

## Understanding the Hydrogenation of 5-HMF in Aqueous Phase

### Exploration of 5-HMF Hydrogenation on Copper Surface in Aqueous Phase using Multiscale Atomistic Simulations

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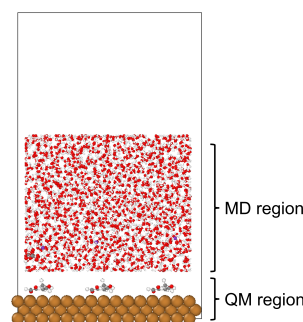
#### In Short

- Investigation of the most favorable reaction path for the conversion of 5-HMF to DMF over Cu(100) surface in explicit solvation model
- Combining DFT and MD methods using multiscale DFT-CES approach to conduct an accurate and efficient simulation of electrocatalytic hydrogenation reaction
- Study the effect of applied potential on the adsorption energy of educt, product, and intermediates in the hydrogenation of 5-HMF to DMF

The negative impacts of fossil fuel on climate change are well known. Therefore, it is essential to explore and develop new sustainable energy resources. In this regard, bio-mass-derived fuels (biofuels) are one of the promising alternatives to fossil fuels. 2,5-dimethylfuran (DMF) is a biofuel with high energy density, good combustion properties, and high octane number, making it a suitable candidate as an alternative fuel [1–3].

DMF can be produced via electrochemical hydrogenation of 5-hydroxymethylfurfural (5-HMF) on metallic catalysts. The selective hydrogenation of 5-HMF to DMF is only achieved by subsequent hydrogenation and hydrogenolysis of the two side functional groups of 5-HMF. Therefore, high-yield production of DMF requires the suppression of undesirable side reactions such as decarbonylation, ring saturation, and ring opening. However, a detailed understanding of the underlying reaction mechanism remains largely elusive for electrocatalytic synthesis. In this project, therefore a comprehensive atomistic understanding will be provided on the reaction mechanisms in the electrocatalytic synthesis of DMF from 5-HMF. The schematic of reaction paths for the hydrogenation of 5-HMF is presented in the Appendix. Quantum mechanical (QM) simulations such as density functional theory (DFT) accurately describe the electronic structure in electrochemical cells. Though the complexity of electrochemical cells limits the investigation of larger systems than a few atoms and a few hundred picoseconds. On the other hand, molecular dynamics simulations (MD) are capable of simulating larger and more complex systems with

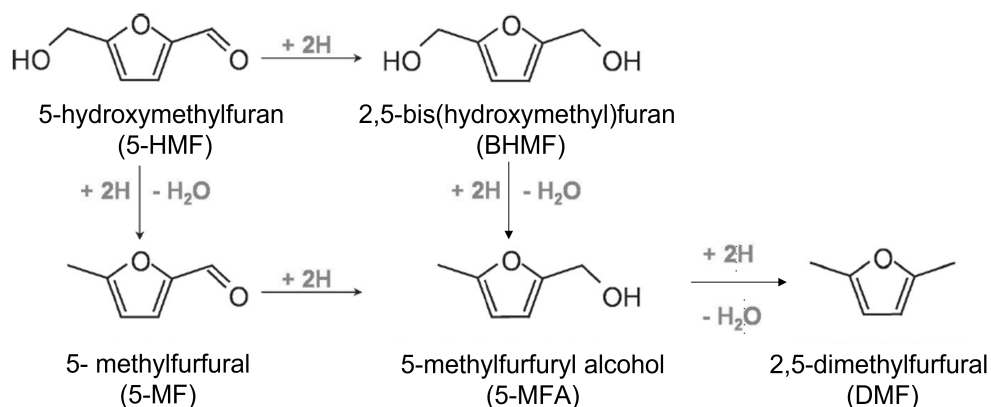
a longer time span to achieve fully equilibrated structural properties. To combine the benefits of both approaches (DFT and MD), we are using the multiscale DFT-CES (DFT in classical explicit solvents) method [4] to study the hydrogenation of 5-HMF. This method provides both a reliable description of the system's polarizability and an appropriate organizational solvent structure using a fully explicit model. In this project, the stable adsorption geometries of 5-HMF, DMF, and the main reaction intermediates (2,5-bis(hydroxymethyl)furan (BHMF), 5-methyl furfural (5-MF), and 5-methylfurfuryl alcohol (5-MFA)) will be calculated by DFT simulations. The effect of aqueous phase and applied potential on adsorption energy will be investigated. Consequently, the stable configurations will be inserted in a DFT-CES simulation to identify the thermodynamically favored reaction path for the electrohydrogenation of the 5-HMF to DMF. In the DFT-CES simulation, the QUANTUM Espresso (QE) and LAMMPS programs are coupled for the DFT and MD parts of simulations, respectively. An exemplary modeled cell using DFT-CES simulation is shown in Figure 1. Figure 1 illustrates the DFT region, describing the adsorbate molecule (5-HMF) and Cu (100) electrode, and the MD region, which consists of water molecules and cation and anion pairs in the electrolyte.



**Figure 1:** Schematic of simulated cell with DFT-CES method for 5-HMF as adsorbate on Cu(100) surface.

By post-processing the data from DFT and DFT-CES calculations, the free energies for different reaction pathways in the explicit solvent model on the Cu (100) electrode will be estimated and compared together. Moreover, the effect of different applied potentials on the reaction mechanism will be analyzed to provide a comprehensive picture of different key determinants in the electrohydrogenation of 5-HMF to DMF on the Cu surface.

**Appendix:**



**Figure 2:** Schematic overview of reaction pathways for electrocatalytic hydrogenation of 5-HMF to DMF.

### WWW

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### More Information

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### Project Partners

Prof. Stefan Ringe's research group (RingeLab) at Korea University

### Funding

DFG, under Germany ExcellenceStrategy- EXC 2163/1, Sustainable and Energy Efficient Aviation, Project-ID 390881007s

### DFG Subject Area

Cluster of excellence, Sustainable and Energy Efficient Aviation (Se<sup>2</sup>a) is a multidisciplinary cluster.