Deactivation of Ni-MoS$_2$ by bio-oil impurities during hydrodeoxygenation of phenol and octanol - DTU Orbit (19/03/2019)

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The stability of Ni-MoS$_2$/ZrO$_2$ toward water, potassium, and chlorine containing compounds during hydrodeoxygenation (HDO) of a mixture of phenol and 1-octanol was investigated in a high pressure gas and liquid continuous flow fixed bed setup at 280 °C and 100 bar. To maintain the stability of the catalyst, sufficient co-feeding of a sulfur source was necessary to avoid oxidation of the sulfide phase by oxygen replacement of the edge sulfur atoms in the MoS$_2$ structure. However, the addition of sulfur to the feed gas resulted in the formation of sulfur containing compounds, mainly thiols, in the oil product if the residence time was too low. At a weight hourly space velocity (WHSV) of 4.9 h$^{-1}$ the sulfur content in the liquid product was 980 ppm by weight, but this could be decreased to 5 ppm at a WHSV of 1.4 h$^{-1}$. A high co-feed of sulfur was needed when water was present in the feed and the H$_2$O/H$_2$S molar ratio should be below ca. 10 to maintain a decent stability of the catalyst. Chlorine containing compounds caused a reversible deactivation of the catalyst when co-fed to the reactor, where the catalytic activity could be completely regained when removing it from the feed. Commonly, chlorine, H$_2$O, and H$_2$S all inhibited the activity of the catalyst by competing for the active sites, with chlorine being by far the strongest inhibitor and H$_2$S and H$_2$O of roughly the same strength. Dissimilar, potassium was a severe poison and irreversibly deactivated the catalyst to <5% degree of deoxygenation when impregnated on the catalyst in a stoichiometric ratio relative to the active metal. This deactivation was a result of adsorption of potassium on the edge vacancy sites of the MoS$_2$ slabs.

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