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Kaluža, Luděk
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Activity of Co, Ni, Mo, CoMo and NiMo sulfided catalysts in hydrodeoxygenation of rapeseed oil

L. Kaluža¹, D. Kubička²

¹Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague 6, Czech Republic; tel. +420 220390270, email: kaluza@icpf.cas.cz; ²Research Institute of Inorganic Chemistry, Litvinov, Czech Republic.

Hydrodeoxygenation of vegetable oils has a potential to become an important process for production of biofuels. The present work deals with hydrodeoxygenation of rapeseed oil over Al₂O₃ supported sulfide catalysts containing Co, Ni, and Mo. The samples of the following composition were studied: monometallic catalysts 10 wt.% Co or Ni and 15 wt.% Mo, and bimetallic catalysts CoMo and NiMo containing 15 wt.% Mo with atomic ratio Ni(Co)/(Ni(Co)+Mo) 0.2, 0.3, and 0.4. The catalysts were prepared by impregnation of commercial Al₂O₃ (344 m²g⁻¹) with aqueous solution of Ni(Co) nitrates and ammonium heptamolybdate followed by calcination in air at 400 °C and in-situ sulfidation in 5 wt.% solution of dimethyldisulfide in isooctane at 320 °C. The reaction was run at 280 °C, 3.5 MPa and 0.25–4 h⁻¹ in a fixed-bed reactor and the reaction products were analyzed by gas chromatography. The deoxygenation reaction of rapeseed oil was described by five pseudo-first-order rate constants (k_1 – k_5) for the reaction scheme triglycerides to octadecanes (k_1); triglycerides to oxygenates (i.e. sum of fatty acids, fatty alcohols, and esters of fatty acids and fatty alcohols; k_2); triglycerides to heptadecanes (k_3); oxygenates to octadecanes (k_4), and oxygenates to heptadecanes (k_5). Because none of the k_1 – k_5 constants represented a convenient and simple measure of the overall deoxygenation activity, the empirical pseudo-first-order rate constants of triglycerides consumption (k_{Tg}), octadecanes formation (k_{C18}) and heptadecanes formation (k_{C17}) were calculated. It was ascertained that the activity k_{Tg} of the catalysts decreased in the order NiMo/Al₂O₃ > Co/Al₂O₃ > Mo/Al₂O₃ > CoMo/Al₂O₃ > Ni/Al₂O₃ showing thus high synergy in activity between Ni and Mo. Furthermore, the catalysts exhibited significantly different product distributions. The Co/Al₂O₃ and Ni/Al₂O₃ catalyzed selectively hydrodecarboxylation (HDC) of fatty acids (reaction intermediates of triglycerides deoxygenation), which was manifested by high k_{C17} (k_5) and practically zero k_{C18} (k_1 , k_3 , k_4). There were not found any products of hydrodeoxygenation of fatty acids, i.e. fatty alcohols or hydrocarbons with an even number of carbon atoms in the reaction mixtures. Over Mo/Al₂O₃, on the contrary, there were only minor concentrations of decarboxylation products and consequently the hydrodeoxygenation (HDO) pathway was nearly the exclusive one ($k_{C17} = 0$). CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts yielded both hydrodeoxygenation and hydrodecarboxylation products suggesting only partial synergy in the relative selectivity HDO/HDC between Co (Ni) and Mo. The partial synergy in selectivity was mainly manifested by the increased k_1 and k_3 constants in comparison to monometallic catalysts. All monometallic catalysts exhibited k_1 and k_3 practically zero and the reaction proceeded essentially only through formation of the oxygenated reaction intermediates, mainly by hydrogenation of triglycerides (high k_2) followed either by HDO (high k_4 , low k_5 , Mo) or by HDC (high k_5 , zero k_4 , Co and Ni). In the Ni(Co)Mo catalysts, the effect of Ni(Co) loading on the activity and selectivity was not significant. L.K. gratefully acknowledges the Czech Science Foundation (grant number P106/11/0902) for financial support. D.K. acknowledges the financial support of the UniCRE centre (CZ.1.05/2.1.00/03.0071) that is supported by the European Regional Development Fund and the state budget of the Czech Republic.