

Hydroconversion of Fatty Acid Derivatives over Ni-Mo Catalysts under Low Hydrogen Pressure

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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 can be directly converted to saturated hydrocarbons over metal catalysts under high hydrogen pressures (4-20 MPa) [1]. To allow for the more efficient utilization of hydrogen during the reaction process, the hydroconversion should ideally be performed under low hydrogen pressures. In our previous work, sulfur-free Ni-Mo supported on Al₂O₃ exhibited a high conversion of vegetable oil to hydrocarbons in the jet fuel fraction even under a low hydrogen pressure less than 1 MPa [2].

Physicochemical properties, in particular, the acid properties of the support will play an important role in catalytic properties in the hydroconversion of vegetable oil. In this study, we carried out the hydroconversion of methyl laurate (ML), one of fatty acid derivatives, under a low hydrogen pressure in order to investigate effects of the support on the catalytic properties in the hydroconversion. Fatty acid derivatives can be obtained through the transesterification of triglycerides with alcohol.

Sulfur-free Ni-Mo catalysts have been synthesized using various types of compounds as a support. The activity and product distribution in the hydroconversion of ML over the Ni-Mo catalysts are summarized in Table 1. It was found that the physicochemical properties of support compounds significantly influenced not only the catalytic activity but the reduction processes of ML. The size of Ni-Mo particles loaded on SiO₂ was decreased with an increase in the surface area of the SiO₂ support, leading to improving the catalytic

activity, while the product distribution was independent of the surface area of SiO₂; C11 hydrocarbons were dominantly produced followed by C12 hydrocarbons. The product distribution in the hydroconversion of ML was strongly dependent on the acid properties of the support. When acidic metal oxides such as SiO₂-Al₂O₃ and TiO₂ were used as a support, the Ni-Mo catalysts exhibited higher catalytic activity and selectivity to C12 hydrocarbons compared with the Ni-Mo catalysts prepared using basic metal oxides such as MgO and ZrO₂.

Furthermore, the Ni-Mo catalysts prepared with zeolites, beta zeolite, ZSM-5, and USY, produced dominantly C12 hydrocarbons followed by C11 hydrocarbons. It is thus suggested that fatty acid derivatives can be adsorbed on the support due to the interaction of the carbonyl group of fatty acid derivatives with the acid sites of the support, leading to accelerating the reduction of the carbonyl group with hydrogen activated on Ni species although, in general, the elimination of the carbonyl group from fatty acid derivatives, decarbonylation or decarboxylation, easily occurs in the hydroconversion of fatty acid derivatives over Ni catalysts.

Table 1 Hydroconversion of ML over Ni-Mo catalysts at 300 °C (4.5 h).

Support	S.A. / m ² g ⁻¹	ML conv. / %	Yield / C-%				
			C12	C11	C2-C10	CH ₄	LA ^a
MCM-41	666	66.5	6.3	41.5	1.7	8.1	0.4
SiO ₂ (Q-6)	313	53.0	9.7	39.1	0.8	5.9	0.2
SiO ₂ (Q-30)	83	47.4	8.3	23.7	2.1	4.4	0.1
SiO ₂ (Q-200)	26	19.6	4.8	13.0	0.5	2.2	0.1
SiO ₂ -Al ₂ O ₃	291	75.0	16.4	45.2	1.1	5.3	0.6
Al ₂ O ₃	92	59.7	7.2	48.3	1.5	8.4	0.4
ZrO ₂	11	42.3	1.9	27.7	2.3	6.1	0.3
MgO ^b	154	55.0	0.3	4.0	1.3	2.9	1.1
*BEA (Si/Al ₂ : 25)	465	72.3	25.0	32.2	1.9	6.7	4.0
ZSM-5 (Si/Al ₂ : 23)	341	73.6	31.4	17.8	4.0	2.8	1.7
USY (Si/Al ₂ : 30)	637	84.1	36.0	21.9	2.4	3.5	2.3

^a Lauric acid; ^b after 1.5 h

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