Selective catalytic conversion of renewable oxygenates to high value products over zeolites and reducible oxides

The thermochemical conversion of biomass to liquids through techniques such as pyrolysis and torrefaction is a promising approach to produce fuels and high value chemicals. The critical challenge lies in the subsequent catalytic upgrading. Biomass decomposition streams commonly contain a wide range of chemical compounds in a mixture that should be upgraded through very different types of chemistry to maximize the overall value of the product. Selectively coupling light C_2 and C_3 compounds to higher value products, for example, while selectively removing oxygen from larger phenolic and furanic species is necessary to avoid large losses of biomass derived products to either low value coke or light gases. Significant advances have been made in recent years to separate the biomass degradation products into streams rich in families of compounds such as light oxygenates, furanics, and phenolics. This separation enables targeted catalytic upgrading to yield specialty chemicals and fuels. Two families of catalysts that have shown considerable promise for the catalytic upgrading of these families of oxygenates are metals supported on reducible oxides and zeolites. In this contribution we will discuss the mechanism required for unique coupling reactions of light acids with other renewable oxygenates over zeolites. Selective acylation reactions can occur under the high temperature and low pressure conditions necessary for coupling with pyrolysis and torrefaction processes. We further show how this reaction can be used to not only increase the carbon efficiency of a process, but also produce high value specialty chemicals.

Lignin-derived phenolic species represent another important class of oxygenates present in biomass derived streams. The nature of the catalytically active site required for the conversion of phenolics over metals supported on reducible oxides, for example Ru/TiO_2, is not well understood. By systematically varying catalyst properties, the catalytic role of cations on the TiO_2 surface promoted by the metal particle can be distinguished from unique sites that lie at the perimeter of the metal nanoparticle for various types of bonds present in biomass-derived phenolic species. We also discuss the unique role of water on sites near the perimeter of the metal particle, and its role in enhancing C-O cleavage rates as well as facilitating ring-rearrangement reactions of furanic species.

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