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Investigation of Electrochemical Synthesis of 2-Methylfuran from Furfural by Molecular Dynamics Simulation

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1. Introduction

2-methylfuran is a promising alternative to fossil aviation fuels due to its higher efficiency and lower hydrocarbon emissions [1]. 2-methylfuran can be produced by means of electrochemical hydrogenation of furfural directly, or by a subsequent reaction after producing furfuryl alcohol. However, other species such as furan and tetrahydrofurfural can be obtained during this process, which are not desirable as an alternative fuel. Therefore, a systematic and tailored synthesis is necessary to achieve sufficient amount of 2-methylfuran that is required to be utilized in the avation industries. In this study, molecular dynamics simulations (MD) were performed to provide a better understanding of furfural and 2-methylfuran behavior in an electrochemical cell. For this purpose, their microstructural and energetic properties were analysed at the electrode surfaces by determining the orientational ordering at the surface, the potential of mean force (PMF), and radial distribution functions (RDF).

2. Simulation Details

The MD simulations were performed with LAMMPS [2] and GROMACS [3]. The simulation system is shown in Fig. 1. It consists of two metal electrodes (from Cu, Ni, Pb), and a liquid phase in between that is composed of water as solvent, furfural molecules and ionized sulfuric acid as electrolyte. The OPLSAA [4] force field was utilized to describe the atomistic interactions of furfural, 2-methylfuran (as shown in Fig. 2), and sulphate ions, while the hydronium ions were modeled using the parameters by Wolf et al. [5]. The TIP3P potential [6] was used to simulate the water molecules, and the compatible surface force fields by Heinz et al. [7] for modeling the electrodes. The approach by Petersen et al. [8] was employed in the LAMMPS simulations to provide a realistic and computationally efficient modeling of electrostatic interactions between electrolyte and polarizable electrodes. The simulations were conducted at 298.15 K and 1 atm pressure conditions with a timestep of 0.5 fs. A cutoff distance of 12 $\mathring{A}$ was used for the electrostatic and Lennard-Jones interactions. The simulation length in the equilibration and production phase was between 9-15 ns for the different systems.
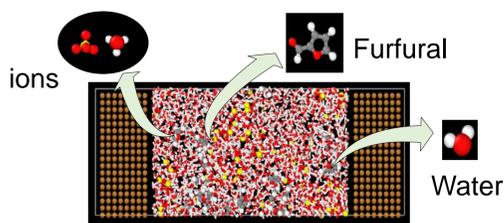

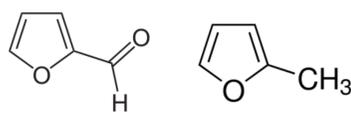**Fig. 1.** The configuration of an electrochemical cell

Fig. 2. Structure of furfural and 2-methylfuran

3. Potential of Mean Force (PMF)

The PMF describes the binding affinity of a solute to the electrode surface. The educt binding affinity in comparison to the product was calculated by: $\Delta\Delta F_{binding} = \Delta F_{educt} - \Delta F_{product}$
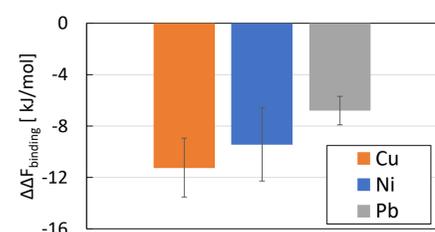

Fig. 3. $\Delta\Delta F_{binding}$ of the educt/product pair at different electrode materials.

For all electrode materials, the educt (furfural) is more strongly stronger binded to the surface than the product (2-methylfuran) (see Fig. 3). This is essential for the reaction to proceed.

The $\Delta\Delta F_{binding}$ is most pronounced for copper as electrode material.

4. Orientation and RDF calculation

The orientation ordering of the furfural molecules towards the surface was analysed by computing the orientation factor *S* as:

$$S = \left\langle \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2}(3cos^2\theta_{i,t} - 1) \right\rangle$$
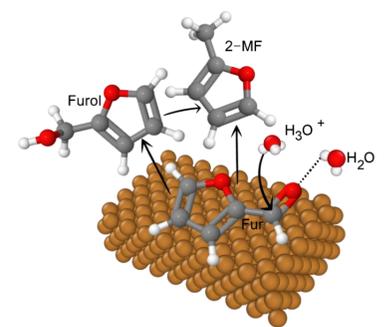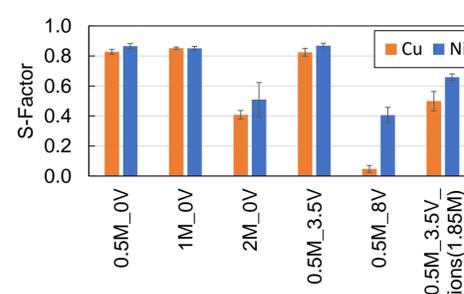

Fig. 4. S-factors of furfural molecules at the working electrode for different concentrations and applied voltage. (S=1: parallel orientation; S = -0.5: perpendicular)

Fig. 5. Scheme of furfural (Fur) hydrogenation to 2-methylfuran (2-MF) or furfurylalcohol (Furol) on a metalic electrode.

Both, the hydrogenation of oxygen in the aldehyde group and the parallel adsorption configuration of furfural on the surface are required reaction conditions for the hydrogenation of furfural to the furfuryl alcohol and/or 2-methylfuran in the presence of protons [9,10].

Fig. 4 illustrates that at lower furfural concentration and without external voltage, the preferable orientation of the furfural molecule is parallel to the surface (see Fig. 5). However, increasing the concentration of furfural, the presence of ions and applied voltage between the electrodes changes the adsorption orientation of the furfural molecules, which will then affect the reaction path.
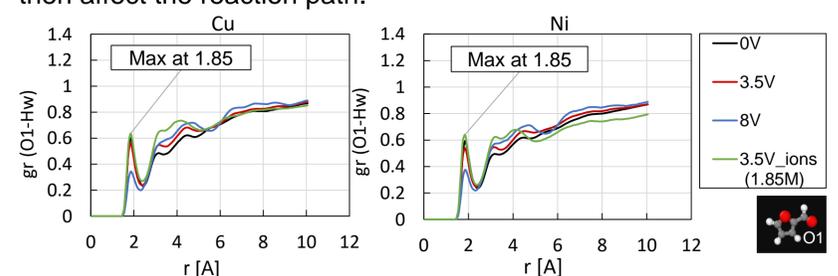

Fig. 6. RDF of aldehyde oxygen (O1) atom in furfural and hydrogen in water for 0.5M of furfural in the electrolyte.

The RDFs (Fig. 6) demonstrate hydrogen bonding between the aldehyde oxygen O1 atom in furfural and hydrogen in water, required for its hydrogenation.

5. Conclusion

In this study, reaction conditions for the production of 2-methylfuran from furfural in an electrochemical cell were investigated. The PMF results demonstrate the tendency of the furfural molecules to pull stronger to the electrode, which is necessary for the reaction progress, and it is most pronounced for Cu electrodes. The RDF calculation shows the hydrogen bonding between water and the aldehyde oxygen in all simulations. This hydrogen bonding leads to the hydrogenation of furfural to furfuryl alcohol and/or 2-methylfuran, when the proton is available in the system. Moreover, the orientation of furfural molecules at the working electrode was calculated for different voltages and concentrations of furfural, showing that increasing the applied voltage and concentration of furfural and electrolyte affects the adsorption trend of furfural. Therefore, it is important to choose a proper combination of electrode material, applied voltage and concentrations to effectively proceed the reaction towards producing 2-methylfuran.

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