

Catalytic Upgrading of Biomass through the Hydrodeoxygenation (HDO) of Bio-oil Derived Model Compounds

TECHNICAL SUMMARY

Lignocellulosic biomass is an attractive renewable source for fuels and chemicals. Of the many conversion alternatives, catalytic fast pyrolysis has emerged as an attractive technology to convert biomass into fuel additives and value-added chemicals. Current pyrolysis oils or bio-oils are incompatible with refinery streams due to their high acid, water, and water content. The key roadblock in its commercial exploitation is development of catalytic platforms for selective deoxygenation along with minimum hydrogen consumption and carbon loss. Current catalytic solutions including zeolites, and conventional hydrotreating catalysts employ high hydrogen pressures, leading to aromatic ring hydrogenation, and hydrogen consumption. This thesis focusses on developing fundamental catalytic understanding on cheaper and earth-abundant reducible transition metal oxide catalysts for selective hydrodeoxygenation (HDO) of bio-oil derived model compounds using reactivity, computation and characterization studies.

The first section focuses on developing structure-reactivity relationships on bulk and supported MoO_3 catalysts for the HDO of lignin-derived model compounds. Characterization studies reveal that MoO_3 undergoes reduction to catalytically inactive MoO_2 at a temperature of 673 K, and stabilization of partially reduced MoO_3 surface through its partial carburization to oxycarbide phase ($\text{MoO}_x\text{C}_y\text{H}_z$) at temperatures < 623 K. Thereafter, it is shown that TiO_2 and ZrO_2 supports prevent the reduction of dispersed oligomeric MoO_x species to catalytically inactive species, enhancing their stability. In addition, the overall catalyst reactivity inversely correlates to the maximum hydrogen consumption temperature during hydrogen temperature programmed reduction (H_2 -TPR) of dispersed MoO_x species. Furthermore, a near-monolayer oligomeric MoO_x dispersion on ZrO_2 support was found to be optimum for HDO reactivity. The second section focuses on developing mechanistic insights into the HDO on bulk and supported MoO_3 with the aid of density functional theory (DFT) computations and kinetic studies. DFT computations were carried out on the elementary steps for HDO of acetone-a model compound on pristine α - MoO_3 (010) surface to reveal dissociative H_2 adsorption on the (010) surface to be the rate-limiting step. Kinetic studies on MoO_3 supported on ZrO_2 reveal the differences in reaction mechanism and the nature of active sites for HDO on $\text{MoO}_3/\text{ZrO}_2$ as compared to bulk MoO_3 . The third section focuses on generalizing the low-temperature (< 523 K) selective HDO on other reducible base metal oxides, specifically cobalt oxide and demonstrates oxides to have significantly higher reactivity than base metals for HDO. Finally, lanthanum strontium cobaltite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$), a perovskite oxide, was demonstrated as a novel HDO catalyst at < 523 K. Overall, this thesis provides a toolkit for developing structure-reactivity relationships on reducible metal oxides for their use as HDO catalysts.

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