

## SYNERGISTIC EFFECTS OF BIMETALLIC Mo-W CARBIDE IN HYDRODEOXYGENATION OF GUAIACOL

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Bimetallic MO-W carbide was synthesized via temperature-programmed reduction to generate a  $\beta$ -Mo<sub>2</sub>C like phase with bulk morphology in order to investigate the synergistic effects of a combination of molybdenum and tungsten in carbide. The solid was characterized using X-ray diffraction (XRD), N<sub>2</sub> physisorption, X-ray photoelectron spectroscopy (XPS), H<sub>2</sub>-chemisorption, and ammonia temperature programmed desorption (TPD-NH<sub>3</sub>). The bimetallic carbide exhibited a significantly higher density of H<sub>2</sub>-activating sites than the corresponding monometallic carbides prepared using the same method. In the HDO of guaiacol at 350°C, MoWC yielded the highest hydrodeoxygenation (HDO) catalytic activity and produced completely deoxygenated products with a selectivity of 92 mol% in which benzene selectivity was 70 mol%. The superior catalytic activity is attributed to the presence of both H<sub>2</sub>-activating sites and oxophilic sites. Under the testing conditions, HDO of guaiacol over monometallic molybdenum carbide followed both direct deoxygenation (DDO) and hydrogenation-dehydration (HYD) pathways, while MoWC strongly favored the DDO route. The catalyst remained highly stable over 8h on stream.

The electronic interaction between Mo and W in MoWC and their effect on the energetics and mechanism of guaiacol HDO was further explored using first principles Density Functional Theory (DFT) calculations. Our calculations showed that oxygen bonded ~ 1 eV stronger on the bimetallic carbide (MoWC) than on the monometallic molybdenum carbide surface, confirming the enhanced oxophilicity of W in the presence of Mo, in agreement with XPS studies. The observed preferential selectivity towards deoxygenated products on MoWC surfaces was further explained by the mechanistic investigation on MoWC and monometallic molybdenum carbide surfaces. Our calculations showed that the DDO pathway was kinetically favored on the bimetallic MoWC surface (leading to benzene), while the HYD and DDO pathways proceeded with competitive barriers on monometallic molybdenum carbide (leading to both cyclohexene and benzene).