

# Molybdenum Trioxide and Molybdenum Carbide as Promising Hydrodeoxygenation Catalysts for Biomass Conversion

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Growing concerns due to rising CO<sub>2</sub> emissions have made biomass an indispensable source of renewable fuels and chemicals due to its net zero carbon emission. However, biomass inherently has high oxygen content, which translates to low energy density, thereby necessitating a deoxygenation step before being utilized as fuels. Recently, MoO<sub>3</sub> and Mo<sub>2</sub>C have emerged as promising earth-abundant cheap catalysts that perform selective hydrodeoxygenation (HDO) at relatively low temperatures ( $\leq 673$  K) and ambient H<sub>2</sub> pressures wherein oxygen is removed as water. However, there exists a significant knowledge gap in understanding the stability of these catalysts and elucidating the active phases responsible for HDO over these catalysts. Furthermore, their applicability for real biomass conversions has not been largely demonstrated.

In this thesis, first, HDO of m-cresol, a biomass-derived model compound, is investigated over bulk and supported MoO<sub>3</sub> catalysts. Detailed reactivity and characterization studies reveal that Mo<sup>5+</sup> species plays a critical role during HDO. Specifically, TiO<sub>2</sub> and ZrO<sub>2</sub> are identified as ideal supports as they feature superior HDO reactivity and stability over bulk MoO<sub>3</sub>. These supports stabilize intermediate Mo oxidation states (i.e. Mo<sup>5+</sup>) while bulk MoO<sub>3</sub> over-reduces to inactive metallic Mo. Translating from model compound studies, MoO<sub>3</sub>/TiO<sub>2</sub> and MoO<sub>3</sub>/ZrO<sub>2</sub> are demonstrated to be effective in converting real biomass (pine) pyrolysis vapors to hydrocarbons (ca. 30 % yield), comparable to conventional zeolites.

In comparison with MoO<sub>3</sub>, Mo<sub>2</sub>C is shown to be significantly more stable and selective for HDO of 4-methylanisole to toluene under identical reaction conditions. Mo<sub>2</sub>C predominantly breaks the stronger phenolic C-O bond while MoO<sub>3</sub> also breaks the weaker aliphatic C-O bond, likely due to the presence of Brønsted acid sites. To close the knowledge gap between these two materials, operando near-ambient XPS is employed for the first time during HDO to gain insights into the surface active sites. Based on this technique, HDO seems to operate via distinct active sites on both these Mo-based catalysts. Finally, in the context of lignin valorization, Mo<sub>2</sub>C is shown to be a viable catalyst for converting real lignin streams to a single product – propylbenzene, a precursor for the production of renewable polymers. Overall, this thesis demonstrates the applicability of Mo-based catalysts in real biomass conversions and provides insights on the working nature of these catalysts, which will enable the design of more effective HDO catalysts.

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