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Preparation of the Natural Zeolite Based Catalyst for Hydrocracking Process of Petroleum Derived Atmospheric Residue

Tserendorj Tugsuu[1], Yoshikazu Sugimoto[2], Byambajav Enkhsaruul[3]

[1]Department of Chemical and Biological Engineering, School of Engineering and Applied Science, National University of Mongolia (NUM), Ulaanbaatar, Mongolia
[2]Energy Technology Research Institute, Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
[3]Department of Chemistry, School of Art and Science, National University of Mongolia (NUM), Ulaanbaatar, Mongolia
Email: tserendorj.tugsuu@yahoo.com

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Abstract

This research focused on preparation catalysts by natural zeolite for hydrocracking and to compare their catalytic reactivity with commercial catalyst. Clinoptilolite type natural zeolite of Tsagaantsav and paraffinic atmospheric residue of Tamsagbulag crude oil were used in this research. The Ni or Fe ion was loaded into the zeolite sample which was enriched and calcined previously, by ion exchange method. It is determined by X-ray diffraction analysis that structure of natural zeolite was not broken down during metal loading. The conversion of feedstock in hydrocracking, in with modified zeolite was used, was 22.5% higher than none catalytic process and 8.9% higher than commercial catalyst. It is proved that both of modified zeolite catalysts worked effectively as a catalyst in hydrocracking of atmospheric residue. Even so the contents of sulfur in middle and heavy fraction were 490 - 615 ppm, after hydrocracking with Ni/zeolite, Fe/zeolite catalysts. This result showed that the Ni/zeolite, Fe/zeolite catalysts were inactive at hydrodesulfurization, because the contents of sulfur in middle and heavy fraction were 370 - 478 ppmafter hydrocracking without catalyst. Process for sulfur removal is needed after hydrocracking with Ni/zeolite orFe/zeolite catalyst.

Keywords

Zeolite Catalyst, Hydrocracking, Catalytic Reactivity, Hydrodesulfurization

1. Introduction

The most important advance in cracking technology in the last seven decades where zeolite catalysts develop has been known. There are 34 known natural zeolites, and about 100 zeolites have been synthesized [1]. Currently more than ten fields of natural zeolite in Mongolian territory have been disclosed and all the resource has been estimated to be 179.1 million ton [2]. Natural zeolite of Tsagaantsav and crude oil of Tamsagbulag had been studied for several years [3] [4]. However, there is no research to prepare a cracking catalyst by natural zeolite for refining process of petroleum in Mongolia. In this study, we have performed a modification of natural zeolite for cracking catalyst and to compare its catalytic reactivity on atmospheric residue of crude oil.

However, initially the cracking process was without catalysts, but the catalyst develop rapidly after using catalyst for cracking process and the using of 2 - 3 functional catalyst for the petroleum refinery [5]. To improve catalytic reactivity of natural zeolite, modifying and synthesis methods were used [6].

2. Experimental

2.1. Materials

In this research we used the natural zeolite of Tsagaantsav to prepare cracking catalyst and the commercial catalyst, which was utilized in Japanese refinery to compare their catalytic reactivity. Also the atmospheric residue of Tamsagbulag crude oil was used as a raw material of hydrocracking.

2.2. Catalyst Preparation

The Ni, Fe ions were loaded into the pore structure of natural zeolite, which was enriched and activated previously, by ion exchange method, which is shown in **Figure 1**.

We prepared a zeolite sample of 1.0 mm in diameter using winnowing fan, after the natural zeolite was swilled out by distilled water many times and cleaned from clay soils. The thermal activation had been made that, half of swilled zeolite calcined at 350˚C for 3 hours [7]. The metal ions in pore of zeolite crystal had been displaced by ammonium ion via adding 0.25 mol/l NH_4Cl solution to the samples of swilled zeolite and activated zeolite. Thus, the zeolite ion exchange capacity was calculated from the variance concentration of ammonium ions. It was modified Ni/zeolite and Fe/zeolite catalyst through the ammonia form of exchange ion in zeolite crystalline valley, ion-exchanged into Ni and Fe form.To do this, at first the 20% solution of $NiCl_2$ and $FeCl_3$ was prepared.Then a 5 g ammonized zeolite was put in a flask, prepare the mixture for the zeolite and salt ratio of 1:5, and heat and stir it with a reflux condenser at 80˚C for 3 hours. Finally modified Ni/zeolite and Fe/zeolite catalyst via the filtered zeolite was disinfected until no chlorine ion and burned at 400˚C for 4 hours.

2.3. Hydrocracking Test

The atmospheric residue of Tamsagbulag crude oil (TBAR) was hydrocracked at 450˚C temperature using a fixed bed reactor that was inserted into an electric

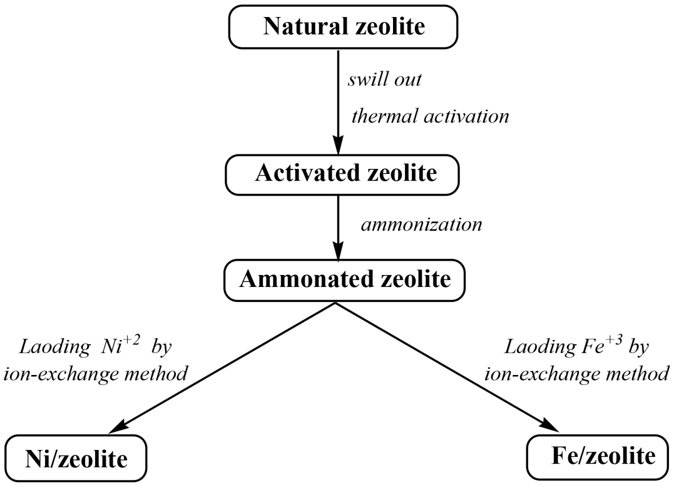

Figure 1. General scheme of method to prepare zeolite catalyst.

furnace with vertically sharking type. About 4 g of atmospheric residue with 200 mg of prepared catalyst were charged into the reactor. The reactor was pressurized by hydrogen gas up to 10 MPa at ambient temperature, and then was heated to the prescribed temperature. Reaction temperature was maintained for 2 hours for every run [8].

2.4. Analysis

2.4.1. XRD Analysis for Modified Zeolite Catalyst

The crystalline structure of the modified zeolite and the bi-functions commercial catalyst was determined using the D500 X-ray diffractometer. The measurements at the 2θ angle of 10˚ to 60˚ had been carried out to measure the accuracy of the 0.01, every 3 seconds. Using copper metal as a source of X-rays.

2.4.2. Determine the Amount of Metal in the Catalyst

A ULVAC PHI 5600 type X-ray photoelectron spectroscopy (XPS) was used to measure the amount of metal in the zeolite catalysts. The Al-K_α with 200 W voltage was used as a source of X-rays. Calculated by 1 s peak intensity at 285.0 eV of carbon and calculated by modifying variance of observed X-ray spectral.

2.4.3. Hydrocracking Product Analysis

After the reaction, gaseous products were subjected to Gas chromatography coupled with thermal conductivity detector (GC–TCD; Agilent, 6890) to estimate its composition. Then, contents of methane, ethane and propane gases were calculated using a calibration of standard gas samples. Initially, atmospheric residue was separated using a distillation method to examine quantitatively its fractional composition. The distillation curve of the liquid product was examined using a GC-FID system (Agilent, model 6890 GC) that was equipped with a fused silica column 5 m long [9]. At first, the toluene insoluble fraction (TIF) was extracted from hydrocracking products. The toluene soluble fraction (TS) was recovered after solvent evaporation, and was then divided into four sub fractions by a distillation method: light fraction (LF), middle fraction (MF), heavy fraction (HF) and bottom. The separated distinct fractions were weighed to check a material balance including the content of gaseous products [10].

3. Results and Discussion

3.1. Catalyst Preparation and Analysis

The Ni or Fe ions was loaded into the zeolite sample after enrichment and activation of natural zeolite by ion exchange method. The quality of adsorption or the ion exchange capacity of natural zeolite was improved from 0.21 mmol/g to 0.41 mmol/g after swill out and thermal activation of natural zeolite.The modified Ni/zeolite, Fe/zeolite catalysts were identified, that the clinoptilolite type zeolite by database in D500 instrument. Results of ammonification for activated natural zeolite shows that ion exchange capacity of the zeolite was 0.41 mmol/g. It means that metal Ni or Fe ions can be loaded 0.41 mmol into 1 g of zeolite by ion exchange method. In **Figure 2**, X-ray diffraction analysis of the modified zeolite catalysts is confirmed that, structure of the natural zeolite was

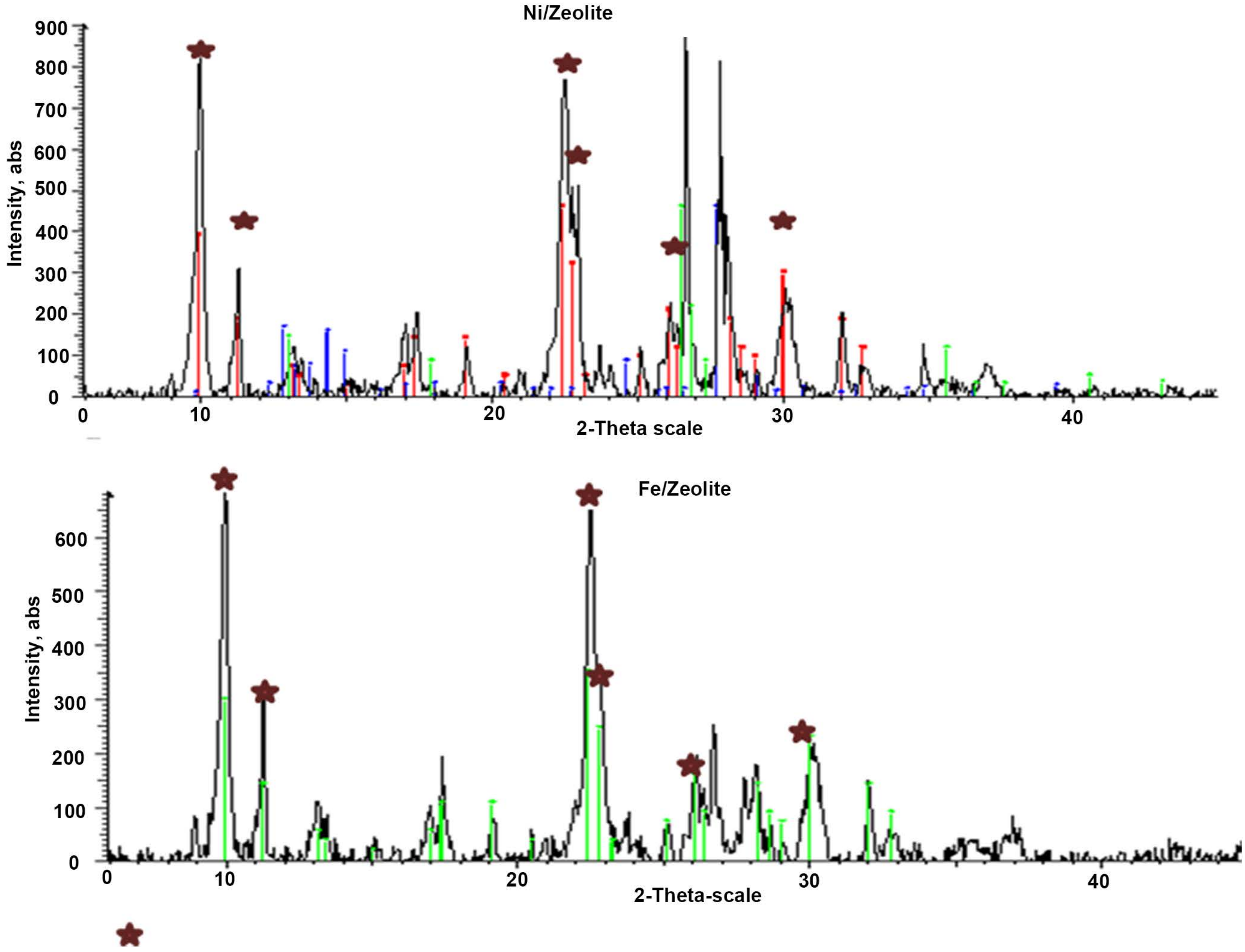

Figure 2. X-ray diffraction pattern of the Ni and Fe ion exchanged zeolite.

not broken down during the metal loading and that, the raw material is Clinoptilolite type natural zeolite.

It makes clear disclosed the crystal structure of zeolite at the interval 10 - 20 and 20 - 40 of 2θ. Also there is no large and agglomerated (>5 nm) metal species in the framework of zeolite. In other words, Ni and Fe metals are too small to be detected by X-ray analysis. It means that metal species loaded into the zeolite are distributed finely during ion exchange.

The researchers assigned that the thermal stability of Tsagaantsav zeolite is 950˚C of temperature [2]. Therefore Ni/zeolite, Fe/zeolite catalysts were possible to use in hydrocracking process, which is carried out at 450˚C - 500˚C of temperature.

Structure of commercial catalyst exhibited almost amorphous by the X-ray diffraction analysis in **Figure 3**. It showed that the metal content in commercial catalyst was lower than ion exchanged zeolite.

The chemical element's content in activated zeolite and ion exchanged zeolites had been determined by X-ray photoelectron spectroscopy (XPS) analysis. The results of analysis are shown in **Table 1**.

TheSi/Alatomic ratio in modified zeolites was around 4.1. It was nearby to data of the clinoptilolite type, which is 4.2. The results of analysis demonstrated that the Ca and K ions in the Tsagaantsav's zeolite were exchange by Ni and Fe ions because the weight contents Ni and Fe were 7.18% and 5.14% in the Ni/zeolite, Fe/zeolite.

3.2. Hydrocracking Test and Product Analysis

Table 2 shows the product distribution after hydrocracking at 450˚C for 2 hours under hydrogen pressure of 10 MPa. As a result of experiments, which used modified zeolite catalysts, the conversion of feedstock, yields of light and middle fraction were higher, the amounts of heavy fraction, bottom and grown up coke lower, than the experiment which used commercial catalyst.

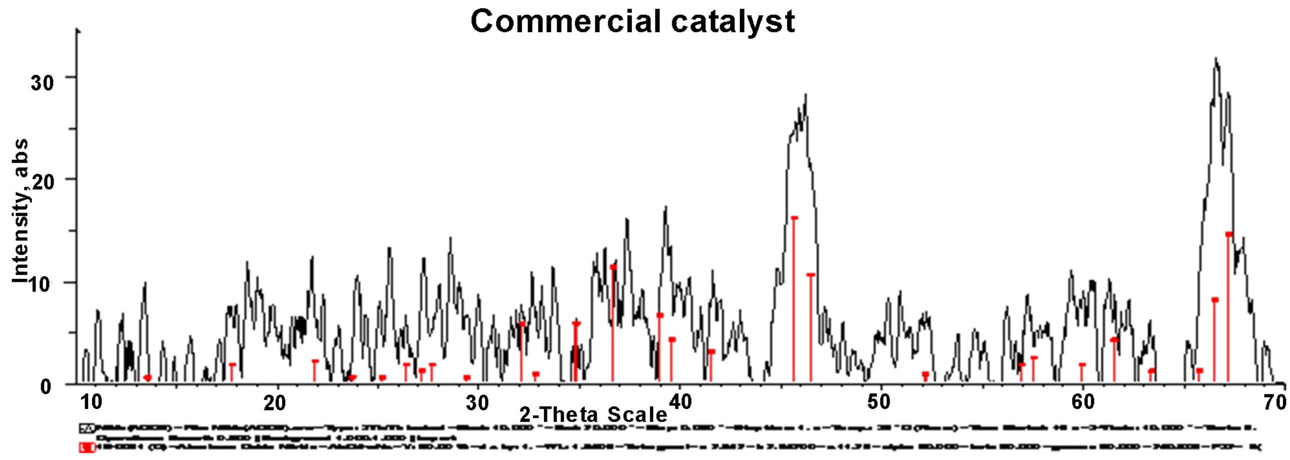

Figure 3. X-ray diffraction pattern of the commercial catalyst.

Table 1. The result of XPS chemical analysisof Ni/zeolite, Fe/zeolite and activated zeolite.

Elements	Activated zeolite		Ni/zeolite		Fe/zeolite	
	Atomic content, %	Weight content,%	Atomic content, %	Weight content, %	Atomic content, %	Weight content, %
Si	25.4	35.08	25.8	34.55	26.2	35.59
Al	6.1	8.12	6.2	8.04	6.4	8.26
O	63	49.59	64.3	49.02	64.9	50.31
Na	4.3	4.87	1.1	1.21	0.6	0.7
K	0.7	1.35	-	-	-	-
Ca	0.5	0.99	-		-	-
Ni	-	-	2.6	7.18	-	-
Fe	-	-	-	-	1.9	5.14
Si/Al	4.16		4.16		4.09	

Table 2. The products distribution after catalytic hydrocracking of atmospheric residue.

Catalyst	Conversion,%	Hydrogen consumption, %	Product distribution					
			C_1-C_3 Gas	LF	MF	HF	Bottom	Coke
Commercial	56.5	0.5	3.7	29.4	22.0	38.0	5.5	2.2
Ni/zeolite	65.4	0.4	3.3	36.6	24.6	27.3	7.4	1.2
Fe/zeolite	62.1	0.2	3.6	33.3	23.8	33.2	4.7	1.6
None	42.9	0.1	3.1	22.9	14.0	35.3	21.8	3.0

Especially the conversion of feedstock was 50% higher than none catalytic process and 15.7% higher than commercial catalyst. It is proved that both of modified zeolite catalysts worked effectively as a catalyst in hydrocracking of atmospheric residue.

The contents of subfractions and n-paraffin (C_9-C_{38}) on some products of hydrocracking by GC-FID analysis were shown in **Table 3**. The content of subfraction < 254˚C was lowest and the content of subfractions < 344˚C and < 496˚C were highest on middle and heavy distillates of product after hydrocracking process, which used the Ni ion exchanged zeolite catalyst. The contents of n-paraffins on middle and heavy distillate, were highest, when used commercial catalyst. It is related the amount of hydrogen for conversion was highest at hydrocracking reaction. In other words the paraffin is cracked to give two smaller paraffins undergo the hydrogen pressure. Also the n-paraffins are expended to the reactions of isomerization, formation of olefin, naphthen and aromatics via surface carbonium-ion intermediates at acidic surface of zeolite catalysts.

The content of sulfur in MF and HF after hydrocracking was determined to evaluate activity of hydrodesulfurization for the commercial and zeolite catalysts. The contents of sulfur in middle and heavy fraction are shown in **Figure 4**.

As the result, the contents of sulfur in middle and heavy fraction were reduced to 19 ppm, 22 ppm after hydrocracking with commercial catalyst, because not

Table 3. The contents of subfractions and *n*-paraffins in hydrocracking products [wt%].

Catalyst	Commercial	Ni/zeolite	Fe/zeolite	none
Subfractions		Middle fraction		
<151˚C	-	-	-	-
<254˚C	42.8	25.6	35.3	30.2
<344˚C	53.9	66.3	59.0	60.5
>344˚C	3.3	8.1	5.7	9.3
n.paraffins	46.3	40.6	41.5	38.7
Subfractions		Heavy fraction		
<254˚C	0.2	-	-	0.7
<344˚C	34.3	16.0	16.0	23.0
<496˚C	63.4	80.0	76.0	73.2
>496˚C	2.1	4.0	8.0	3.1
n.paraffins	41.1	32.1	32.0	39.3

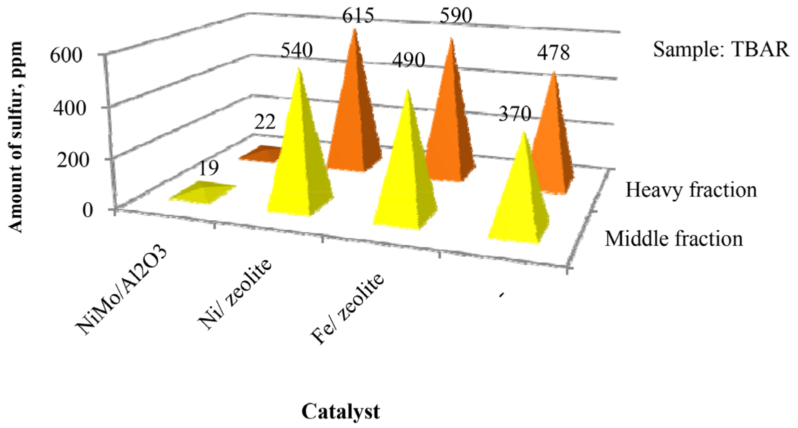

Figure 4. Influence of catalyst on content of sulfur in middle and heavy fraction after HC.

only cracking reaction but also hydrodesulfurization was being hold excellent during the process. Even so the contents of sulfur in middle and heavy fraction were 490 - 615 ppm after hydrocracking with Ni/zeolite, Fe/zeolite catalysts. This result was evidenced the Ni/zeolite, Fe/zeolite catalysts were inactive at hydrodesulfurization, because the contents of sulfur in middle and heavy fraction were 370 - 478 ppm after hydrocracking without catalyst. Therefore there is a need for the sulfur removal process from products after hydrocracking with Ni/zeolite or Fe/zeolite catalysts.

4. Conclusions

Prepared Ni/zeolite and Fe/zeolite catalysts were used in the hydrocracking process of TBAR and their catalytic reactivityof cracking and hydrodesulfurization reaction were compared with the bi-function commercial catalyst and none catalyst process.

In the none catalyst process, the conversion was minimum (42.9 wt%), the amount of residue was the highest (21.8 wt%). Therefore, it is necessary to use active catalysts in the hydrocracking process. The research showed that, prepared zeolite catalysts were more active in hydrocracking reaction than commercial catalyst and none catalysis process.

It is possible to use Ni/zeolite and Fe/zeolite as a catalyst in the hydrocracking process (450˚C - 500˚C) because the heat resistance of Tsagaantsav's zeolite is 950˚C.

Ni/zeolite and Fe/zeolite catalysts were inactive in hydrodesulfurization reaction. The desulfurization process is required after hydrocracking with prepared zeolite catalysts.

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