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THE COMPARISON OF SULFIDE ALUMINA-SUPPORTED CATALYSTS IN RAPESEED OIL HYDRODEOXYGENATION

Luděk Kaluža[1] and David Kubička[2]

[1] *Institute of Chemical Process Fundamentals of CAS, v. v. i.; Rozvojová 135; 165 02 Prague 6–Suchdol; Czech Republic*

[2] *Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology, Prague, Czech Republic*

The Al_2O_3 (S_{BET} 344 m^2g^{-1}, S_{Meso} 243 m^2g^{-1}, V_{micro} 70 $mm^3\ g^{-1}$, V_{Total} 0.41 cm^3g^{-1}, D_{BJH}s 3.8 and 5.0 nm) supported monometallic Co, Ni and Mo and bimetallic CoMo and NiMo catalysts were compared in rapeseed oil hydrodeoxygenation (HDO) reaction after in situ sulfidation. The reaction was described by five pseudo-first order rate constants (k_1–k_5) for the simplified reaction scheme: triglycerides (Tgs) to octadecane (k_1); Tgs to oxygenates (Oxs; i.e., sum of fatty acids, fatty alcohols, and esters of fatty acids and fatty alcohols) (k_2);Tgs to heptadecane (k_3);Oxs to octadecane (k_4), and Oxs to heptadecane (k_5). The empirical pseudo-first order rate constant of the hydrocarbons (Hcs) product formation (k_{Hc}) increased in the order Ni/Al_2O_3 ~ Co/Al_2O_3 < $CoMo/Al_2O_3$ ~ Mo/Al_2O_3 << $NiMo/Al_2O_3$ showing hence a significant synergy between Ni and Mo. All monometallic catalysts exhibited k_1 and k_3 practically zero and the reaction proceeded essentially through the formation of the oxygenated reaction intermediates (high k_2). The Co/Al_2O_3 and Ni/Al_2O_3 catalyzed selectively hydrodecarboxylation (HDC) of fatty acids (high k_5). Over Mo/Al_2O_3, the HDO pathway, however, was nearly the exclusive one (high k_4). $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts yielded both HDO and HDC products suggesting partial synergy in the relative selectivity HDO/HDC between Co(Ni) and Mo. In the Ni(Co)Mo catalysts, the effect of Ni(Co)/(Ni(Co) + Mo) atomic ratio 0.2–0.4 on the activity and selectivity was not significant. [1]

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Table 1. Catalytic activities k_{Hc} and k_1-k_5 in rapeseed oil HDO/HDC (280 °C, 3.5 MPa).

Catalysts	k_{Hc} ($kg\ kg^{-1}\ h^{-1}$)	k_1	k_2	k_3	k_4	k_5
Co/Al_2O_3	0.2	0.03	4.45	~0	~0	0.20
Ni/Al_2O_3	0.2	~0	1.87	~0	~0	0.26
Mo/Al_2O_3	0.8	~0	3.48	~0	1.21	0.10
$0.2CoMo/Al_2O_3$	0.6	0.50	1.53	0.20	0.55	0.32
$0.3CoMo/Al_2O_3$	0.6	0.10	2.61	0.10	0.81	0.69
$0.4CoMo/Al_2O_3$	0.7	0.18	2.75	0.59	1.04	0.80
$0.2NiMo/Al_2O_3$	2.6	0.06	6.25	0.78	4.49	0.62
$0.3NiMo/Al_2O_3$	2.5	0.05	4.23	1.48	4.03	0.09
$0.4NiMo/Al_2O_3$	2.6	0.61	3.43	1.42	3.35	0.10

Reference:

[1] Kaluža, L.; Kubička D. Reaction Kinetics, Mechanisms and Catalysis, 122 (1), **2017**, 333-341.