

Synthesis and Characterization of Atmospheric Residue Hydrodemetalization (Ardhm) Catalyst for Crude Oil Processing

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Abstract: Synthesis and characterization of atmospheric residue hydrodemetalization (ARDHM) catalyst for crude oil processing have been carried out. The catalyst was synthesized by loading of small amount of Ni and Mo metals onto the Indonesian natural zeolite from Klaten (ZA sample). The natural zeolite was treated with 3M HCl solution to produce the ZAA sample. The Ni and Mo metal was impregnated onto the ZAA sample using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ followed by $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ precursor solution, then calcined at 450°C for 5 h and reduced at 400°C for 3 h produced the NiMo/ZAA catalyst. The zeolite samples were characterized by means of total acid amount determined by pyridine vapour adsorption, the TO_4 site ($T = \text{Si}$ or Al) analyzed by Infra Red Spectrometer (IR), Crystallinity by X-ray Diffraction (XRD), and surface performance by Scanning Electron Microscope (SEM), and metal content measured by Atomic Absorption Spectroscopy (AAS). The catalyst activity was tested in hydrodemetalization process using nickel porphyrin, thiophene or pyridine as petroleum residue model compounds carried out at 360, 370, 380 and 390°C, LHSV 0.2 h⁻¹. The HCl treatment to the ZA sample caused dealumination, did not defect the crystalline matter and increased total acid amount. Loading of Ni and Mo metal onto the ZAA sample increased acidity, did not defect the crystalline of mordenite and also did not block the zeolite pore. Nickel removal from nickel porphyrin (Np) was easier than N removal from pyridine; on the other hand, nickel removal from nickel porphyrin was more difficult than S removal from pyridine. The spent catalyst was deactivated by coke deposition and it can be regenerated and reused.

Key words: Hydrodemetalization, Indonesian Natural Zeolite, Nickel Porphyrin, thiophene, pyridine.

I. Introduction

Increasing world-wide demands of transportation fuels is challenging the petroleum industry to optimize refinery operation for improving its performance. Petroleum cuts containing vanadium, sulfur and nitrogen compounds had to be removed in order to produce cleaner and better performance of transportation fuels [1]. The present energy resources and environmental problems open up a challenge for the development of new hydrotreating catalysts which would be more efficient than the existing ones for sulfur and nitrogen removal from various petroleum cuts. A practical method of meeting improved quality fuels need of improving the operation of hydroprocessing unit that produced finished products. This unit is a heterogeneous catalytic process in which crude oil fraction are contacted with hydrogen at elevated pressure and temperature in order to remove impurities, primarily sulfur and nitrogen, and convert aromatic compounds to their corresponding naphthenic compounds.

There is an assumption that an improved catalyst will result in improved hydroprocessing unit utilization. This improvement may be approached either by promoting increased throughput at the some operating conditions or increased impurity removal at the severe operating conditions. Recent findings have shown that hydroprocessing catalyst with high surface acidity have also a higher activity [2-3]. Currently employed hydroprocessing catalysts consist of active metals, such as molybdenum and nickel supports on γ -alumina. These catalysts were commercially used for hydrodemetalization and hydrodesulfurization of petroleum heavy fractions [4-5] as well as Palladium and nickel or molybdenum supported on HY-zeolite [6-7]. However, research about utilization of Indonesian natural zeolite as a support material instead of alumina and synthetic zeolite have not been widely explored and applied in industry. It is well known that Indonesian natural zeolite has higher surface acidity than alumina, furthermore, zeolite acidity is easier to improve [8-9]. Increasing Lewis acidity is thought to contribute overall increase in activity, increased Bronsted acidity enhances catalysis of specific steps in hydrodemetalization [10].

Based on the above consideration, the authors proposed a research of synthesis and characterization of the atmospheric residue hydrodemetalization (ARHD) catalysts for crude oil processing. This research relates to a novel catalyst for the hydrodemetalization of heavy crudes and residues and a process for the catalysts preparation and characterization. In the commercial unit it is known that metals content in petroleum hydrocarbons may be reduced by hydrotreatment with a catalyst. Among the catalysts effective for this purpose are those which combine metallic compounds of atoms coming from Group VIB of the Periodic Table with metallic compounds of Group VIII. These compounds are usually dispersed over a carrier or support, such as

alumina, silica or a silica-alumina as well as synthetic zeolite (Y-zeolite). In spite of the fact that Indonesia has abundant natural zeolites, the authors undertaken an activated Indonesian natural zeolite as a support material of the hydrodemetalization catalysts. The Ni and Mo metals were loaded on to the zeolite surface by wet impregnation method. The catalyst properties in hydrodemetalization process of some petroleum model compounds were then evaluated. The results are described herein.

II. Experimental

2.1. Natural zeolite activation

An Indonesian natural zeolite from Klaten consisted mainly of mordenite type crystalline (ZA sample) was treated with 3 M HCl solution as proposed in the previous paper [11].

2.2. Catalyst Preparation

The catalyst was prepared by loading a small amount of Ni metal onto the Indonesian natural zeolite using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor solution by impregnation method. The ZAA sample was mixed with 50 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 wt.% based on Ni metal) in demineralized water. The mixture was laid still for 3 h, after which the solvent was evaporated. After drying at 120°C for 3 h, the nickel-containing sample was then mixed with 50 mg of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in demineralized water for 3 h, then the solvent was evaporated. The Ni-Mo containing sample was then calcined under nitrogen gas stream at 450°C for 5 h followed by reduced under hydrogen gas stream at 400°C for 3 h (produced NiMo/ZAA catalyst).

2.3. Catalyst Characterization

X-ray diffractograms were obtained with a Rigaku Geigerflex spectrometer. A TO_4 (T = Si or Al) site in the zeolite samples was analyzed by a Shimadzu FTIR 8201-FC spectrometer. The zeolite sample acidity was determined by adsorption of pyridine base vapour. Surface area, total pore volume and radius were analyzed using a NOVA-1000 Surface Area Analyzer. The surface performance of the zeolite samples was observed by a JEOL JSM-6360LA Scanning Electron Microscope (SEM).

2.4. Hydrodemetalization Process

The atmospheric residue of crude oil models such as nickel porphyrin (Np), thiophene and pyridine were used to test the catalyst activity. The hydrodemetalization process was carried out in a semi-batch reactor system. The catalyst (1.0 g) was placed in a stainless steel reactor (i.d = 2 cm, o.d = 2.5 cm). The feed was heated in other reactor and flowed into catalyst reactor using hydrogen gas. The reaction temperature was varied at 360, 370, 380 and 390°C. The liquid and gas products were separately collected every 5 min. range time and analyzed by GC, GC-MS and Atomic Absorption Spectrophotometer (AAS). The kinetics and thermodynamics parameters were then evaluated.

III. Results and Discussion

The HCl treatment towards the ZA sample caused dealumination of the zeolite framework and reduced the amorphous materials as described in the previous paper [9].

Determination of total acid sites (acidity) in the zeolite samples was carried out by adsorption of pyridine base vapour and gravimetrically calculated as total amount of the adsorbed base on the acid sites of zeolite. The total acid amount of the ZA, ZAA and NiMo/ZAA sample was 0.18, 0.44 and 1.06 mmol/g sample. This result informed that HCl treatment increased total acid amount of zeolite sample due to the reduction of amorphous material that covered the crystalline matter of the zeolite. Loading a small amount of metal onto the zeolite also increased total acid amount of the sample. This phenomenon caused by the fact that the Ni and Mo metal have degenerated empty orbitals that acted as Lewis acid sites.

Surface performance of the NiMo/ZAA sample analyzed by SEM was shown in Figure 1. The micrograph showed that the crystalline matter was observed and the metals loading did not cause pore mouth blocking.

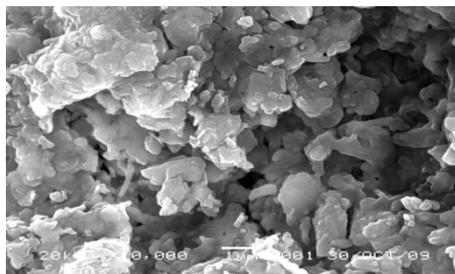


Figure 1 Surface performance of NiMo/ZAA catalyst

Shown in Table 1 results of HDM products at several temperatures, LHSV 0.2 h⁻¹ using the NiMo/ZAA catalyst. From Table 1 it can be seen that in the range of 360 to 390°C, nickel removal from nickel porphyrin feed is easier than nickel removal from that in addition of a small amount of thiophene as well as pyridine. The available of thiophene as well as pyridine caused the competition in adsorption between nickel and sulphur (in thiophene) as well as nickel and nitrogen (in pyridine) in the catalyst surface. This condition caused the decrease of nitrogen adsorption by the catalyst. The increase of temperature caused the increase of nitrogen adsorption in the catalyst surface. This due to the increase of feed molecule activity that interacted with catalyst surface active sites and undergone adsorbed by the supply of energy via the increase of the temperature.

Table 1 Results of HDM products at various reaction temperatures, LHSV 0.2 h⁻¹.

Feed	Nickel removal at various temperature (wt.%)			
	360°C	370°C	380°C	390°C
Nickel porphyrin (Np)	54	73	88	96
Np + thiophene (1% v/v)	38	48	65	70
Np + pyridine (1000 ppm)	12	19	27	33

Table 2 showed the kinetics parameter of rate constant, k of relative reactivities of S, N and Ni-containing compounds. It can be seen that in the range of 360 to 390°C, nickel removal from nickel porphyrin (Np) was easier than N removal from pyridine; on the other hand, nickel removal from nickel porphyrin was more difficult than S removal from pyridine. These phenomena were caused by the fact that hydrodenitrogenation (HDN) consumed hydrogen in large excess of the stoichiometric requirements, since the HDN apparently requires full ring hydrogenation to destroy the aromaticity of the heterocyclic nitrogen compounds prior to nitrogen atom removal. On the other hand, S removal from thiophene was easier than that of nickel removal from nickel porphyrin may be caused by the position of S in a S-containing molecule is located in the outside of aromatic ring, thus it needed lower energy than that of nickel removal in the Np compound.

Table 2 Pseudo-first order rate constant, k of S, N and Ni-containing compound removal

Compound	Pseudo-first order rate constant, k, (min ⁻¹)
Nickel porphyrin	1.82
Thiophene	2.14
Pyridine	1.08

Table 3 shown the activities of fresh, spent and regenerated catalysts of the NiMo/ZAA on nickel removal reaction from nickel porphyrin compound at 390°C. This data showed that after being used in the hydrodemetalization process the activity of catalyst was reduced or undergone deactivated as shown by the decrease of the rate constant, k of nickel removal. The rate of deactivation can be significantly reduced by increasing the hydrogen pressure, and therefore heavier feed stocks require higher hydrogen pressure. Lighter feeds caused deactivation predominantly by coke lay down on catalyst surface. This catalyst was easily and almost completely regenerated by burning the coke. In an attempt to reuse the spent catalyst in this research, the authors undertaken regeneration process of the spent catalyst by purging with hydrogen gas at 1000°C. The result showed that activity of the regenerated catalyst was increased closed to the activity of the fresh catalyst. This indicated that the spent catalyst was deactivated majority by coke deposition on it surface, thus it could be easily burned out. For deactivation caused by metals deposition on the catalyst surface, regeneration techniques have not been developed, and thus, for residue processing, catalyst life may be as short as 6 months. Hence deactivation caused by metal deposition is more serious than deactivation due to coke deposition if coke deposition is not excessively rapid.

Table 3 Rate constant in nickel porphyrin reaction at 390°C

Catalyst	Pseudo-first order rate constant, k, (min ⁻¹)
Spent catalyst	0.19
Regenerated catalyst	1.67
Fresh catalyst	1.82

IV. Conclusions

Attempting to utilize natural zeolite as a catalyst support, modification and characterization of Indonesian natural zeolite from Klaten was carried out. Its property in atmospheric residue hydrodemetalization (ARHDM) process was evaluated, using nickel porphyrin (Np), thiophene and pyridine as petroleum residue model compounds.

The results obtained in this work showed that the Indonesian natural zeolite from Klaten mainly consisted of mordenite type crystalline matter. HCl treatment was found to remove some of impurities in the sample, also caused dealumination and enhanced total acidity. Loading of small amount of metal (Ni and Mo)

onto the zeolite did not significantly defect the crystalline matter and blocked the zeolite pore, and also increased total acidity. In the range of 360 to 390°C, nickel removal from nickel porphyrin (Np) was easier than N removal from pyridine; on the other hand, nickel removal from nickel porphyrin was more difficult than S removal from pyridine. The spent catalyst was deactivated by coke deposition and it can be regenerated and reused.

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