

Upgrading n-Heptane *via* Catalytic Hydroisomerisation

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Abstract

An atmospheric pressure upgrading of n-heptane was carried out in a temperature range of 300 to 450°C over an *in situ* developed molybdenum carbide phase supported over sulphated zirconia. Although a decreased in surface area with increased in pore volume were observed after carburization, the physicochemical data showed no noticeable alteration to the zirconia structure or the sulphate species. The catalyst formed a good system with high selectivity to iso-heptanes under either low temperature or high space velocity. It therefore has promising features that could offer mitigation to some of the challenges faced by the petroleum refineries with noble metals promoted zeolites.

Keywords: n-heptane, hydroisomerisation, carbide catalyst, stability, sulphated zirconia.

1.0 INTRODUCTION

n-Heptane constitutes one of the principal compositions of gasoline extracts that could be upgraded to higher anti-knocking fractions. The key industrial option for achieving this specific role is the hydroisomerisation process. Under normal operations, n-heptane feed is heated at moderate temperature (250-400°C) over a bifunctional heterogeneous catalyst[1]. High hydrogen pressure of at least 20kPa is usually employed to ensure optimal conversion and limit side reaction interferences[2].

The petroleum refineries have today emphasized on the exploitation of modified zeolitic substances as catalyst materials. Platinum and/or Palladium promoted mordenite (MOR), ZSM-5 and BETA zeolites are the most widely exploited [3-6]. However, the numerous challenges associated with their production and utilization account for the search for a better alternative. The promoters (Pt/Pd) are associated with the production of hydrogenolysis species to very high selectivity. Restricted diffusion problems with the parent zeolites promote Bronsted acid sites assisted hydrocracking. The net effect been very low selectivity to both mono- and multiple-branched heptanes. When coupled with the expensive acquiring and/or production costs, the materials could be considered unprofitable.

In the present study, we have focused on the evaluation of *in situ* generated molybdenum carbide phase supported with sulphate modified zirconia. The effect of a number of operating parameters on the activity of this new system has been critically studied to establish optimal activity. Our reasons for selecting this system include the previous history of the carbide materials as promising catalysts for hydroconversion processes such as hydrodesulphurization and hydrodenitrogenation. Their resistance to catalyst poison and thermal stability are the key favourable factors in this regard[7, 8]. They are also much cheaper than modified zeolites. On the other hand, sulphated zirconia has shown good isomerisation properties at low operation temperatures, especially during n-butane upgrading. We believed the surface modification with carbide to enhances not only isomerisation properties but long term thermal stability. Unlike the zeolitic catalysts, diffusion limitation problems are strictly very low with powdered materials like the developed system and there is also an improved chance of handling the hydrogenolysis and hydrocracking difficulties, particularly due to moderate acidity of sulphated zirconia and optimal carbide loading.

2.0 EXPERIMENTAL

The preparation of the precursor, active phase, subsequent characterization and catalyst testing were carried out as reported in our previous studies [9]. However, details have been captured below for easy reference.

2.1 Preparation of $\text{MoO}_3/\text{SO}_4^{2-}$ - ZrO_2 Precursor

An accurate weight (4.60 g) of hydrated ammonium heptamolybdate ($[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, Fisher Scientific, Laboratory grade reagent) which gives 25 wt% $\text{MoO}_3/\text{SO}_4^{2-}$ - ZrO_2 (computed based on Mo content) was completely dissolved in 100 cm^3 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 cm^3/min at 550°C for 3 h and stored in a pre-cleaned sample bottle under laboratory conditions.

2.2 Carburisation of the Precursor by *In situ* Method

In situ catalysts carburisation was generally carried out in the reaction system, prior to hydroisomerisation studies. The procedure eliminates any possible transition associated with catalyst exposure to air after carburisation.

0.2 g of a catalyst sample diluted with 0.5 g of SiC phase stabilizer was placed into the quartz reactor, between quartz wool plugs, and introduced into the reaction system. Carburisation was carried out with 1:4 CH_4 to H_2 mixture at a total flow of 100 $\text{cm}^3\text{min}^{-1}$ by raising the reactor temperature to 650°C (ramp rate of 20°C/min) and maintained for 2 h 15 min. All carburised samples were cooled to desired reaction temperature in a H_2 flow of 20 mL/min.

2.3 Physicochemical Chemical Elucidations

The physicochemical properties of the catalyst were established using BET and BJH methods, X-ray diffractions (XRD) and X-ray photoelectron spectroscopy (XPS).

For the BET and BJH studies, the sample was degassed at 200°C overnight to remove physically adsorbed water molecules, retained ammonia gas at the surface from calcinations and any other adsorbed gases. The degassed sample was reweighed and the BET and BJH measurements carried out 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 N_2 isotherm using the BET method while pore volume data was generated using the BJH method.

Phase identification and crystallinity studies were carried out by x-ray diffraction studies, with the aid of Bruker-AXS model x-ray diffractometer with Cu $\text{K}\alpha$ 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.

The XPS measurements were carried out with an Omnicron spectrometer, equipped with an EA-125 hemispherical electron multichannel analyser, with a Mg K α X-ray beam source, a radiation energy of 1253.6 eV at 75 W. The samples have been prepared by pressing them into 12 mm diameter pellets; they were mounted in a steel support and were outgassed in a vacuum chamber (10^{-6} Pa) 10 h before the analysis. The measurement reference was Zr 3d_{5/2} 182.3 eV.

2.4 Catalyst Testing

Hydroisomerisation reactions of the n-heptane were initially carried out at 350, 400, 450°C using the *in situ* carburized catalyst under similar hydrogen flow at 1 atm. The reactions were later repeated for a 6 h period to evaluate the catalyst stability. The GHSV was 2.95 h^{-1} . Effect of contact time was evaluated by performing the reactions at 450°C while varying the contact times in the range 0.32 to 0.65 h. Effect of space velocity (hydrogen flow) was evaluated at 350°C. The automatically collected reaction products and unreacted reactants were analysed with the aid of Perkin-Elmer 8410 Gas Chromatograph (GC) with flame ionisation detection (FID).

3.0 RESULTS AND DISCUSSION

3.1 Catalyst Characterization

Table 1 reports the data generated from BET and BJH analysis. It was established that a decreased in active BET surface area could be observed after the carburisation process but with significant increased in the total pore volume. This factor implies the interaction of the carburization atmosphere with the catalyst to have a pronounced effect on the size and distribution of the carbide and/or oxide particles over the sulphated zirconia support.

Sample	BET, m ² /g	BJH Pore Volume cm ³ /g
25MoO ₃ /SO ₄ ²⁻ -ZrO ₂	124	0.0149
β-Mo ₂ C/SO ₄ ²⁻ -ZrO ₂	98	0.1726

Table 1: Results of BET and BJH studies.

Figures 1a and b showed the x-ray diffraction patterns of ammonium heptamolybdate tetrahydrate before and after calcinations, respectively. The pre-calcined material yields patterns that are specific to a monoclinic form of (NH₄)₆Mo₇O₂₄·4H₂O (Figure 1a), which upon treatment with carburization atmosphere at 550°C for 3 h produced new patterns (Figure 1b) that are characteristic of orthorhombic MoO₃. This confirms that the calcinations conditions were appropriately selected.

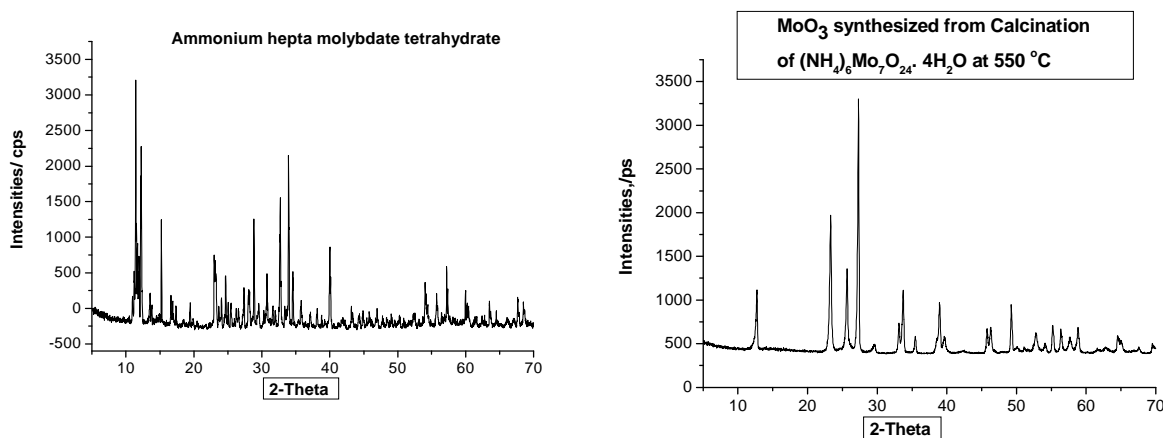


Figure 1a: XRD patterns of ammonium molybdate. Figure 1b: XRD patterns of calcined ammonium molybdate.

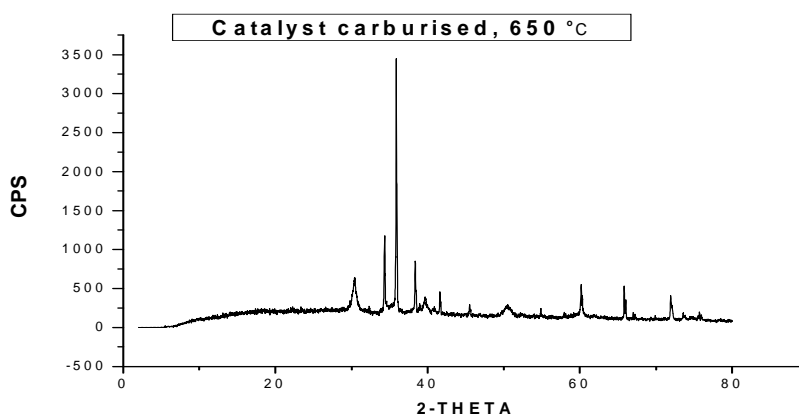


Figure 2: XRD of carburized Molybdenum oxide supported sulphated zirconia diluted with SiC.

A significant increased in crystallinity could be observed in Figure 2. This is associated with the conversion of the oxide to the carbide phase. Weak partly-resolved peaks at 34.5, 37.9, 39.5, 61.5 and 69.6° are features of the β - Mo₂C[9]. The most intense peaks 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° [9]. 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 that very sharper compared to oxide sample (Figure 1b).

The x-ray photoelectron spectra of Mo 3d and C1s are illustrated in Figures 3 and 4. From Figure 3, the weak peak around 228.2eV correspond to β -Mo₂C formation, however the presence of other peaks beyond 230eV corresponding to partial reduction of MoO₃ indicated surface re-oxidation of the carbide phase on exposure to air. The presence of carbidic carbon was supported by the C1s peak with intensity of around 283.8eV (Figure 4). Beyond this are peaks with binding energies between 285 and 290 eV, corresponding to species of deposited coke, possibly during carburization process [9].

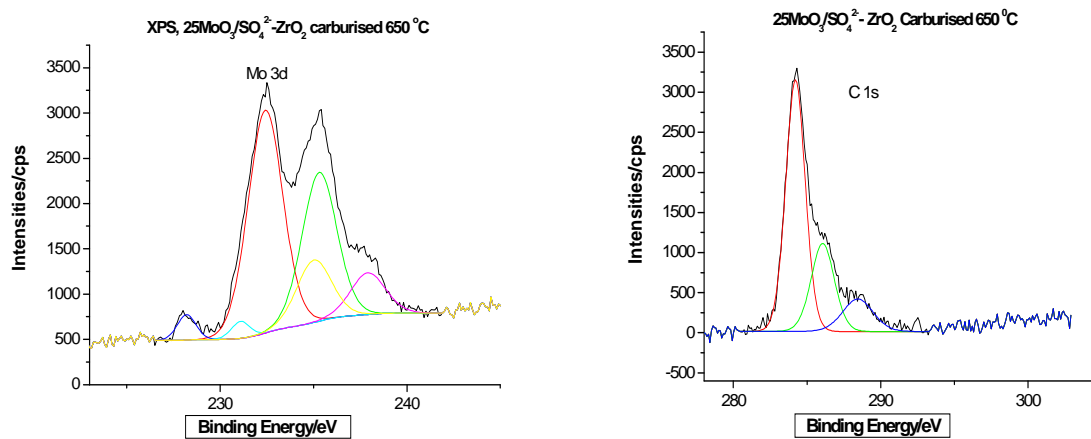


Figure 3: Mo 3d XPS spectra after carburization. Figure 4: C1s XPS spectra after carburization.

3.2 Reaction Studies

One of the important parameter that influences the activity of any hydroisomerisation catalyst is the working reaction temperature. As shown in Figures 5a and b, increasing the reaction temperature favors catalyst activity (i.e conversion of n-heptane). At 350°C the conversion was 40% but increased to 55% when the temperature was raised to 450°C (Figure 5a). This trend has a negative effect on the selectivity to both mono- and multiple branched heptanes, their concentration decreased whereas selectivity to lower facile hydrocracking species was favored (Figure 5b). At 350°C the maximum isoheptanes selectivity was 95% but felt to 84% at the highest working temperature (Table 2) The result is in good agreement with a number of literatures for other n-alkanes under comparable reaction conditions [6, 10, 11]. At higher temperatures the intermediate iso-heptane carbenium ions underwent facile cracking producing mainly methane, propane and n- and i-butane species. Hydrogenolysis over the carbide surfaces could also be a contributing factor under this conditions. An important behavior noticed with the designed catalyst system is its stability over time. At a particular temperature, the catalytic conversions and isomer yields were fundamentally the same irrespective of whether or not, the reaction was carried for longer period. This property is desirable for prospective industrial catalyst. It can be an indication of possible resistance to poisons in the feed as well as active sites protection under thermal treatment.

Reaction Temperature, °C	Isomer Selectivity, %
350	95.0
400	89.4
450	84.0

Table 2: Effect of temperature on selectivity to isoheptanes

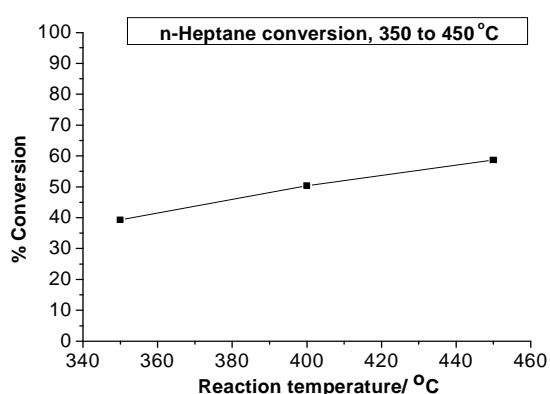


Figure 5a: n-Heptane conversion.

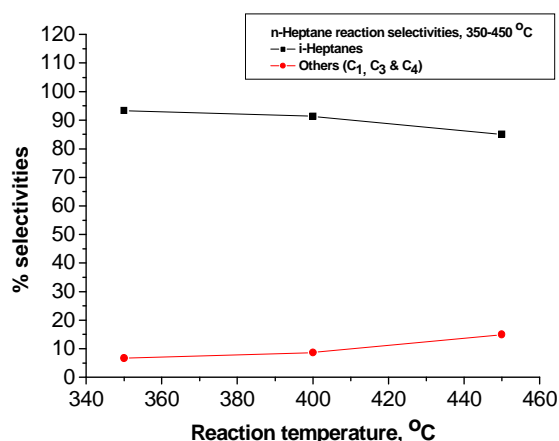
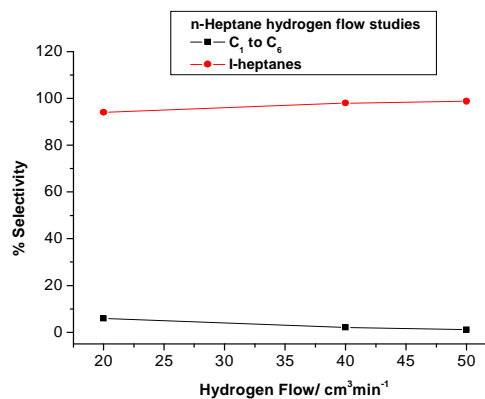
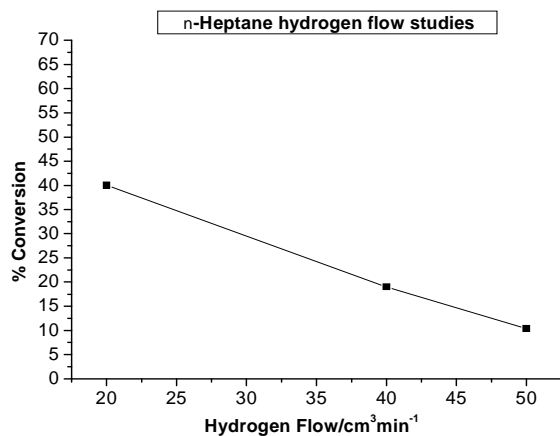


Figure 5b: Reaction products selectivities.

Another important parameter that favors isoheptanes production is the reaction space velocity. Higher space velocities limit the chance of hydrocracking and/or hydrogenolysis by allowing a balance on the catalyst surface. According to Figure 6a increasing the hydrogen flow (i.e. space velocity) caused an overall decreased in the conversion of n-heptane. At 50 ml/min, the activity decays to nearly 10%. On the other hand, the overall production of isoheptanes increased, reaching 99% at 50 ml/min (Figure 6b). The isomer distribution indicates lower hydrogen flow rates to generate multiple-branched heptanes as dominant reaction products (up to 70%). However, at higher flow rates 2 and 3-methylhexanes were the dominant products. The observed trend is also in good agreement with previous literature data [6, 9, 10].



Figures 6a and b: Role of space velocity (Hydrogen flow) on conversion (left) and products selectivities (right) at 350°C.

4.0 CONCLUSION

n-Heptane was successfully hydroisomerised into both mono- and multiple branched heptanes over an *in situ* prepared molybdenum carbide supported sulphated zirconia catalyst system. The catalyst exhibited resistance to deactivation after long time reaction with no observable phase or structural transition. This behavior suggests the possibility of employing this material as a replacement to the zeolitic substances under commercialization. Temperature and hydrogen flow/space velocity influenced the catalytic performance, with low temperature and high space velocities being much favorable for suppressing hydrocracking and hydrogenolysis. Thus, enhancing isomer yield.

5.0 REFERENCES

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