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

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The Al₂O₃ (S_{BET} 344 m²g⁻¹, S_{Meso} 243 m²g⁻¹, V_{micro} 70 mm³ g⁻¹, V_{Total} 0.41 cm³g⁻¹, D_{BJHS} 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/Al₂O₃ ~ Co/Al₂O₃ < CoMo/Al₂O₃ ~ Mo/Al₂O₃ << NiMo/Al₂O₃ 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/Al₂O₃ and Ni/Al₂O₃ catalyzed selectively hydrodecarboxylation (HDC) of fatty acids (high k_5). Over Mo/Al₂O₃, the HDO pathway, however, was nearly the exclusive one (high k_4). CoMo/Al₂O₃ and NiMo/Al₂O₃ 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 ₂ O ₃	0.2	0.03	4.45	~0	~0	0.20
Ni/Al ₂ O ₃	0.2	~0	1.87	~0	~0	0.26
Mo/Al ₂ O ₃	0.8	~0	3.48	~0	1.21	0.10
0.2CoMo/Al ₂ O ₃	0.6	0.50	1.53	0.20	0.55	0.32
0.3CoMo/Al ₂ O ₃	0.6	0.10	2.61	0.10	0.81	0.69
0.4CoMo/Al ₂ O ₃	0.7	0.18	2.75	0.59	1.04	0.80
0.2NiMo/Al ₂ O ₃	2.6	0.06	6.25	0.78	4.49	0.62
0.3NiMo/Al ₂ O ₃	2.5	0.05	4.23	1.48	4.03	0.09
0.4NiMo/Al ₂ O 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.