

# First-Principles-Based Kinetic Modeling of Brønsted and Lewis Acidic Zeolites or the Catalytic Conversion of Furans to Aromatics

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Polyethylene terephthalate (PET) plastics and fibers are produced through the reaction of terephthalic acid with monoethylene glycol. Current renewable PET products can only claim to be 30% renewable, as the terephthalic acid which makes up *ca.* 70% of its structure are still derived from petroleum sources. In order to achieve 100% bio-derived PET materials, a renewable route to terephthalic acid is needed. The discovery of a mechanism by which biomass-derived furans and ethylene react to form aromatics over solid acid zeolites has provided a potential pathway for the renewable production of terephthalic acid.

Computational studies of this system revealed a tandem reaction scheme, whereby furans and ethylene undergo a concerted Diels-Alder cycloaddition to form an oxanorbornene intermediate, which successively dehydrates to an aromatic. The role of Brønsted acidic zeolites has been shown, through first-principles density functional theory (DFT) calculations, to be on the dehydration reaction of the tandem scheme.

Direct comparisons between these DFT calculations and experimental observations have remained a challenge, due to the complicated nature of these systems, however. Experimentally, interesting behaviors were observed, whereby adding catalyst to the reactor caused an increase in aromatic production rate at low catalyst loadings, but had no effect on the rate at high catalyst loadings. Additionally, studies extended beyond well-understood Brønsted acidic zeolites to framework-substituted Lewis acid zeolites demonstrated this same behavior.

In this dissertation, DFT calculations are connected to experimental observations through the parameterization of microkinetic models of the reactor systems. A systematic approach is taken to create combined quantum mechanical, molecular mechanical model of zeolite active sites and the surrounding pore, which significantly improves the accuracy of adsorbate interactions with zeolites, without significantly increasing the computational costs. These improved zeolite models are used to parameterize microkinetic models of Brønsted acidic zeolites, providing fundamental explanations for the aforementioned experimental observations, but also to investigate the fundamental role of Brønsted acid strength on reactivity of these materials.

A study of Sn, Ti, and Zr, framework-substituted zeolites provides insights into the role of the active site of these materials for the aromatization of furans. The ability to isolate elementary reaction steps computationally is used to investigate the effects of Lewis and Brønsted acid sites in these materials on the Diels-Alder cycloaddition and dehydration reactions separately. Their overall contributions to furan aromatization are also examined. Finally, framework-substituted, Zn-containing zeolites are studied for their ability to catalyze the aromatization of oxygenated furans. Little is known about the active site in these materials, and so possible structures are explored for their intrinsic properties and their effect on reactivity.