

Promotion of Heterogeneous Acid and Base Catalysts for Biomass Upgrading

by

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Technical Summary

As the chemical industry decarbonizes and shifts away from petroleum-based feedstocks, renewable lignocellulosic biomass has received interest as an alternative carbon source for chemicals production. Homogeneous acids and bases have been shown to be active for a wide variety of chemical reactions useful in converting bio-based substrates to existing and novel chemicals; however, the costly separations associated with homogeneous catalysts have necessitated the study of solids with similar properties to fulfill the same role. Indeed, many natural or synthetic solid materials contain acidic or basic active sites that can catalyze a variety of organic transformations. In this work, we studied how acid-catalyzed reaction rates can be enhanced by modifying reaction and catalyst conditions beyond the active site itself. We have also leveraged the acid-base pairs on alkaline earth oxides to generate novel monomers for chemically recyclable plastics.

First, we show how applied electrochemical potentials can be used to enhance Brønsted acid-catalyzed dehydration reactions over a molybdenum oxide film on an yttria-stabilized zirconia pellet. Brønsted acid-catalyzed dehydrations of isopropanol and 2-butanol were found to increase by 2.5× and 1.3×, respectively, upon a +1.5 V polarization of the molybdenum oxide film. We hypothesize that this promotion originates from generation of Brønsted acid sites localized to the three-phase boundary at the catalyst/gas/electrolyte interface and/or acid site strengthening due to electrical polarization. This work demonstrates an alternative handle to promote catalytic turnover, which with further understanding, could be applied toward other Brønsted acid-catalyzed chemistries.

Next, we sought to understand how solvent and framework polarity affect Lewis-acid catalyzed aldol addition reactions in microporous Hf-BEA zeolites using the self-aldol addition of ethyl pyruvate (EP) as a probe reaction. Initial rates were measured using toluene and acetonitrile as solvents and hydrophobic Hf-BEA-F and hydrophilic Hf-BEA-OH catalysts. Apparent first-order rate constants span two orders of magnitude across the four systems; at 363 K, the highest rates were observed over hydrophobic Hf-BEA-F in toluene, while the lowest rates were observed in hydrophilic Hf-BEA-OH in acetonitrile. Despite the substantial rate constant variation across the four systems, apparent enthalpies for Hf-BEA-F in both solvents and Hf-BEA-OH in acetonitrile were within the error of each other (~ 70 kJ mol⁻¹). Reactions performed using Hf-BEA-OH with toluene featured a higher apparent enthalpic barrier of 83.8 kJ mol⁻¹. The differences between the systems are attributed to hydrogen-bonding interactions between the EP molecules and polar silanol nests during catalysis in toluene using Hf-BEA-OH, which hinder EP

adsorption to the active site in the hydrophilic framework. These findings show that aldol addition kinetics are not significantly modified by solvent polarity in hydrophobic frameworks beyond site-blocking effects; however, silanol nests in hydrophilic frameworks significantly alter substrate adsorption to the active site.

Finally, acid-base pairs on supported alkaline earth oxide catalysts were used for the first-reported continuous catalytic synthesis of the α -methylene- δ -valerolactone (MVL), the monomer of the chemically recyclable acrylic plastic poly-MVL, via a gas-phase aldol condensation of δ -valerolactone (DVL) and formaldehyde (FA). In particular, CaO supported on SiO₂ catalyzed the reaction with >95% selectivity to MVL at conversions of ~30% (613 K, 0.4 mol% DVL, 1.2 mol% FA, 5 wt% CaO/SiO₂ catalyst). Selectivity to MVL remained >75% even at DVL conversion between 50-75%. This work shows the first continuous and scalable synthesis of the MVL monomer, which represents an important step toward the large-scale production of this chemically recyclable plastic.

These results show that reactivity over solid acid and base catalysts can be tuned beyond modification of the catalyst active site alone. Rigorous analysis of these systems can allow for the development of new biomass upgrading schemes with higher reactivities that can eventually lay the groundwork for a more sustainable chemical industry.

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