**The Comparison of Sulfide Alumina-Supported Cytalysts in Rapeseed Oil HydrodeOxygenatic**

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

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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.