

MECHANISTIC INSIGHTS INTO THE HYDRODEOXYGENATION OF BIOMASS-DERIVED FURANS TO VALUE-ADDED FUELS AND CHEMICALS

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Biomass upgrading technology to value-added fuels and chemicals has been intensely studied in recent years, owing to concerns over the sourcing, availability, and environmental impacts of conventional fossil resources with ~50% gigatons of CO₂ emitted annually. Although recent advances in hydraulic fracturing have introduced shale gas as an inexpensive source of natural gas and < C₄ olefins, new production routes will be needed to make up for shortages in larger (C₃₊) products, e.g., aromatics and liquid fuels. In effort to find long-term solutions, lignocellulosic biomass has emerged as a potential carbon-neutral feedstock for the production of C₃₊ compounds from its C₅ and C₆ sugars. However, in contrast with fossil fuels, these biomass-derived sugars are highly oxygenated (~50% O by weight), and strategies for selective oxygen removal are required to create “drop-in” replacements for petrochemicals. A common strategy is to first dehydrate sugars to a class of oxygenated furans, known as platform chemicals, e.g., furfural and 5-hydroxymethylfurfural, from which a myriad of valuable products can be formed. However, the generation of valuable, renewable fuels and chemicals from platform chemicals requires the selective removal of C-O bonds through hydrogen addition, a process known as hydrodeoxygenation (HDO). The aim of this thesis is to design and develop active and selective HDO strategies for several key reactions through detailed mechanistic understanding and characterization of both heterogeneous and homogeneous catalytic systems. In particular, routes to liquid fuels such as 2-methylfuran and linear oxygenates such as 2-hexanol and adipic acid (AA) are discussed in detail.

Alkylated furans, e.g., 2-methylfuran and 2,5-dimethylfuran, are attractive compounds to synthesize due to their high energy densities, high octane numbers, and suitable characteristics as fuels or drop-in fuel additives. However, side reactions from their oxygenated counterparts produce a number of undesired byproducts under reaction conditions, and mechanisms for selective HDO to alkylated furans are not well-understood. This dissertation investigates a mildly oxidized Ru/RuO_x/C catalyst which has achieved remarkable activity for HDO of furfural to 2-methylfuran when secondary alcohols are used as hydrogen donors for catalytic transfer hydrogenation. By employing isotopic labeling techniques and surface characterization, we demonstrate that atomically mixed Ru and RuO_x are central to obtaining high HDO selectivity (~61%), where Lewis acid sites (RuO_x) facilitate Meerwein-Ponndorf-Verley reduction,

and metal sites (Ru) are responsible for *in situ* hydrogen production and transfer. Molecular-level understanding of both the catalyst surface and the underlying reaction pathways, including furan ring activation, are presented through kinetic measurements and *in situ* catalyst characterization.

Furan ring-opening can lead to a variety of valuable polymer precursors and linear oxygenates. Of particular interest is the hydrogenolytic ring-opening of biomass-derived tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) to AA, a valuable C₆ diacid used for Nylon 66 synthesis. Although several reports suggest that metal/metal oxide catalysts, e.g., Rh-ReO_x and Pt-MoO_x, are highly selective for furan ring-opening, we demonstrate that these materials drive significant overhydrogenation of carboxylic acid groups, precluding them from use for AA production from THFDCA. This work addresses this issue by developing a novel, metal-free pathway by combining hydriodic acid and molecular H₂ in organic acid media, forming AA with the highest yield reported to date (~89%). Kinetic and reactivity measurements indicate first-order relationships in proton and iodide concentrations and H₂ partial pressure. We moreover employ spectroscopic techniques and kinetic modeling to elucidate the synergy between molecular H₂ and iodide, the latter of which plays a key role in selective C-O bond scission and H₂ activation. We extend this system to a variety of solid acids, e.g., Nafion and zeolites, which significantly reduces the levels of corrosion during reaction. A variety of both metal-based and metal-free ring-opening mechanisms are proposed and discussed.