes or alkynes to any detectable concentration could be attributed to the role of high hydrogen atmosphere used during the reaction. Production of methane to the highest selectivity shows the reaction to much likely proceeds over the β -Mo₂C surfaces (i.e *via* hydrogenolysis, see scheme 1), because the high energy requirement for acid sites hydrocracking limits the chance of methane formation over the sulphated zirconia support. However, the formation of C_{3,i} and n-C₄ and C₅ species could be Bronsted acid sites mediated. One possibility involved the generation of n-, mono- and multiple branched octane carbenium ions (see scheme 2), that underwent facile β -fission yielding these compounds in the presence of hydrogen.



Scheme 1: Possible catalytic route to methane production over the β -Mo₂C surfaces via radical assisted hydrogenolysis.



Scheme 1: Possible catalytic route to iso-octanes and iso-octane carbenium formation and subsequent hydrocracking over both the β -Mo₂C and SO₄²⁻ZrO₂ surfaces.

The *in situ* prepared catalyst shows very high stable conversions and selectivities, prompting the choice of the carburization option as more reliable. At a particular temperature, the n-octane conversion and reaction products selectivities were linearly constant. This property provides an insight into thermal resistance and non-destructive behavior of the *in situ* system. Table 2 below reports the effect of temperature on the activity. At 350°C the conversion was 15% but increased linearly to 50% at 450°C. The results is in good agreement with the features of key hydroconversion catalyst systems [14-17]. High temperature favors the endothermic reaction under controlled conditions.

Table 2: Effect of changing reaction temperature on catalytic conversion at 1 atm.

Reaction Temperature, °C	Conversion, %
350	15
400	21
450	50

The hydroconversion selectivities are presented in Table 3 given below. Propane and butanes are key important components of LPG that were produced to significant concentrations, especially at elevated temperature of 450°C. Therefore, the catalyst system is highly prospective for LPG synthesis. However, the production of higher liquid hydrocarbons (i.e C₆ to i-C₈) must be taken into account.

Table 3: Products distribution from n-octane hydroconversion at 1 atm.

Reaction Temperature, °C	C ₃ species, %	C ₄ species, %	C ₅ species, %	All other species, %
350	15	25	30	30
400	17	28	17	48
450	25	30	15	30

4.0 CONCLUSION

The study demonstrated that, molybdenum carbide supported sulphated zirconia could be employed as a catalyst for production of LPG range alkanes. It provides an important insight for extending biomass-to-petrol technology to include light hydrocarbon fuels production. *In situ* catalyst preparation favors the formation of most active, stable and reliable material due to hindered air exposure. The participation of both the support and supported materials showed the catalyst to be *bifunctional* in its action.

5.0 REFERENCES

1. Edmonds, J. and J. Reiley, Global Energy-Assessing the Future. 1985.
2. Lutz, C., B. Meyer, and M.I. Wolter, The global multisector/multicountry 3-E model GINFORS. A description of the model and a baseline forecast for global energy demand and CO₂ emissions. International Journal of Global Environmental Issues, 2010. 10(1): p. 25-45.
3. Azar, C., K. Lindgren, and B.A. Andersson, Global energy scenarios meeting stringent CO₂ constraints—cost-effective fuel choices in the transportation sector. Energy Policy, 2003. 31(10): p. 961-976.
4. Nakićenović, N., A. Grübler, and A. McDonald, Global energy perspectives. 1998: Cambridge University Press.
5. Marland, G., et al., Global, regional, and national fossil fuel CO₂ emissions. Trends: A compendium of data on global change, 2003: p. 34-43.
6. Marland, G. and R.M. Rotty, Carbon dioxide emissions from fossil fuels: A procedure for estimation and results for 1950–1982. Tellus B, 1984. 36(4): p. 232-261.
7. Patten, D.M., Intra-industry environmental disclosures in response to the Alaskan oil spill: a note on legitimacy theory. Accounting, Organizations and Society, 1992. 17(5): p. 471-475.
8. Loughlin, T.R. and E.V.O.S.T. Council, Marine mammals and the Exxon Valdez. 1994: Academic Press San Diego.
9. Blumer, M., G.t. Souza, and J. Sass, Hydrocarbon pollution of edible shellfish by an oil spill. Marine Biology, 1970. 5(3): p. 195-202.
10. Prins, M.J., K.J. Ptasiński, and F.J. Janssen, Exergetic optimisation of a production process of Fischer-Tropsch fuels from biomass. Fuel Processing Technology, 2005. 86(4): p. 375-389.
11. Rigby, A.M., Process for producing hydrocarbons from a hydrocarbonaceous feedstock. 2008, EP Patent 1,935,845.
12. Perego, C. and A. Bosetti. Biomass to fuels: the challenges of zeolite and mesoporous materials. in Proceedings of the 16th International Zeolite Conference Joint with the 7th International Mesoporous Materials Symposium. 2010.
13. Galadima, A., et al., Supported Molybdenum Carbide as n-Hexane Upgrading Catalyst. Chemistry and Materials Research, 2013. 3(11): p. 73-78.
14. Gopal, S. and P.G. Smirniotis, Factors affecting isomer yield for n-heptane hydroisomerization over as-synthesized and dealuminated zeolite catalysts loaded with platinum. Journal of Catalysis, 2004. 225(2): p. 278-287.
15. Calemma, V., S. Peratello, and C. Perego, Hydroisomerization and hydrocracking of long chain n-alkanes on Pt/amorphous SiO₂-Al₂O₃ catalyst. Applied Catalysis A: General, 2000. 190(1): p. 207-218.
16. Calemma, V., et al., Hydrocracking and hydroisomerization of long-chain n-paraffins. Reactivity and reaction pathway for base oil formation. Industrial & engineering chemistry research, 2004. 43(4): p. 934-940.
17. Lucas, A.d., et al., Hydroisomerization of n-octane over platinum catalysts with or without binder. Applied Catalysis A: General, 2005. 282(1): p. 15-24.