Metal sulfides-catalyzed hydrodeoxygenation of phenol and triglycerides

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As high demands of alternative fuels due to the scarcity of fossil fuels, biofuels e.g. biodiesel, biooil, biogas have been employed over 10 years through the conversion of biomass [1] by suitable catalytic reactions. Among of them, hydrodeoxygenation (HDO) has been used in various applications such as biomass upgrading into valuable chemicals, biodiesel quality improvement, and bio-hydrotreated diesel (BHD) production. HDO catalysts involve with metal, metal oxides, and metal sulfides on supports e.g. γ-Al_2O_3, SiO_2, graphite. Co, Ni, Cu, Mo, and their oxides or sulfides are conventional catalysts aside from noble metals e.g. Pt, Pd, Ru, Rh.

Metal sulfide catalysts for HDO reaction are typically synthesized through the sulfurization with H_2S. However, H_2S is a severely toxic gas and high cost in comparison to other industrial gases, thus special equipment and handling are necessary. Therefore, the use of low cost and water-soluble sulfiding agent provides some advantages such as encouraging sulfurization with metal salt solution, simple scaling up, and lower cost production. Moreover, the presulfurization is not required when performing continuous reactor system. In our work, we used thiourea ($CS(NH_2)_2$) as the sulfur source to prepare unsupported MoS_2, MoS_2/γ-Al_2O_3, unsupported sulfided NiMo, and sulfided NiMo/γ-Al_2O_3. The synthesis approach required low temperature in a range of 250-500 ^oC in air. The higher purity and crystallinity of samples could be achieved if the calcination was performed at higher 350 ^oC under inert or vacuum atmosphere. As-synthesized catalysts were characterized by XRD, FT-IR, SEM, and N_2 adsorption-desorption. The catalytic activities have been studied on 2 reactants. The HDO of phenol, a model compound of lignin, leads to cyclohexane as the final product, while palm oil (triglycerides) as the reactant yields long chain C15-C18 alkanes (BHD).

Structural details of as-synthesized catalysts, i.e. local structure of metal cations, active sites, have been planned to study by XAS at the Synchrotron Light Research Institute (Public Organization), Thailand. The data fitting to model structures will be performed on Athena and Artemis [2]. Besides the metal sulfides, nanostructured copper phosphates have been developed for potential catalysts in HDO process, and analyzed by XAFS spectroscopy [3]. We expect the better understanding of physical, chemical and catalytic properties of MoS_2 and sulfided NiMo system along with other related catalysts on HDO reaction to design, optimize, and develop novel catalysts for HDO and related reactions in the future works.

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[1] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, Chem. Soc. Rev. **41,** 8075 (2012).
[2] B. Ravel, M. Newville, J. Synchrotron Rad. **12,** 537 (2005).
[3] P. Khemthong, P. Daorattanachai, N. Laosiripojana, K. Faungnawakij, Catal Commun. **29,** 96 (2012).