

Ring Opening of Decalin over Zeolite-Supported Ni-Co-Mo Catalysts

U.I Gaya¹⁺, B.Y. Jibril², Y.M. Al-Wehaibi², R.S. Al-Hajri² and J.T. Naser²

¹ Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B. 3011 Kano State, Nigeria

² Department of Petroleum and Chemical Engineering, Sultan Qaboos University, Postcode 123, P.M.B. 36, Alkhoud, Muscat, Oman

Abstract. The applicability of different zeolite-supported Ni-Co-Mo for hydrocracking was tested using decalin as model light oil, towards the use of the supported catalysts in heavy crude upgrade. The study aimed at surmising the hydrocracking ability of the metals, the influence of the support, the products and mechanism of the reaction. The metals (Ni-Co-Mo) were dosed up in atomic mass fractions (0.300 : 0.175 : 0.525, respectively) by impregnation and calcinations onto the supports to produce 5 wt%, 10 wt %, 15 wt % and 20 wt% contents. Support materials were varied based on SiO₂/Al₂O₃ ratio (1:50; 1:5; 1:1; 1:20; 1:280) using as received commercial CBV5524G, CBV300, CBV901, CBV21A, CBV28014, respectively. SiO₂ and Al₂O₃ -supported metals were also prepared to check backgrounds. Catalysts were characterised by X-Ray Diffractometry (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. Reactivity experiments were performed at 250 °C, in a microwave operated batch reactor of 100 ml capacity, under autogenous pressure for 90 min. Ring opening of decalin and the formation of varied products was studied using FTIR spectroscopy and Gas Chromatography-Mass Spectrometry (GC-MS). Ring opening products were mostly alkyl cyclohexene, Z/E-disubstituted alkenes, ethers but in addition a phenolic characterised by its distinctive FTIR absorption bands, was selectively formed over Ni-Co-Mo/CBV901. Reaction mechanisms for product formation are speculated, which include α - and β - scission of the decalinic fused ring.

Keywords: Zeolite, hydrocracking, decalin, Ni-Co-Mo.

1. Introduction

Many parts of the world are endowed with immense reserve of heavy crude oil which remains untapped or even unexplored owing to the difficulty of recovery, pumping, transportability and poor value [1-3]. Heavy crude oil is a type of unconventional oil characterized by high density, viscosity and asphaltene content, usually associated with other impurities such as sulphur, waxes and carbon residue that may have to be removed before being refined [4]. Consequently, this translated as poor market for the heavy crude oil. On the other hand, light crude deposits are threatened with depletion and the will to purchase them also constantly declined. It is therefore a renewed initiative to explore and tap denser crude reserves. Accordingly, it becomes crucial to synthesize catalysts with promising performance for hydroprocessing such unconventional crudes.

Hydroprocessing catalysts containing different components or support materials have been synthesized by several workers. Minja and Ternan [5] modified Co-Mo/Al₂O₃ heavy oil hydrocracking catalysts by the addition of 20 wt % hydrogen-mordenite zeolite. The turnover frequency for HDM per nm² was greater for catalysts containing greater amounts of mordenite. The catalyst performance was attributed to the catalyst acidity (confirmed by temperature-programmed desorption of benzofuran) and changes in catalyst pore geometry. Nares et al. [6] upgraded heavy crude oil from the Gulf of Mexico at high H₂ pressure (10.8 MPa), using separately supported commercial heterogeneous catalysts (MoCoP/Al₂O₃ or MoWNiCoP/Al₂O₃) and unsupported ones (Mo, Fe, and Mo-Fe). Weismann et al. [7,8] and Cavallaro et al. [9] attempted improving

⁺ Corresponding author.

E-mail address: gayau2841@buk.edu.ng

the quality of heavy oil in a combustion tube enveloped by a high pressure vessel using supported Ni-Mo. In the first test conventional in situ combustion tube packing was used alone. To the best of our knowledge, most of the cracking formulae used by the previous workers composed of binary metals, ternary metal-nonmetal or single metal catalysts in supported or unsupported forms. We present our evaluation of the cracking ability of ternary metal (Ni-Co-Mo) catalysts supported on different zeolites using decalin (decahydronaphthalene) as model oil. Although decalin occurs in minute quantities in crude petroleum it makes a good choice for preliminary observations of the cracking ability of these catalysts.

2. Experimental

2.1. Catalyst Preparation

5 wt% Ni-Co-Mo was supported on zeolites by impregnation in a solution containing atomic mass fractions of metals namely $W_{Ni} = 0.300$; $W_{Mo} = 0.525$; $W_{Co} = 0.175$, using BDH AnalaR $Ni(NO_3)_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The CBV zeolite powders used in the study, their surface area (S_a) and silica-alumina mole ratio (SAR) are as follows.

- CBV5524G or NH_4 -ZSM-5; SAR = 50, $S_a = 425 \text{ m}^2/\text{g}$
- CBV901 a H-Zeolite-Y type powder; SAR = 1, $S_a = 80 \text{ m}^2/\text{g}$
- CBV21A is an NH_4 -Mordenite powder; SAR = 20, $S_a = 400 \text{ m}^2/\text{g}$
- CBV28014, also an NH_4 -ZSM-5; SAR = 280, $S_a = 400 \text{ m}^2/\text{g}$
- CBV300 is an NH_4 -zeolite-Y; SAR = 5, $S_a = 925 \text{ m}^2/\text{g}$

Zeolyst powders were loaded with 5 wt % Ni-Co-Mo by constant agitation of mixed metal solutions for 24 h under room condition (25 °C), followed by drying at 83 °C and calcination in the presence of air at 500 °C for 4h. The calcined material was made into uniform sizes of 500 micron using Glenammer sieves. The 5 wt% Ni-Co-Mo supported zeolites were characterized by XRD.

2.2. Hydrocracking Experiments

Hydrocracking experiments were carried out in batch mode Milestone microwave Start D using decalin (15.5 mL) as a model hydrocarbon. 5 mL ethanol (previously diluted by water in 1:1 ratio) was used as H-donor while the water acts as enhancer. The microwave reactor was operated at 250 °C under autogenous pressure for 90 min. The resulting sample from the hydroprocess was dried with Na_2SO_4 and centrifuged at 1000 rpm for 5 min. The top layer was a dark orange coloured oil. The bottom layer consisted of a plain orange waxy residues which were separated at high retention times (15.9, 17.5, 37.3 and 52.5 min) using Perkin Elmer Clarus 600 GC, which was installed with DB-5 column and hyphenated with quadrupole MS detector. The top fairly translucent layer was analysed by FTIR, GC-MS and UV-Vis spectrometry. FTIR-spectrometer was operated at spectral range of $4000-400 \text{ cm}^{-1}$. The GC-MS was a Varian GC. 3800 coupled to a Varian Saturn 2200 ion trap equipped with a Varian Factor Four VF-5ms column (30 m \times 0.25 mm i.d., 0.25- μm film thickness) and operated using Chemstation software. In the FTIR analysis, liquid product was dropped as film between two NaCl discs using glass capillary tube. As -Cl cannot absorb on NaCl plates, methylene chloride was used for cleaning.

3. Results and Discussion

3.1. Catalyst Characterisation

The 5 wt% metals supported catalysts were analysed by FTIR and XRD, to ascertain functional groups and identify any changes in the zeolitic phase respectively. The X-ray diffractometer used in the analysis was Philips PW1710 automated powder diffractometer having nickel-filtered $Cu \text{ K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation and scanned over 2θ ranges of 5 to 40 degrees. The IR spectra were recorded on Perkin Elmer BX FTIR spectrometer controlled by spectrum software. Catalyst powder (1%) was mixed with previously dried KBr and pressed into pellet. The catalysts show asymmetric stretching Si-O near 1100 cm^{-1} , bending Si-O near 790 cm^{-1} , weak asymmetric stretching of Si-OH at 460 cm^{-1} , and symmetric OH stretching at 1635 cm^{-1} .

XRD micrograph has shown that the zeolite powders retain their identities after supporting the metals. CBV 300 for example was identified as zeolite-Y using JCPDS. Fig. 1 shows the XRD micrograph of 5 wt%

Ni-Co-Mo/CBV300. From the figure, this powder appears to contain amorphous phase to highly crystalline phases. The micrograph is similar to that of Ni-CO-Mo/CBV901 (another zeolite-Y) and Ni-CO-Mo/CBV (mordenite). On the other hand, 5 wt% Ni-Co-Mo/CBV28014 and 5 wt% Ni-Co-Mo/CBV5524G (both ZSM-5 based) showed relatively poor crystallinity.

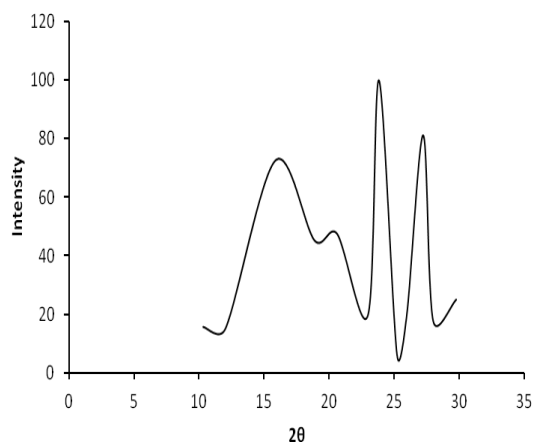


Fig. 1: XRD micrographs of the supported metal catalysts

3.2. Products of Hydrocracking

Cyclohexene derivatives were detected by GC-MS at different retention times (RT min): 3-ethylcyclohexene (RT = 6.898 min), 3-propylcyclohexene (RT = 6.404 min), 1-propyl or 1-butyl cyclohexene (RT = 6.410). Tetralin (1,2,3,4-tetrahydronaphthalene) was observed near 7.474 min. The presence of these cyclohexene products can be corroborated by the analysis of the FTIR absorption spectra of decalin before and after hydrocracking. The starting compound decalin was detected at 5.37 min. Decalin shows absorption at 2919 cm^{-1} for sp^3 C-H anti-symmetric stretching while absorption at 2851 cm^{-1} is due to C-H symmetric stretching. Absorptions at 1449 cm^{-1} , 666 cm^{-1} and 452 cm^{-1} are for C-H bending vibrations. After the hydrocracking reaction, several compounds were formed. The FTIR absorption frequencies of the functional groups of these compounds are displayed in Fig. 2.

Absorption frequency of acyclic C=C was at 1648 cm^{-1} (medium, broad band). The emergence of absorption band at 839 cm^{-1} which was absent in decalin spectrum, shows the presence of alkene. The absorption frequency at 971 cm^{-1} shows the presence of trans-double bond which in turn indicates the presence of R-CH=CH-R (E). The absorption frequency at 741 cm^{-1} shows the presence of cis-disubstituted alkene with structure R-CH=CH-R (Z). The lone peak 1138 cm^{-1} shows the presence of symmetrical ether (R-O-R). This is confirmed by C-O-C absorption band at 853 cm^{-1} . The pair of absorption bands near 1333 cm^{-1} and 1224 cm^{-1} shows the presence of phenolic C-OH (Ph-OH). This is confirmed by the weak absorption at 3300 cm^{-1} [10] and by electronic absorption spectrum at 274 nm. This appears to be selective transformation as this functional group was not detected except on hydrocracking over 5 wt% Ni-Co-Mo/CBV901. Similarly, the other zeolite-Y based supported Ni-Co-Mo (5 wt % Ni-Co-Mo/CBV300) yielded spiro[4.5] decane which could only be detected on using DB-5 column (installed on Clarus 600 Perkin Elmer GC-MS) at 6.02 min. Incidentally, spiro [4.5] decane has also been reported by Haas et al. [11] in the hydrogenolysis of decalin over Ir/ and Pt/silica catalysts, which supports this premise.

3.3. Reaction Mechanisms

The following reaction mechanism may be speculated for the hydrodecomposition of decalin in presence of ethanol as H-donor. One of the decalin rings can open at C atom α - or β - to one of the fused carbon atoms. In the former case 1-butylcyclohexane is formed while the latter results in the formation of 3-(or 1)-cyclohexene.

The hydrogen for hydrocracking is supplied by ethanol and steam used in the process but this resulted in the formation of ethers and organic alcohols. Tetralin is probably directly formed from decalin as Wang et al. [12] have earlier proposed the mechanism in the ring opening of naphthalene.

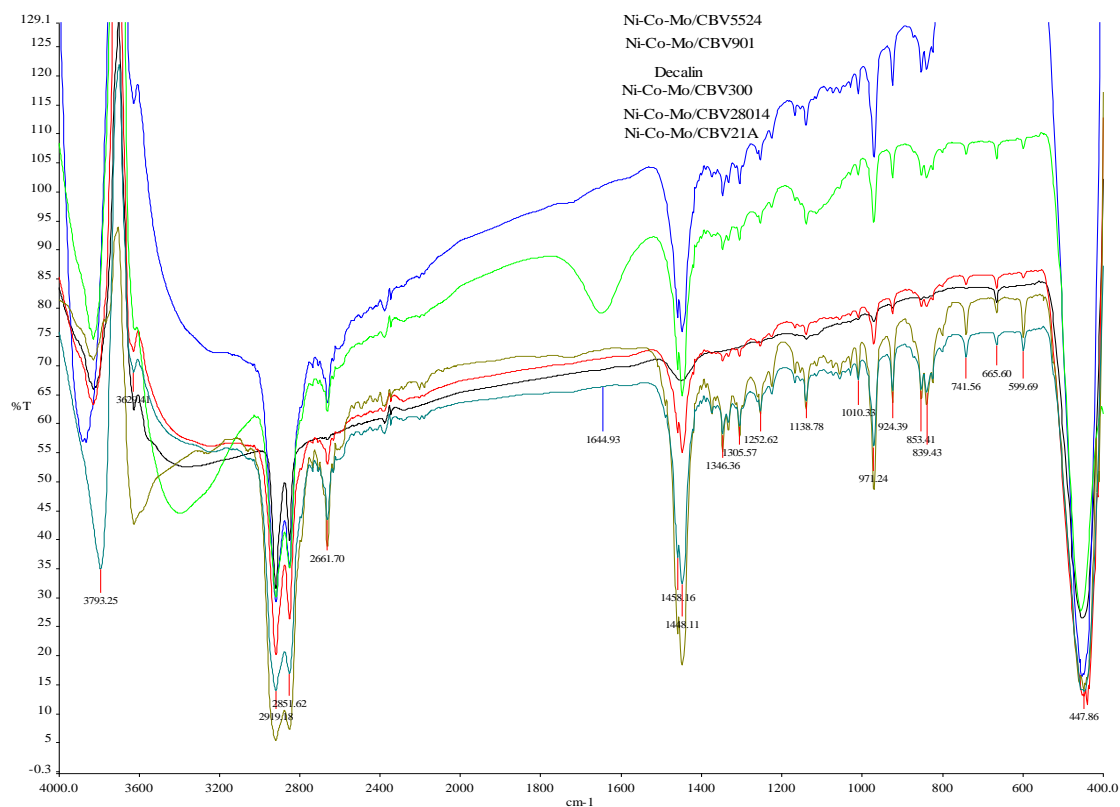


Fig. 2: Overlay of the FTIR spectra of the products of decalin before and after hydrocracking over 5wt% Ni-Co-Mo/CBV zeolites

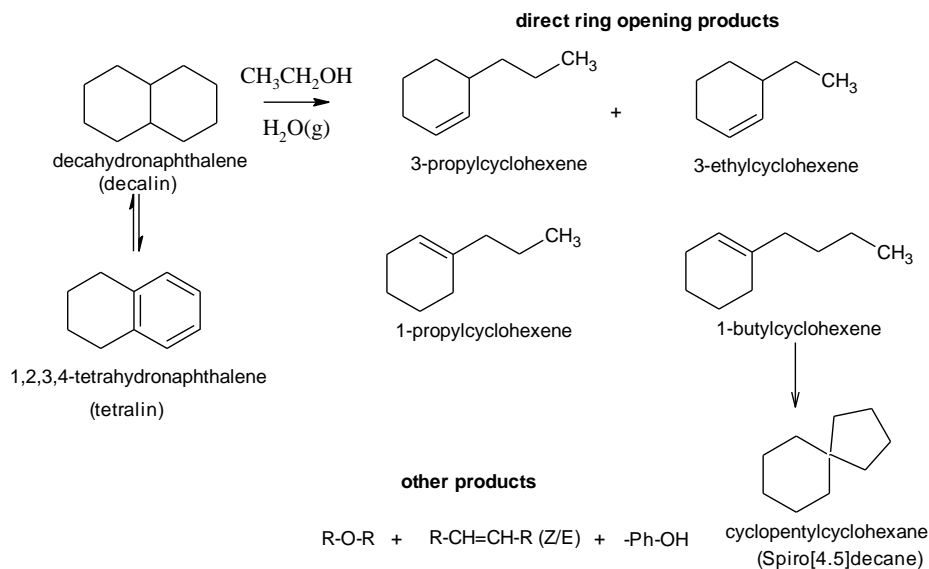


Fig. 3: XRD micrographs of the supported metal catalysts

4. Acknowledgements

Umar gratefully acknowledges The Research Council (TRC) of Sultan Qaboos University for funding this work under postdoctoral fellowship scheme as well as Bayero University Kano for granting the postdoctoral leave and sponsoring presentation of the work at the 2012 ICECB.

5. References

- [1] S.W. Hasan, M.T. Ghannam, N. Esmail, Heavy crude oil viscosity reduction and rheology for pipeline transportation, *Fuel* 2010, **89**: 1095–1100.
- [2] H. Al-Sulaimani, S. Joshi, Y. Al-Wahaibi, S. Al-Bahry, A. Elshafie, A. Al-Bemani, Microbial biotechnology for enhancing oil recovery: Current developments and future prospects, *Biotechnol. Bioinf. Bioeng.* 2011, **1**: 147-158.

- [3] Y. Al-Roomi, R. George, A. Elgibaly, A. Elkamel, Use of a novel surfactant for improving the transportability/transportation of heavy/viscous crude oils, *J. Pet. Sci. Eng.* 2004, **42**: 235-243.
- [4] J.G. Speight, The desulfurization of heavy oils and residua, 2nd Ed., Marcel Dekker Inc., New York, 2000.
- [5] H.R. Nares, P. Schacht-Hernández, M.C. Cabrera-Reyes, M. Ramírez-Garnica, O. Cazarez-Candia, *Petroleum Society's 7th Canadian International Petroleum Conference (57th Annual Technical Meeting)*, Calgary, Alberta, Canada, June 13 – 15, 2006.
- [6] R.J.A. Minja, Marten Ternan, Hydrocracking Boscan heavy oil with a Co-Mo/Al₂O₃ catalyst containing an h-mordenite zeolite component, *Energy & Fuels* 1991, **5**: 117-122.
- [7] M. Greaves, T.X. Xia Downhole upgrading of wolf lake oil using THAI/CAPRI processes - tracer tests, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2004, **49**: 69-72.
- [8] J.G. Weissman, R.V. Kessler, R.A. Sawicki, Down-Hole Catalytic Upgrading of Heavy Crude Oil, *Energy & Fuels* 1996, **10**: 883-889.
- [9] A.N. Cavallaro, G.R. Galliano, R.G. Moore, S.A. Mehta, M.G. Ursenbach, E. Zalewski, P. Pereira, In situ upgrading of Llançanelo heavy oil using in situ combustion and a downhole catalyst bed, Paper presented at the Petroleum Society's 6th Canadian International Petroleum Conference (56th Annual Technical Meeting), Calgary, Alberta, Canada, June 7 – 9, 2005.
- [10] D.L. Pavia, G.M. Lampman, G.S. Kriz, J.R. Vivyan, Introduction to spectroscopy, Brooks/Cole, 2009
- [11] A. Haas, S. Rabl, M. Ferrari, V. Calemma, J. Weitkamp, Ring opening of decalin via hydrogenolysis on Ir/- and Pt/silica catalysts, *Appl. Catal. A: Gen.* 2012, **425–426**:97– 109.
- [12] Q. Wang, H. Fan, S. Wu, Z. Zhang, P. Zhang, B. Han, Water as an additive to enhance the ring opening of naphthalene, *Green Chem.* 2012: 1-6.