HDO of model molecules derived from lignin catalyzed by molybdenum oxides: influence of the support and copper promoter

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Abstract

Bulk and supported molybdenum catalysts, in addition to the effect of copper as a promoter, were investigated on the activity, selectivity, and stability of molybdenum oxide in the hydrodeoxygenation of molecules derived from lignin. The catalytic performance was correlated with physicochemical properties using ICP-OES, XRD, XPS, Raman spectroscopy, N_2 physisorption, TPR, H_2O-TPD, and oxygen chemisorption. The results showed that under the studied conditions, both the use of support and the addition of copper promoted the activity of molybdenum oxides, preserving the selectivity regardless of the tested molecule. The characterization studies showed that the species formed were mainly $CuMoO_4$ in bulk samples, MoO_3, over titania and silica samples, and metallic copper, Cu_2O, and MoO_2, over activated carbon samples. The H_2O-TPD and O_2 chemisorption results indicate that the inclusion of copper to molybdenum oxide promoted the reduction of molybdenum, the creation of oxygen vacancies, and the formation of H•, factors that favored the selective cleavage of the C–O bond. The hydrodeoxygenation of phenol promoted benzene formation (selectivity above 98%), indicating that the route followed was direct deoxygenation. Guaiacol was more reactive than anisole but had a lower rate of HDO due to a steric constraint. The distribution of products showed that the preferred route for anisole was demethylation, followed by deoxygenation, providing the formation of phenol and benzene. While for guaiacol, the main route was demethoxylation, providing phenol as the main product.

Keywords: Hydrodeoxygenation, Biomass-derived molecules, MoOx, Copper