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

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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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> (344 m<sup>2</sup>g<sup>-1</sup>) 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<sup>-1</sup> 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/Al<sub>2</sub>O<sub>3</sub> > Co/Al<sub>2</sub>O<sub>3</sub> > Mo/Al<sub>2</sub>O<sub>3</sub> > CoMo/Al<sub>2</sub>O<sub>3</sub> > Ni/Al<sub>2</sub>O<sub>3</sub> showing thus high synergy in activity between Ni and Mo. Furthermore, the catalysts exhibited significantly different product distributions. The Co/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> 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/Al<sub>2</sub>O<sub>3</sub>, 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/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> 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.