

# Computational Insights into DMF Conversion to p-Xylene: Ethylene or Ethanol?

Pavlo Kostetsky<sup>1</sup>, Ivo Teixeira<sup>2</sup>, Michail Stamatakis<sup>3</sup>, Shik Chi Edman Tsang<sup>2</sup> and Giannis

Mpourmpakis<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15621, USA

<sup>2</sup>Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, UK

<sup>3</sup>Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

## Abstract:

Production of renewable, biomass-based chemical feedstocks has recently emerged as an important area of research, with high industrial relevance<sup>1,2</sup>. A number of biomass-based 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 upgraded to p-xylene, an important precursor in the production of polymers. DMF can be converted to p-xylene by a Diels-Alder (DA) reaction with ethylene, using acidic heterogeneous catalysts. 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 Brønsted acid-catalyzed (BA) reactions<sup>3</sup>. In this work we investigate an alternative, ethanol-based route for DMF conversion to p-xylene using BA zeolite catalysts. 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 attribute the improved performance to the generation of a water molecule in the first step of the mechanism, which is ethanol dehydration to ethylene. This water molecule is absent in the ethylene route. The presence of 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. Moreover, we demonstrate that the sequence of the reactions in the ethanol route follows a proton affinity<sup>4</sup> thermodynamic preference of the reacting species. Importantly, our calculated (using the energetic span model<sup>5</sup>) activation energy difference between the two routes is in excellent agreement with kinetic experiments.

## References:

1. Kunkes, E. L.; Simonetti, D. A.; West, R. M.; Serrano-Ruiz, J. C.; Gartner, C. A.; Dumesic, J. A., *Science* **2008**, 322, 417-421.
2. Williams, C.L.; Chang, C.C.; Do, P.T.; Nikbin, N.; Caratzoulas, S.; Vlachos, D.G.; Lobo, R.F.; Fan, W.; Dauenhauer, P.J.; *ACS Catal.* **2012**, 2, 935-939.
3. Nikbin, N.; Do, P.T.; Caratzoulas, S.; Lobo, R.F.; Dauenhauer, P.J.; Vlachos, D.G.; *J. Catal.* **2013**, 35-43.
4. Kostetsky, P.; Maheswari, J. P.; Mpourmpakis, G., *J. Phys. Chem. C* **2015**, 119, 16139-16147
5. Kozuch, S.; Shaik, S., *Acc. Chem. Res.* **2011**, 44, 101-110.