Supported Molybdenum Carbide as n-Hexane Upgrading Catalyst

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Abstract

Catalytic upgrading of n-hexane to corresponding isomers was successfully achieved at 1 atm using molybdenum carbide supported sulphated zirconia as hydroisomerisation catalyst. The characterization data generally indicated the formation of the carbide phase from molybdenum oxide precursor to proceeds stepwise at high temperatures, with increase in crystallinity after carburization. There was also limited destruction to the structural composition of the sulphated zirconia support. Production of isomerised hexanes increased with increase in space velocity but decreased significantly with increase in either hydroisomerisation temperature or contact time. Overall, the catalyst shows good upgrading properties towards n-hexane, suggesting its potentials as gasoline upgrading catalyst.

Keywords: Molybdenum carbide, sulphated zirconia, n-hexane, upgrading, potentials.

1. INTRODUCTION

Since the first application of petrol (i.e gasoline) in automobile engines, the issue of its anti-knocking properties remained crucial. Several options have been tried and later abandoned due a number of factors ranging from environmental pollution to costs and destruction to catalytic converters in the automobile engines. Additives such as tetra ethyl lead (TEL), methyl cyclopenta dienyl molybdenum tricarbonyl (MCT), ethers, alcohols and aromatics were the key additives before 90's. Emissions associated with burning of these substances have severe health consequences including death and mental deformations as well as engine destruction on the other hand, therefore rendering their application as a negative issue to petroleum refineries across the globe [1-4]. The emergence of the hydroisomerisation option in the later years was considered as a way forward. The hydroisomerisation process does not involved the addition of any pollutant to the gasoline, but rather constitutes the conversion of the linear alkanes in the gasoline feed to their corresponding isomers with high anti-knocking properties (i.e higher octane numbers) at high hydrogen pressue (usually > 20 bars). Heterogeneous solid acids promoted with active species of metals, especially Pt and Pd loaded zeolites like mordenites, have been the major catalytic materials in used by many refineries. Although these catalysts have recorded wide global utilization with documented literature of successful applications, the acquiring and processing costs and many other challenges have accounted for the need to shift to most suitable replacements. Production of hydrocracked and hydrogenolysis species, poor thermal stability, low resistance to sulphur and nitrogen poisons in the reaction feed and recycling and reusability problems are among the key difficulties identified by the refineries [4-9].

In the current study, we investigated the potentials of molybdenum carbide supported sulphated zirconia as replacement catalyst. n-Hexane was similarly selected as the model compound for the hydroisomerisation process. Since a catalyst suitable for hydroisomerisation must contain both the acid and metal functions, the acidity of sulphated zirconia coupled with dehydrogenation-hydrogenation properties of molybdenum carbide could be good features of desired catalyst. Carbides of molybdenum have been key important catalysts for petroleum refining, especially during hydrotreatments. They are good for hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxidation (HDO) and many other refinery reactions, thus suggesting their potentials as hydroisomerisation catalysts.

2. EXPERIMENTAL

2.1 Preparation of Molybdenum Oxide Supported Sulphated Zirconia

An accurately weighed 4.60 g of ammonium heptamolybdate tetrahydrate ([$(NH_4)_6Mo_7O_{24}.4H_2O$], Fisher Scientific, Laboratory grade reagent) which gives 25 wt% MoO_3/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

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

200 mg of a catalyst sample diluted with 500 mg of SiC stabilizer was placed into the quartz reactor, between quartz wool plugs, and loaded into the reaction system. Carburisation was carried out with 1:4 CH_4 to H_2 mixture at a total flow of 100 cm^3min^{-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 Catalyst Characterization

The catalyst was characterized 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 kα 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 Catalytic Reactions

Hydroisomerisation reactions of the n-hexane 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. RESULTS AND DISCUSSION

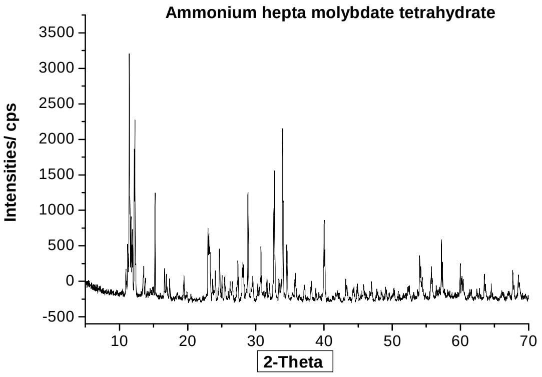
3.1 Catalyst Characterization

Table 1 shows the results obtained from BET and BJH analysis. The data indicated a decreased in active surface area after the carburisation process but with significant increased in the total pore volume. This suggests the carburisation process to possibly influenced 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_2C/SO_4^{2-}-ZrO_2	98	0.1726

Table 1: Results of BET and BJH studies.

Figures 1 and 2 showed the x-ray diffraction patterns of ammonium heptamolybdate tetrahydrate before and after calcinations, respectively. The uncalcined sample shows diffraction patterns corresponding to a monoclinic form of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Figure 1), which upon calcination at 550°C for 3 h produced new diffraction features (Figure 2) that are characteristic of orthorhombic MoO_3. This implies that the calcinations conditions were appropriately selected.



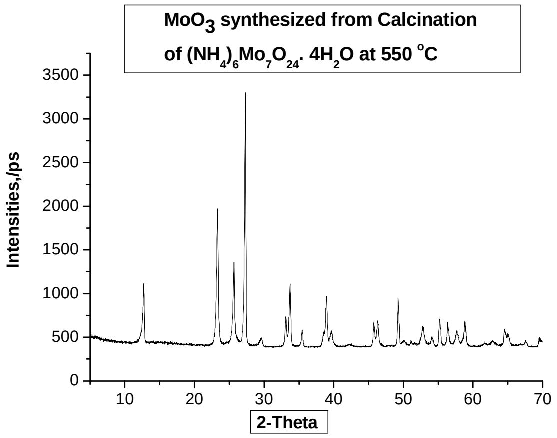


Figure 1: XRD patterns of ammonium molybdate. Figure 2: XRD patterns of calcined ammonium molybdate.

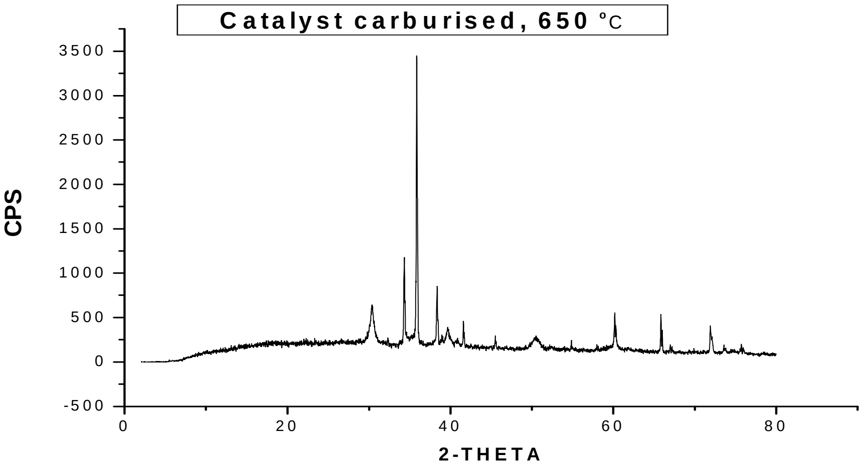


Figure 3: XRD of carburized Molybdenum oxide supported sulphated zirconia diluted with SiC.

A significant increased in crystallinity could be observed in Figure 3. This is associated with the conversion of the oxide to the carbide phase. Weak peaks at 34.5, 37.9, 39.5, 61.5 and 69.6^{o} are characteristic of the β- Mo_2C [10-12]. The most intense peaks are features of the SiC diluant. The diffraction pattern also showed diffraction angles at 30.2, 35.4, 50.2 and 60.1^{0} of 2θ, with the strongest peak at 30.2^{o}. These peaks are characteristics of tetragonal zirconia. It could be seen that, the influence of the higher temperature conditions produced both zirconia and β- Mo_2C peaks that very sharper compared to oxide sample (Figure 2).

The x-ray photoelectron spectra of Mo 3d and C1s are illustrated in Figures 4 and 5. From Figure 4, the weak peak around 228.2eV correspond to β-Mo_2C formation [13-14], however the presence of other peaks beyond 230eV corresponding to partial reduction of MoO_3 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 5). Beyond this are peaks with binding energies between 285 and 290 eV, corresponding to species of deposited coke, possibly during carburization process.

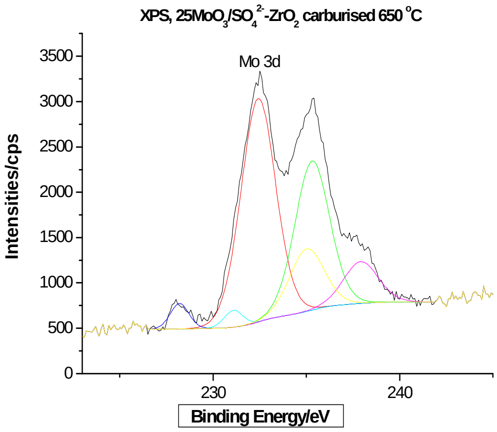


Figure 4: Mo 3d XPS spectra after carburization.

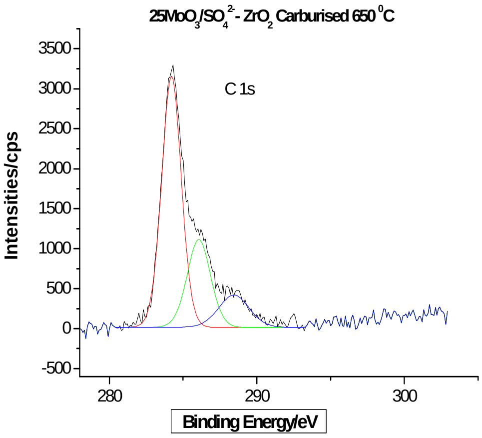


Figure 5: C1s XPS spectra after carburization.

3.2 Hydroisomerisation Reactions

Figures 6 and 7 showed the effect of changing reaction temperature on the conversion and selectivities respectively. Increasing the reaction temperature resulted in an increase in the conversion of n-hexane (Figure 6). At 350°C, the conversion was 45.02% but rose to 50.05 and 55.01% at 400 and 450°C, respectively. The production of hydrogenolysis/hydrocracking species also increased with temperature but the production of isohexanes decreased as the temperature was raised (Figure 7).

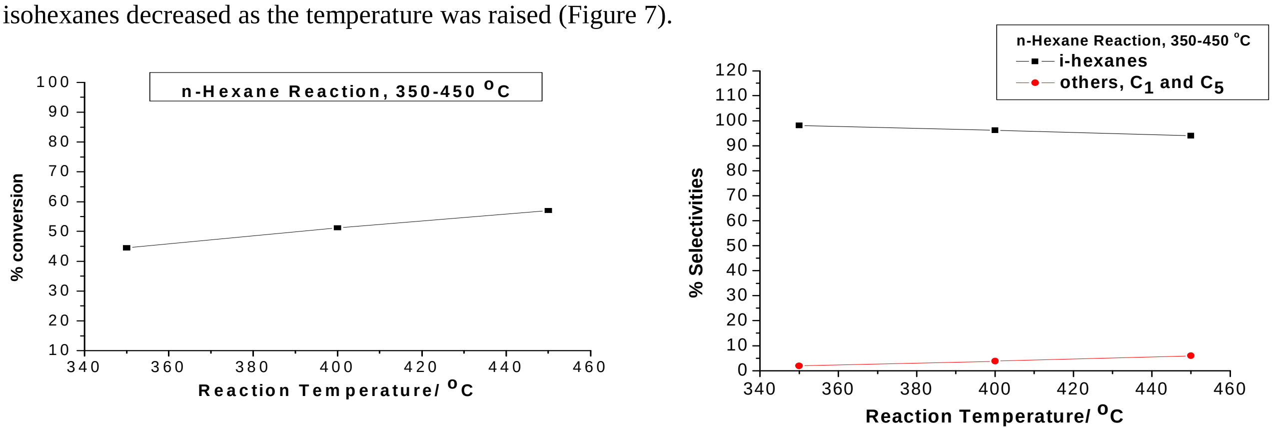
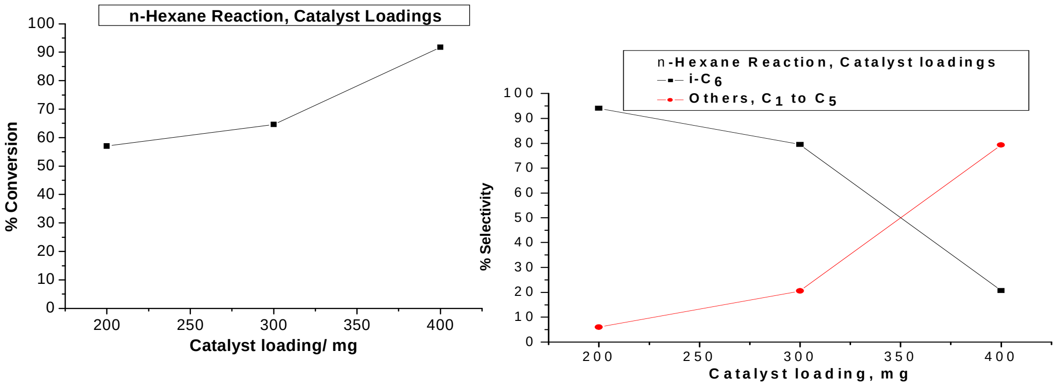


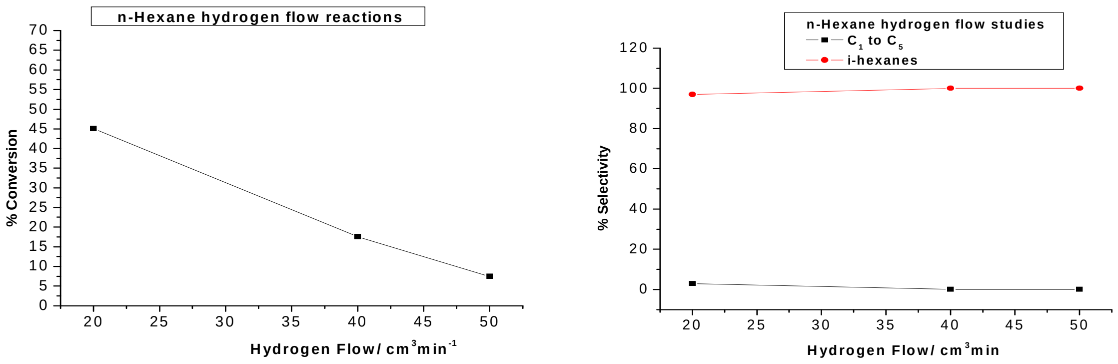
Figure 6 and 7: Effect of temperature on n-hexane conversion (left) and products reaction selectivity (right).

Figures 8 and 9 showed the effect of changing the catalyst weight (i.e contact time) on the conversion and selectivity, respectively. The conversion of n-hexane increased with increased catalyst loading. At 200 mg, the conversion was ~55%, but rose to ~65 and ~93% at 300 and 400 mg loadings, respectively (Figure 8). On the other hand, reaction selectivity to isohexanes dropped while the formation of hydrocracking/hydrogenolysis species increased (Figure 9). The trend of the results is in good agreement with that obtained with n-heptane and could be correlated with a number of previous studies [9]. The results also indicate that n-hexane was initially converted into iso-hexanes, which undergo successive degradation into lighter alkanes by hydrocracking/hydrogenolysis [9].



Figures 8 and 9: n-Hexane conversion (left) and product selectivities (right) with catalyst loading (i.e contact time) at 450°C.

The effect of changing space velocity on the catalyst activity with space velocity during n-hexane hydroisomerisation was monitored under the conditions stated earlier and results are illustrated as Figures 10 and 11. In a trend similar to literature studies with other catalysts, n-hexane conversion decreased with increasing hydrogen flow rate (Figure 10) while the selectivity to isomerisation products increased (Figure 11). At 20 mL/min the conversion was 45.02% but decreased to 17.6 and 7.5% at 40 and 50 mL/min, respectively. On the other hand, the iso-hexane selectivity was initially 96.9% but increased linearly to ~100% at 50 mL/min of hydrogen. The results showed that, at high space velocities, isoalkanes became stabilised while cracking is suppressed [15-16].



Figures 10 and 11: Change in n-hexane conversion (left) and product selectivities (right) with hydrogen flow (space velocities) at 350^{o}C.

4. CONCLUSION

The various characterization results indicated the carburization of molybdenum oxide over the sulphated zirconia surfaces to be a feasible process with limited destruction to structural or activity properties of either the active phase or the support. Production of isomerised hexanes with very high selectivity at low temperature, high contact time and/or low catalyst loading indicates the potentials of the designed catalyst system as gasoline upgrading catalyst.

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