

## DEVELOPMENT OF CARBON-COATED ALUMINA SUPPORT FOR HYDRODEMETHALLIZATION

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### Introduction

Coke is easily deposited on surface of catalyst support during the hydrodemetallization (HDM) of heavy oil, which is one of the important reasons to deteriorate the catalytic activity. In order to decrease such a deposition on the surface of catalyst support, we tried to make pyrolytic carbon coating on the surface of alumina support. It is known that carbon has a lower surface affinity with coke than alumina catalyst support. Therefore, it is expected that the carbon coating on the catalyst support surface suppresses the coke deposition during HDM. Influence of the pyrolytic carbon coating on the porosity, the HDM performance, and the deposition amount of coke were carefully examined. We confirmed that the pyrolytic carbon coating on the catalyst support was effective to reduce the amount of coke deposition during HDM.

### Materials and Methods

#### Coating carbon on alumina

In order to prepare the carbon-coated alumina (CA), pyrolytic carbon coating on alumina was carried out using ethylene gas as a carbon source. The pyrolysis temperature was 600, 700 or 800°C. The amount of carbon coating was quantified by thermogravimetric analysis (TGA) in air. Porosity of the prepared CAs was examined from nitrogen adsorption and desorption isotherms at 77 K.

#### Preparation NiMo catalyst

NiMo catalyst composed of NiO and MoO<sub>3</sub> was supported on CA as follows. First, an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O was impregnated into CA. Then, the impregnated CA was dried at 150°C and calcined at 300°C in air. In this study, the amounts of supported Ni and Mo were set to be 2 wt% and 8 wt%, respectively.

#### HDM reaction and fraction

Lower Fars crude-atmospheric residue (LFC-AR) was used as a target oil for HDM reaction in this study. The reaction was carried out using a batch reactor. The prepared catalyst was sulfurized prior to the HDM reaction. HDM reaction conditions were at 300 rpm of stirring speed, at 9 MPa of initial hydrogen pressure, at 370°C of reaction temperature, and for 1 h of reaction time. Three-cycle HDM reactions were performed using the same HDM catalyst. The reaction oil was fractionated using an open column.

#### Analysis of catalyst and oil

The amount of coke deposited on catalysts after the HDM reaction was measured by TGA in air. In order to evaluate HDM activity of catalysts, the vanadium (V) concentration in the oil after the

reaction was examined by ICP-MS.

## Results and Discussion

Figure 1 shows the amount of carbon coating on alumina of CAs prepared at different pyrolysis temperatures. A clear correlation was observed between the pyrolysis temperature and the amount of carbon coating. Furthermore, the combustion temperature of coated carbon changed depending on the carbon coating temperature. It was found that CA coated at higher temperatures was more resistant to oxidation.

In Figure 2, nitrogen adsorption and desorption isotherms of the prepared CAs together with those of parent  $\text{Al}_2\text{O}_3$  are shown. The decreases of nitrogen adsorption amount indicate a pore blocking (especially for mesopores) by the coated carbon, and the degree of the pore blocking increased with an increase of the carbon coating temperature. For 600°C-pyrolysis sample (600CA), the change of pore structure was not remarkable as compared from other CA samples. From these results, we deposited NiMo catalyst on 600CA and the parent  $\text{Al}_2\text{O}_3$ , and analysed the HDM activity to clarify the effect of the carbon coating on suppressing coke deposition of the catalyst.

Quantitative results of V in feed and each oil after HDM reaction by ICP-MS are shown in Figure 3. The amount of V in feed LFC-AR was about 750 ppm. After the HDM reactions, V content decreased and the reduction rate was larger for NiMo/ $\text{Al}_2\text{O}_3$ .

As shown in Table 1, the amount of coke deposited on NiMo/600CA in each HDM reaction cycle was less than that on NiMo/ $\text{Al}_2\text{O}_3$ . This result indicates that, by the carbon coating on alumina, the coke deposition on the catalyst during HDM reaction was suppressed.

## Conclusions

Although the HDM activity was lowered to some extent, the carbon coating on alumina support was found to be effective to suppress the coke deposition on the support during HDM reaction.

## References

1. Matsuyama E. (1962). Pyrocarbon. *Tanso* 31, 28-34 [in Japanese].

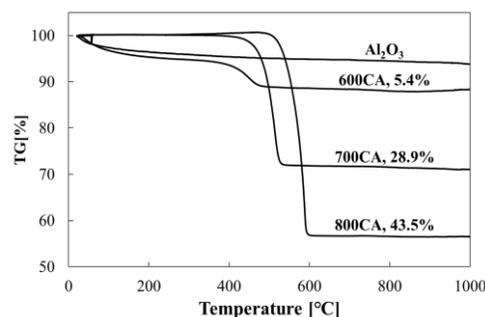


Figure 1. TGA curves in air for each CA before HDM reaction

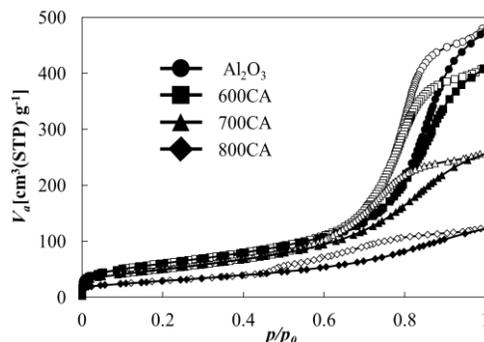


Figure 2. Nitrogen adsorption and desorption isotherms at 77 K of each catalytic support

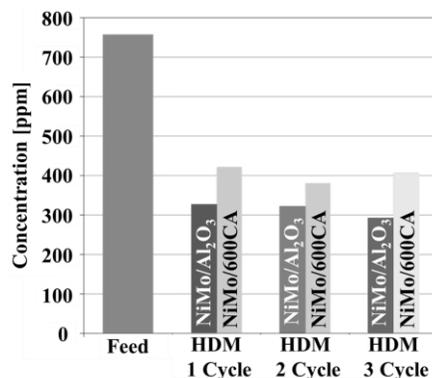


Figure 3. Residual concentration of vanadium before and after HDM reaction

Table 1. The amount of coke deposited on the catalyst after HDM reaction cycles

	1 Cycle	2 Cycle	3 Cycle
NiMo/ $\text{Al}_2\text{O}_3$	15.1%	16.1%	17.6%
NiMo/600CA	13.5%	15.7%	14.2%