Hydroconversion of fatty acid derivatives over Ni-Mo catalysts prepared with zeolite support

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Abstract: Ni-Mo catalysts have been synthesized with beta zeolite as a support, and were applied to the hydroconversion of methyl laurate (ML). It was found that Brønsted acid sites played important roles in improving the catalytic activity and enhancing the reduction of carbonyl group of fatty acid portion of ML. When beta zeolite was used as a support after the acid- or base-treatment, the catalytic acidity was improved in comparison with the Ni-Mo catalyst supported on parent beta zeolite. Furthermore, when acid- or base-treated beta zeolite was used as a support, *n*-dodecane was selectively produced compared with *n*-undecane.
Keywords: Ni-Mo catalyst, zeolite, hydroconversion.

1. Introduction

In recent decades, the production of biofuels such as biogasoline and biodiesel from biomass resources has been focused on from the viewpoint of the use of environmentally benign fuels. Vegetable oils or microalgae oil can be directly converted to saturated hydrocarbons over metal catalysts under high hydrogen pressures (4-20 MPa)[1,2]. To allow for the more efficient utilization of hydrogen during the reaction process, the hydroconversion should be ideally performed under low hydrogen pressures. We successfully synthesized a sulfur-free Ni-Mo catalyst with high catalytic activities in the hydroconversion of vegetable oil and a fatty acid derivative even under low hydrogen pressures less than 1 MPa[3,4].

In our previous studies, it was found that physicochemical properties including surface area and acid properties of support materials would play an important role in improving the catalytic activity as well as the reduction rate due to an increase in active sites and enhancement the interaction between a catalyst and a reactant. In this study, we synthesized zeolite-supported Ni-Mo catalysts since zeolites have high specific surface area and strong acid sites. We also carried out the hydroconversion of methyl laurate (ML, $C_{11}H_{23}COOCH_3$), one of fatty acid derivatives, in order to investigate effects of the support on the catalytic properties in the hydroconversion.

2. Experimental

Supported Ni-Mo catalysts were prepared by incipient-wetness method with a mixture of $Ni(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ aqueous solutions. The resultant was dried at 90ºC overnight and further dried at 200ºC for 3 h. In order to effects of zeolite supports on catalytic properties, zeolites were treated with acidic or basic aqueous solutions before the loading of the metal species.

The hydroconversion of ML was carried out as follows: A catalyst (0.15 mL) was placed with quartz sand at a stainless reactor, and pretreated at 370ºC for 6 h under a hydrogen pressure of 0.4 MPa; ML was introduced into the reactor with the liquid hourly space velocity (LHSV) of 12 h^{-1} under the conditions at 300ºC with a hydrogen pressure of 0.4 MPa. The products were analyzed by gas-chromatographs equipped with FID or TCD.

3. Results and discussion

Figure 1 shows the hydroconversion of ML over Ni-Mo catalysts under the conditions at 300ºC with a hydrogen pressure of 0.4 MPa. Beta zeolite with a Si/Al_2 molar ratio of 25 was used as a parent material. The Ni-Mo catalyst prepared with beta zeolite showed a higher conversion of ML compared with the Ni-Mo catalyst supported on pure silica beta zeolite, indicating that acid sites of the zeolite support enhanced the hydroconversion of ML probably due to the interaction between the acid sites and ML. When beta zeolite was treated with HNO_3 or tetraethylammonium hydroxide (TEAOH) aqueous solution before the loading of Ni and Mo species, the catalytic activity was improved in comparison with the Ni-Mo catalyst prepared with parent beta zeolite. When beta zeolite is base-treated, mesoporous-like voids can be formed through the dissolution of silica portion of zeolite, leading to high dispersion of metal species on the support and to improving in the diffusion of the substrate. By contrast, when beta zeolite was used as a support after the treatment with NaOH aqueous solution, the catalytic activity was drastically declined. After the removal of Na^+ from beta zeolite treated with NaOH aqueous solution by NH_4^+ ion-exchange, the catalytic activity was improved due to the re-generation of acid sites.

Ni-Mo/BEA catalyst produced selectively *n*-undecane (n-$C_{11}H_{24}$) followed by *n*-dodecane (n-$C_{12}H_{26}$) derived from the fatty acid portion. It is indicated that hydrodecarboxylation and/or hydrodecarbonylation of the fatty acid portion of ML dominantly took place under the present conditions, and that simultaneously, stepwise reduction of the fatty acid portion through the formation of alcohol proceeded to produce *n*-dodecane. CO can be hydrogenated to CH_4 over Ni particles. In addition, hydrocarbons with the carbon number of 2-10 were little produced, indicating that the hydrocracking of hydrocarbon products would not proceed over the zeolite-supported Ni-Mo catalyst. When beta zeolite was used after the treatment with HNO_3 or TEAOH aqueous solution, *n*-dodecane was dominantly produced followed by *n*-undecane. In addition, a molar ratio of *n*-dodecane/*n*-undecane over the beta zeolite support treated with NaOH was increased in comparison with the parent beta zeolite support. It is thus suggested that the reduction of carbonyl group of fatty acid portion would be enhanced on zeolite with Brønsted acid sites tuned by acid- or base-treatment.

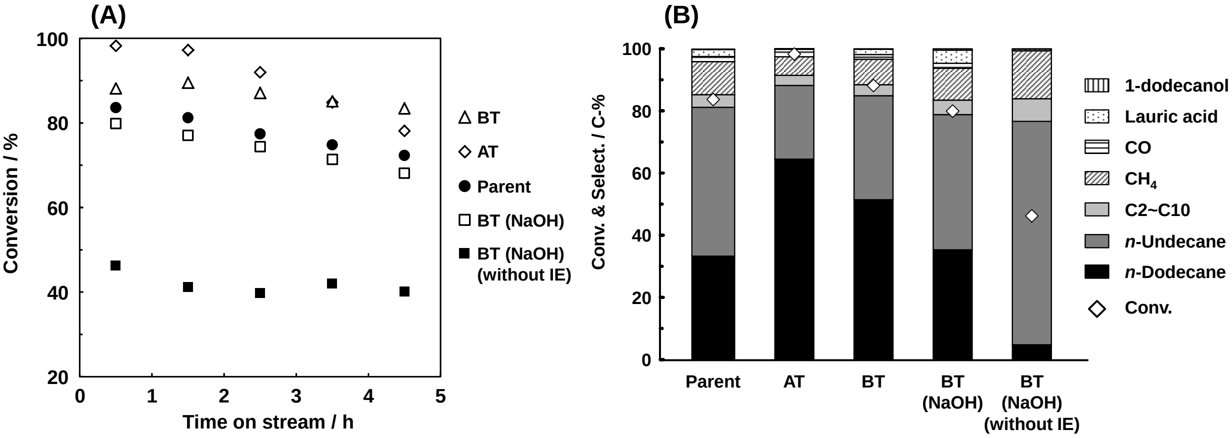

Figure 1. Hydroconversion of ML over zeolite-supported Ni-Mo catalysts. (A) ML conversion and (B) product distribution. AT, acid-treated beta zeolite; BT, base-treated beta zeolite; IE, ion-exchange.

4. Conclusions

In the hydroconversion of ML over zeolite-supported Ni-Mo catalysts, acid- or base-treatment of beta zeolite prior to the loading of Ni and Mo species played important roles in improving the catalytic activity and the reduction ability. Beta zeolite treated with HNO_3 or TEAOH aqueous solution improved the conversion of ML in comparison with parent beta zeolite. In addition, in the product distribution, acid- or base-treated beta zeolite support increased a *n*-dodecane/*n*-undecane molar ratio probably due to the interaction between ML and fine-tuned acid sites of beta zeolite

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