

# Modification of Zeolite Acid-Base Properties for the Selective Catalytic Dehydration of Biomass-Derived Lactates to Acrylates

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Motivated by concerns about anthropogenic climate change, extensive research efforts in recent years have focused on the synthesis of fuels and chemicals from non-edible lignocellulosic biomass, which is a renewable and abundant carbon source. The increasing utilization of shale natural gas in place of petroleum has caused a decline in the production of key olefin platforms, particularly propylene and butadiene. This change in feedstock distribution provides an opportunity for the development of new, sustainable routes to partially oxidized, C<sub>3+</sub> commodity chemicals from biomass resources. Synthesizing the same final products, or drop-in substitutes, from oxygen-rich lignocellulose, rather than oxygen-poor hydrocarbon platforms, requires the development of new catalytic technologies for selective deoxygenation and dehydration. Similar to petroleum refineries, the "biorefineries" of the future will produce a variety of valuable fuels and chemicals through the application of these novel catalytic deoxygenation and dehydration processes to a defined set of flexible, biomass-derived platform molecules. Lactic acid has been proposed as a model platform species because it can be efficiently and renewably produced from cellulose-derived glucose, and directly valorized into numerous products including 2,3-pentanedione, acetaldehyde, lactide, 1,2-propanediol, and acrylic acid.

Acrylic acid, along with its esters and derivatives, is a major commodity chemical (>8 million tons/year) currently produced almost entirely via the selective oxidation of petroleum-derived propylene. Acrylate-based polymers are used in paints, absorbents, coatings, adhesives, and other specialty chemicals, and the market for these products is projected to grow at >5% per annum in the coming years. While the synthesis of acrylate products via lactic acid dehydration is conceptually straightforward, achieving selective conversion has proven challenging. Despite almost 10 years of intensive research, the maximum reported yield is below 80% and reaction rates are too low for the process to become economically competitive with petroleum-based methods. The slow development of effective dehydration catalysts can be largely attributed to a lack of detailed investigation of the surface-mediated reaction mechanism. Mechanistic insights based on rigorous experimental evidence will aid in the identification of key surface-adsorbate interactions and descriptive parameters for lactic acid dehydration, enabling the rational design of more active, selective, and durable catalyst materials.

This dissertation elucidates the molecular-level reaction mechanism for the conversion of lactates (lactic acid and methyl lactate) in the gas phase over alkali metal-exchanged zeolite catalysts. The comprehensive proposed mechanism can be divided into three inter-related parts. First, we show how the dissociative adsorption of organic acids and esters on sodium-exchanged faujasite (NaY) changes the acid/base properties of the material in situ by generating extrinsic Brønsted acidic sites on the zeolite

framework. The catalytic characteristics of these extrinsic sites are compared to intrinsic sites, i.e. those on proton-exchanged zeolites, using both spectroscopic and kinetic investigations. Second, we identify the active sites and key mechanistic steps for both lactate dehydration and the major side reactions, decarbonylation to acetaldehyde and decomposition to coke. Dehydration must pass through dissociatively adsorbed sodium lactate, and conversion to adsorbed sodium acrylate is mediated by Lewis acid sites on NaY. By contrast, the extrinsic Brønsted acidic sites exclusively catalyze the side reactions. The rate-limiting step for dehydration is shown to be dependent on the reaction conditions, and the effects of this finding on the reaction rate and selectivity are explored. Third, pyridine is applied as a model alkaline additive to quench the unselective Brønsted acid sites, and this approach is shown to improve dehydration selectivity. However, the inclusion of pyridine also introduces a new mode of catalyst deactivation, as strongly adsorbed pyridine accumulates in the micropore network and blocks reactant access to active sites. Finally, these mechanistic insights are applied to the development of novel sodium phosphate-treated NaY zeolites, which exhibit dehydration selectivities of up to 90%. The alkaline phosphate species is shown to play multiple roles, as it increases the extent of dissociative adsorption and quenches extrinsic Brønsted acid sites, but also leads to the accumulation of sodium acrylate on the surface through strong acid/base interactions. The broader implications of these insights for the rational design of selective lactate dehydration catalysts, as well as the upgrading of multi-functional biomass-derived molecules in general, are discussed in detail.