

## Abstract

In this doctoral thesis, I investigated the electrochemical reduction of furfural in an acidic medium. The main purpose was to expand knowledge of the factors influencing the course and selectivity of the electrochemical reduction. To achieve this, I used several electrochemical and analytical methods. Electrochemistry coupled with mass spectrometry (EC-MS) played a central role, allowing me to measure the resulting products in situ.

First, I examined how electrode structure affects the electrochemical reduction of furfural on copper. I compared nanostructured copper nanoparticles on carbon (Cu/C) with a polycrystalline copper disk (Cu disk). Electrode structure proved to be an important factor. Copper nanoparticles were more active in producing the higher-value product 2-methylfuran (2-MF) and in the side hydrogen production reaction than the copper disk. Underpotential lead deposition revealed that the surfaces differ in the amount of individual crystal faces, which likely explains the different selectivity. Several defect sites were also present on the copper nanoparticles.

I further investigated the electrochemical reduction of furfural on palladium-on-carbon (Pd/C) nanoparticles. Using the EC-MS methodology, I obtained partial currents for both products under selected conditions of the electrochemical reduction of furfural, as well as for the side reaction of hydrogen production. This allowed me to determine Tafel slopes for each reaction and gain insight into the reaction mechanism. The results indicate that the electrochemical reduction of furfural at palladium electrodes proceeds mainly via a Langmuir-Hinshelwood type mechanism. Additionally, I demonstrated the blocking effect of furfuryl alcohol (FA) on further reduction and showed that FA is a precursor for 2-methylfuran at palladium electrodes.

I also examined whether the choice of support material affects the electrochemical reduction of furfural. I compared palladium nanoparticles on carbon with palladium nanoparticles on titanium oxynitride on graphene oxide (Pd-TiON<sub>x</sub>/rGO). The titanium oxynitride sample was less oxyphilic and had a greater tendency to adsorb protons. I determined the total zero charge potential from N<sub>2</sub>O reduction, which was slightly shifted in the cathodic direction for the titanium oxynitride sample, indicating a more negatively charged surface compared to palladium on carbon. In the electrochemical hydrogenation of furfural, Pd-TiON<sub>x</sub>/rGO was more active in producing 2-MF and in side hydrogen production.

In the final part, I investigated the effect of adding an ionic liquid to the catalyst surface as a surface modifier to improve selectivity. I selected 1-methyl-3-propylimidazolium dicyanamide

(MPI DCA) for this purpose. The formation of a film on the surface of the MPI DCA electrode increased selectivity for 2-MF formation and inhibited side hydrogen production.