

# Understanding the p-Xylene Formation Mechanism from Dimethylfuran and Ethanol

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Renewable, biomass-based chemical feedstocks as alternatives to petrol-based commodities are of high industrial relevance<sup>1,2</sup> and have attracted recent attention. A number of platform chemicals have been identified as industrially-important, including cyclic oxygenates such as 2,5-Dimethylfuran (DMF)<sup>2,3</sup>, which can be catalytically converted to p-xylene, an important precursor in the production of polymers. Acidic heterogeneous catalysts can catalyze the conversion of DMF to p-xylene by a Diels-Alder (DA) reaction with ethylene. The reaction can be divided into two stages: DA cycloaddition and cycloadduct water elimination (dehydration), with the DA being the rate-controlling step in the Bronsted acid-catalyzed (BA) reactions<sup>3</sup>. In this work we propose an alternative route for DMF conversion to p-xylene using BA zeolite catalyst and ethanol as the dienophile source. Using electronic structure calculations, we elucidate the detailed reaction pathways and associated energetics and demonstrate that the ethanol-based pathway is preferred to ethylene in terms of overall reaction rates. We demonstrate that the sequence of reactions in the ethanol route follows a proton affinity<sup>4</sup> thermodynamic preference of the reacting species, initiated by ethanol dehydration to ethylene. Improved performance is rationalized by the generation of a water molecule in this first step of the mechanism. While absent in the ethylene route, the presence of additional water in the system reduces the entropy loss in key elementary steps and facilitates proton transfer reactions. As a result, activation free energy barriers for the catalytic cycle decrease relative to the ethylene pathway. The calculated activation free energy difference (using energetic span model) between the two routes is in excellent agreement with kinetic experiments.

## References:

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