## Catalytic Cracking of Fat by Hierarchical Zeolite-Containing SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Using Curie Point Pyrolyzer

<u>Atsushi Ishihara</u>, Takashi Tsukamoto, Tadanori Hashimoto and Hiroyuki Nasu *Mie University, Tsu City, Japan* 

## \*E-mail: ishihara@chem.mie-u.ac.jp

Biodiesel is produced using ester exchange reaction with fats and methanol (FAME), but a large quantity of glycerin as a byproduct has been generated, which has been a significant problem [1]. Therefore, catalytic cracking of fats to get gasoline is suggested. In catalytic cracking, a catalyst with high product selectivity as well as improved activity is required. We have already reported that catalysts composed of zeolite and matrix composites having hierarchical structure [2,3] were effective for the catalytic cracking of heavy carbonaceous materials [1,3]. In this study, we paid attention to matrix where there were few scientific studies until now and prepared a catalysts for cracking of heavy oils and fats. The reactions were evaluated using Curie point pyrolyzer (CPP) which was demonstrated to be very easy evaluation method for catalytic cracking [1, 3].

Tetraethyl orthosilicate, aluminium tri-secbutoxide, malic acid, ethanol, H<sub>2</sub>O, zeolite ( $\beta$ , ZSM-5, Y) were used for the reagents in the preparation of the two-layered catalyst [1,2].

Three-layered catalysts were prepared by the combination of silica-gel derived from the gel skeletal reinforcement method [4] and twolayered catalysts described above.

Soybean oil was used for a raw material of this experiment. CPP was used as the reaction device, and the catalytic cracking was conducted on the following conditions: The quantity of a catalyst was 1.5 mg, soybean oil 0.2 mg, reaction temperature 500 or 590 °C. Products were analyzed by GC-FID.

The pore volumes increased, indicating that more mesopores were introduced into catalysts with the hierarchical structure. In addition, it was found that the catalyst with three-layered structure had more mesopores. These results suggested that the reduction of pores of threelayered catalysts by the calcination was inhibited more effectively than that of twolayered catalysts

When the reaction was performed at 500°C activities of catalysts having hierarchical structures were improved. It is thought that the diffusion of soybean oil molecule was promoted in the presence of large mesopores of the catalysts having hierarchical structure. ZSM-5 zeolite-containing catalysts showed Olefin/Paraffin, high iso-/nand verv Multi/single branch ratios, compared with  $\beta$ zeolite and Y zeolite containing catalysts, indicating that ZSM zeolite-containing catalysts provided gasoline fractions of good quality. At reaction temperature 590°C, gasoline selectivity increased in three layered catalysts when  $\beta$  zeolite was used. Specifically when two-layered catalyst in the three-layered catalyst included SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> matrix, the catalyst showed very high conversion 45% and very high gasoline selectivity 60%.

Gasoline yields increased with increasing conversion as shown in Fig. 1. It was shown that preparing a catalyst with high activity is very important to get the higher gasoline yield. In addition, the gasoline yield was able to be plotted on the same straight line when the same type of zeolite was used, indicating that the product selectivity would depend on the type of zeolite and that the activity would strongly depend on the existence of the matrix.



Fig. 1 Conversion vs gasoline yield in catalytic cracking of soybean oil at 500°C and 590°C.

## REFERENCES

[1] A. Ishihara et al., J. Mol. Catal., A: Chem., 396 (2015) 310.

[2] A. Ishihara et al., J. Catal., 295 (2012) 81.

[3] T. Sonthisawate, A. Ishihara et al., Fuel Processing Technol., 142 (2016) 337.

[4] A. Ishihara, H. Oono, T. Hashimoto, H. Nasu, Micropor. Mesopor. Mater., 233 (2016) 163.

## Acknowledgment

This work was supported by JSPS KAKENHI.