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ScienceDirect

Procedia Earth and Planetary Science 11 (2015) 325 – 331

Procedia
Earth and Planetary Science

Global Challenges, Policy Framework & Sustainable Development for Mining of Mineral and Fossil Energy Resources (GCPF2015)

Mesoporous Alumina Supported NiMo Catalysts for Residue Conversion

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Abstract

Mesoporous alumina catalyst supports with high surface area (upto458m^2/g) and pore volume (upto1.55cm^3/g) have been synthesized through Sol-gel process using non-ionic block copolymers as a template. Nitrogen gas adsorption, FT-IR and transmission electron microscopy were performed to determine the structure of these synthesized materials. Hydro processing of vacuum residue with prepared NiMo catalysts supported on mesoporous alumina was conducted in a batch reactor. The hydro processing reactions were performed at 400-420˚C with hydrogen pressure of 100bar. High conversions with low coke formation and high quality of liquid products (12.46wt% of naphtha, 31 wt% of middle distillates, 21wt% of VGO and 36wt% of residue) is obtained with the catalyst having large pore diameter and high pore volume.

Peer-review under responsibility of organizing committee of the Global Challenges, Policy Framework & Sustainable Development for Mining of Mineral and Fossil Energy Resources.

Keywords: Mesoporous alumina; vacuum residue; hydroprocessing.

1. Introduction

Residue hydro processing is the most attractive process for refineries to produce high yield of middle distillates to meet the growing demand of transportation fuels. However, it is not as simple process as conventional hydro treating. Vacuum residue (VR) is the heaviest fraction of petroleum residue fractions. The presence of high concentration of asphaltene and metals makes the VR as a challenging feed to upgrade. The catalyst system used for hydroprocessing are generally composed of CoMo/NiMo alumina supported catalysts designed for hydrodesulphurisation (HDS), hydrodemetallisation (HDM), asphaltene conversion (HDAs) and hydrocracking (HCR).The main problem with these catalysts is catalyst deactivation[1-2]caused by coking and deposition of heavy metals. By understanding the catalyst deactivation mechanisms in heavy oils and asphaltenic fraction one can improve the catalysts with increased catalyst life cycles.

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Peer-review under responsibility of organizing committee of the Global Challenges, Policy Framework & Sustainable Development for Mining of Mineral and Fossil Energy Resources.
doi:10.1016/j.proeps.2015.06.068

It has been already reported in literature that diffusion of large molecules such as asphaltene and organometallic compounds through the catalyst pores to reach its active sites is the limiting step in heavy oil hydrocracking reactions. Therefore, the pore size and pore volume of the catalyst plays a crucial role in improving the catalyst life cycle and decreasing the rate of catalyst deactivation. It has been found that mesoporous materials favour the access of asphaltenes from the heavy oils into the active sites of the catalyst thereby promoting asphaltene conversion (HDAs), hydrodemetallization (HDM) and residue conversion reactions.

In the present study, mesoporousaluminas were synthesized using non-ionic surfactant as structure directing templates. Then the catalytic activity studies of the NiMo-catalyst supported on these mesoporous alumina in the upgrading of VR as feedstock has been investigated.

2. Experimental

2.1. Support synthesis

Aluminum isopropoxide (alfaaesar 98%) and P123 triblock copolymer (sigma-aldrich) were used as aluminum source and non-ionic surfactant respectively. The solvents used for the synthesis are isopropanol and sec-butanol.

The mesoporousaluminas have been prepared by using sol-gel route. The molar composition for the synthesis of AL-I is: - 1.0 aluminum isopropoxide: 0.1 surfactant: 0.25 DPA (dipropylamine): 2.0 water and 18.2 isopropanol. The surfactant was dissolved in half of the required amount of isopropanol and the aluminum isopropoxide was added into this solution. Then a solution containing water, DPA and remaining solvent was added drop wise to above made solution with constant stirring at room temperature. The resulting gel was stirred for 2h and then left for 24h at room temperature. The synthesized alumina paste was separated by filtration and washed with a mixture of ethanol and water (2:1), followed by drying at 353K for 48h. Then the sample was calcined at 773K for 4h at rate of 3˚C/min. The sample is denoted as AL-I.

For the synthesis of AL-II, 0.2mol of surfactant was dissolved in 12.5mol of sec-butanol. Then 1mol of aluminum isopropoxide was added. After 2h of stirring at room temperature, a dilute solution of water in sec-butanol was added drop wise with constant stirring. The as-synthesized product was then stirred at room temperature for 3h followed by drying at 80˚C for 24h. Finally, the dry powder was calcined at 550˚C for 4h. The calcined material is assigned as AL-II.

2.2. Catalyst preparation

The catalysts were prepared by the incipient wetness impregnation method with successive impregnation of the precursor salts, ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) and nickel nitrate ($Ni(NO_3)_2.6H_2O$). The final composition of the catalyst was 10wt% MoO_3 and 3wt% NiO. The intermediate drying was done at 110˚C for 6h and calcined at 450˚C for 4h. RHC-I and RHC-II are the NiMo catalyst supported on mesoporous alumina AL-I and AL-II respectively.

2.3. Support and catalyst characterization

Mesoporousalumina supports and catalysts were characterized by N_2-physiosorption, X-ray diffraction (XRD), and Transmission electron microscopy (TEM). Nitrogen adsorption-desorption analysis at liquid nitrogen temperature (-196˚C) was obtained with BEL MAXSORP equipment. Prior to the analysis, the samples were degassed for 2h at 300˚C. The FT-IR absorption spectra of the prepared alumina samples were obtained with a Nicolet-87000 FT-IR spectrophotometer in the range of 4000-500cm^{-1}. The powder X-ray diffraction (XRD) patterns were obtained on an X-ray Diffractometer D8 Advance, Bruker AXZ GMBH using a CuKa radiation (k = 0.15418 nm). TEM studies of supports and sulphided catalysts were performed using a Technai G2 instrument. The catalyst support and sulphided catalysts were ultrasonically dispersed in ethanol and n-heptane respectively. The suspension was collected on carbon coated grids.

2.4. Catalytic activity

The catalytic activity tests were performed in a batch reactor at 400-420˚C and 100 bar of total pressure for 6h with constant stirring. Prior to catalytic activity studies, the catalysts were activated by

sulphidation under atmospheric pressure of the oxidic catalysts using ex-situ sulphidation apparatus. For this, hydrogen was passed through a container containing CS_2, and then the saturated mixture of CS_2 and hydrogen was passed through the reactor at 400˚C for 2h. The sulphided catalyst (2.0g) was then transferred in an inert atmosphere to a batch reactor. Solid and liquid products were separated from the catalyst after the reaction and the metal, sulphur and asphaltene contents of the liquid products were analysed. The spent catalysts were washed with hot toluene by the soxhlet process and dried at 110˚C for 4h before characterization.

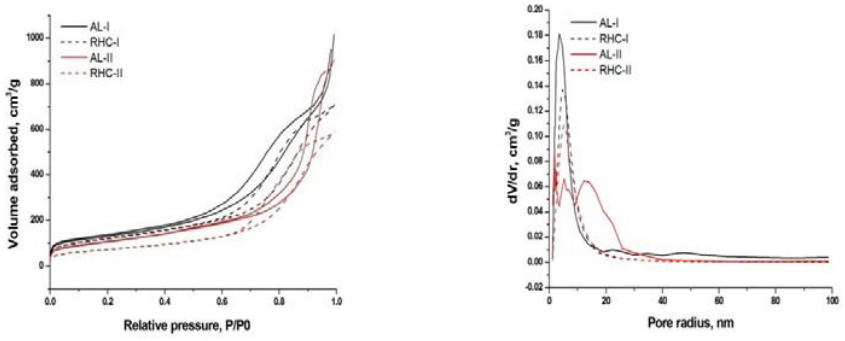
2.5. Analytical procedures

ASTM-D4124-09 was used for SARA analysis of the feed. Metals (Ni, V) were analysed in the feed and products using ICP-AES (Leeman Model DRE, PS-3000UV). The total sulphur content was analysed with oxford model Lab-X 35000 using x-ray fluorescence. The elemental carbon, nitrogen, hydrogen was analysed using an ElementerVario Micro CHNS analyzer. The density and dynamic viscosity of the liquid products were measured according to the ASTM D7042 by the Viscometer SVM 3000 (Anton Paar). Asphaltene is determined according to ASTM- D-3279 method. Catalyst weight loss due to combustion of the spent catalyst has been measured by thermogravimetric (Perkin Elmer TGA4000) analysis. For this experiment, the burning of coke was carried out in a 50ml/min air atmosphere. 10mg of sample was placed in platinum crucible and heated from ambient temperature to the final temperature of 900˚C at rate of 10˚C/min. Boiling point distribution of the feed and the products were determined by thermogravimetric analysis (TGA).

3. Result and discussion

3.1. Support and catalyst characterization

Figure1 shows the nitrogen adsorption-desorption isotherms and pore size distribution of the calcinedγ-alumina samples and supported NiMo catalysts. Their surface area, pore volume and pore size distribution are listed in table1.



(a). (b).

Fig.1. Nitrogen sorption isotherms (a) and pore size distributions (b) of mesoporous alumina supports and NiMo- catalysts.

N_2-sorption isotherms are Type IV(IUPAC designation) which confirms the presence of mesopores. For mesoporous alumina supports AL-I and AL-II, a H_3-type of hysteresis loop is observed, indicating the presence of plate like pores. A narrow pore size distribution is observed in PSD plots. The pore volume of 1.55 and 1.40cm^3/g for AL-I and AL-II are large for synthesized samples. The hysteresis loops are shifted to higher P/P0 which indicates that the capillary condensation occurs in large mesopores. The pore volume of alumina support (AL-I) is reduced from 1.55 to 1.42 cm^3/g with impregnation of metals.

Table1.Textural properties of the calcined mesoporous alumina supports and as-prepared NiMo-catalysts.

Samples	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Pore diameter (nm)
AL-I	458	1.55	13.55
AL-II	385	1.40	14.51
RHC-I	397	1.42	13.20

RHC-II	324	1.04	13.02

Infrared spectra (in figure2) of dried (before calcinations) and calcined alumina materials show the presence of hydroxylation level on the surface of synthesized samples. The symmetric stretching vibration corresponding to Al-O-H bond was observed at 3443 and 3456cm^{-1}. Absorption bands at 486 and 625cm^{-1} were due to the vibrations of Al-O-Al, while peaks at 742 and 1070cm^{-1} can be assigned to the bending vibration of Al-O and O-H respectively.

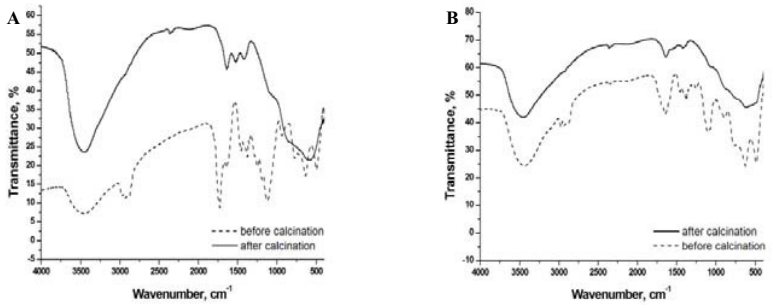


Fig. 2. FT-IR Spectra of mesoporous alumina supports A) AL-I and B) AL-II.

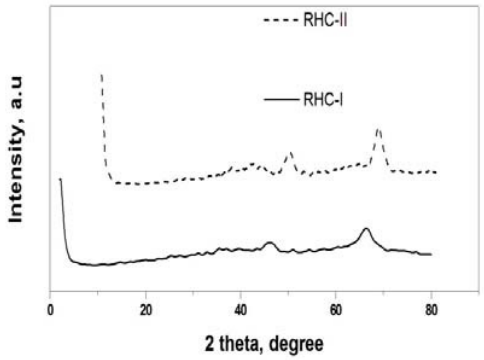


Fig.3. XRD spectra of RHC-I and RHC-II.

XRD diffraction pattern (figure3) of the both catalysts indicates that active metal molybdenum and promoter are well dispersed into the alumina support. The absence of peaks at 2θ=25-27˚ showed amorphous phase of molybdenum oxide.

The morphology analysis of the calcined alumina supports and NiMo catalysts (after sulphidation) were performed and their TEM images are displayed in figure4

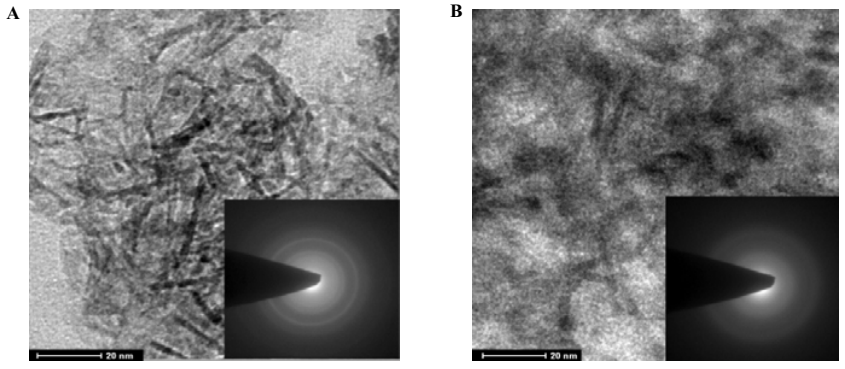


Fig.4. Images of Transmission electron microscopy (TEM) of A) calcined mesoporous alumina material (AL-I) and B) supported catalyst RHC-I.

The observation of plate-like particles in TEM image of mesoporus alumina support AL-I is consistent with the H_3-type of hysteresis observed in its corresponding isotherm (figure1a).TEM photographs of the sulphided RHC-I represents the block thread-like fringes corresponds to the MoS_2 slabs. SAED patterns also confirm the amorphous (diffuse rings) nature of the synthesized materials.

3.2. Feedstock characterisation

The main physicochemical properties of the feed are described in table 2. The vacuum residue had large amount of hetero atoms like vanadium and nickel. The content of vanadium metal is more than nickel content and insoluble content is ~22wt%. Therefore, VR used for this work is highly contaminant and highly viscous material. The more concerned of this feed is its high insoluble material which adversely effects the catalyst deactivation during reaction.

Table2. Properties of the feedstock studied

Properties	Vacuum Residue
Physical properties	
Density g/ml at 15˚C	1.055
Viscosity (Cst) at 100˚C	25794
API Gravity	2.50
Elemental Analysis (wt%)	
C	82.96
H	7.42
N	0.876
S	5.45
Metal (wppm)	
Ni	65
V	240
SARA Fraction (wt %)	
Saturates	8.89
Aromatics	25.88
Resins	43.25
n-C_7 insoluble	21.98

3.3. Catalytic activity

The hydro treating activities of the AL-I and AL-II supported NiMo catalysts were studied for vacuum residue. The HDS, HDM and HDAs activities are compared in figure5. This figure indicates that NiMo catalyst (RHC-I) supported on the mesoporous alumina AL-I had higher HDS and HDM activities than the catalyst supported on AL-II. The larger pore diameter and higher pore volumes might be the reason for the higher HDS and HDM activities of the RHC-I.

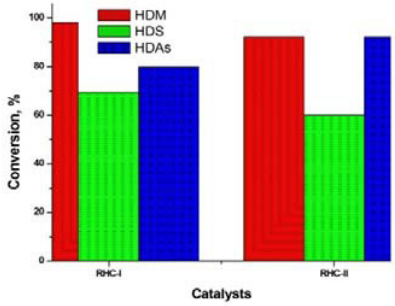


Fig.5.Hydrotreating activities of the RHC-I and RHC-II.

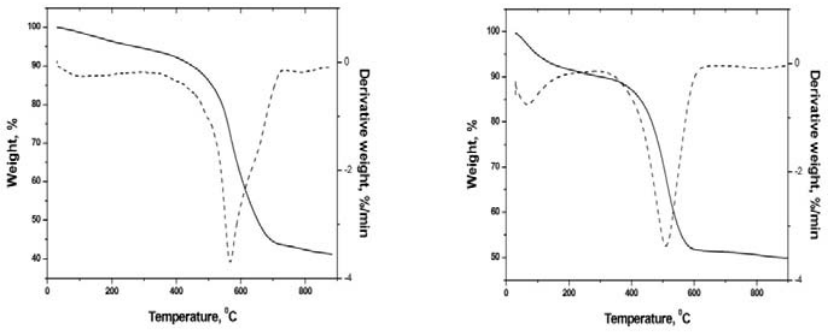
The VR used for the present study was highly asphaltenic. Therefore, significant formation of coke deposits on the catalysts during reaction was expected. The RHC-I had a better performance for asphaltene conversion (HDAs) than the RHC-II. The pore volume in RHC-II was lower than RHC-I showing that not only the pore size is important but also the volume of pores.

The hydrocracking activities of the catalysts were also studied by TGA. The results are reported in table3. The catalyst RHC-I with large pore diameter and higher pore volumes exhibited higher cracking activities i.e. lower amount of materials having boiling temperature higher than 550˚C was produced.

TGA analysis of the spent catalysts was also measured. The spent catalyst obtained after reaction were washed using toluene as solvent by the soxhlet process. The weight loss and its derivative with temperature are presented in figure 6.

Table 3. Hydrocracking activities of the catalyst RHC-I and RHC-II.

Properties	RHC-I	RHC-II
Kinematic Viscosity, mm^2/s	9.91	17.24
Density, g/cm^3	0.90	0.92
API	25.82	22.67
Product Distribution, wt%		
<150˚C	12.46	9.93
150-350˚C	30.62	30.24
350-550˚C	20.64	17.91
>550˚C	36.29	41.29



(a) (b).

Fig.6. TGA & DTG profiles of Spent Catalysts A) RHC-I, B) RHC-II.

Both the derivative curves show two principal weight losses. The first peak is at around 100˚C and second peak position for the RHC-I and RHC-II is at 570 and 510˚C. The second peak is very sharp and prominent. The weight loss at first peak is for the loss of water and second peak is due to coke burning. It can be stated that carbon deposited on the catalyst (RHC-I) is relatively hard in nature

4. Conclusions

Sol-gel method is used to synthesize mesoporous alumina as catalyst support with larger pore diameter as well as higher pore volume. By using amine in the presence of non-ionic surfactant, high surface area of 458m^2/g, pore volume 1.55cm^3/g and pore diameter 13.55nm has been obtained. NiMo-catalyst were prepared with mesoporous alumina as supports and tested in hydroprocessing reaction at temperature 400-420˚C and 100 bar of H_2 pressures. Hydrocracking as well as hydrotreating activities of the catalysts were driven by pore volume and pore size distribution of the catalytic supports. Significant conversions were observed with the RHC-I due to its large pore volume and pore size.

References

1. Maity S K, Perez V H, Ancheyta J, Rana M S, Centeno, G. Petroleum Science and technology 2007, 25, 241-249.
2. Maity S K, Blanco E, Ancheyta J, Alonso F, Fukuyama. Fuel 2012, 100, 17-23.
3. Puron H, Pinilla J L, Berrueco C, Fuente J A, Millan M. Energy&Fuels 2013, 27, 3952-3960.
4. Niesz K, Yang P, Somorjai G A. ChemComm 2005, 1986-1987.
5. Huang B, Bartholomew C H, Woodfield B F. Microporous and Mesoporous Materials 2013, 177, 37-46.
6. Fulvio P F, Brosey R I, Jaroniec M. Applied Materials & Interfaces 2010, 2, 588-593.