Overcoming Technology Barriers with Tailored Catalysts: Design of Molecularly Functionalized Heterogeneous Catalysts for Selective Reductions of Biomass-derived Materials (FunCat)

Future success in biomass-based economy requires rapid solutions for converting compounds available from biomass to value-added building blocks for materials and for the chemical industry. These rapid solutions can only be obtained by new catalytic methods. These methods need catalysts that do not yet exist.

This multidisciplinary project aims at development of new catalysts for the processing of biomass-based raw materials. We specifically aim at the development of selective reduction catalysts since most biobased raw materials are highly oxidized, and reduction will render them more useful as building blocks.

The project focuses on the development and even design of ligand-modified heterogeneous metal catalysts. The ligands are molecules that adsorb on the metal surface, modifying and amplifying the catalytic efficiency of the solid metal catalyst. In other words, the ligand molecules act as active co-catalysts. The theoretical and experimental studies focus on co-operation of ligands and the metal, and the effect of this cooperation on the efficiency and selectivity of reduction reactions.

The teams will bring their own expertise to the project: the team led by Prof. Honkala will focus on density functional theory calculations and the development of structure-reactivity models for the new catalysts. The group of Prof. Pihko focuses on synthetic chemistry, including synthesis of ligands for characterization of catalysts and reactivity studies. Based on atomic-level understanding on the properties of the ligands and how they impact the activity and selectivity in studied reactions, we seek to obtain key descriptors to facilitate fast optimization and tailoring of catalysts for a variety of reduction reactions relevant to biomass-based raw-materials.

The experimental research has focused on synthesis of ligands and their tests in selected reactions, such as reduction of ketones. A small library of ligands has been successfully synthesized and screened with different metals in test reactions. The test reactions do show selectivity, but low selectivities compared to literature selectivities, with the best results obtained on platinum. catalysts. The origin of these selectivity problems lies with the activation of platinum catalysts. The catalysts are typically activated under very harsh conditions requiring high temperatures with hydrogen. These conditions that are not easy to reproduce and also appear to be unsafe for scale-up. For these reasons, we have now switched the research towards metals that are safer to activate and use on a large scale, such as Pd and Ni catalysts. For unearthing the structure-activity relationships, we have focused on in diastereoselective reduction reactions of model compounds such as allylic alcohols to probe their sensitivity to the to the ligand environment. The model compounds have been synthesized and the initial tests revealed that homogenous catalysts, such as rhodium catalysts, appeared to give better selectivities than heterogeneous catalysts. The effect of the ligands has not yet been systematically explored, however.

In our calculations, we have used a quinoline-based ligand molecule to modify the catalytic properties of platinum because it binds strongly enough onto a platinum surface and have mildly attractive ligand-ligand interactions. We demonstrate that the presence of ligand allows hydrogen to dissociate via a so-called heterolytic pathway forming a positive proton and negative hydride. Heterolytic dissociation may have an impact on a reaction mechanism, which in turn influences activity and selectivity of a catalyst. Herein, we have considered levulinic acid semi hydrogenation as a model reaction on a bare and ligand-modified Pt surface. Our results show that while the presence of a ligand changes the reaction mechanism, the quinoline-based ligand does not improve activity, but it may influence the selectivity of the reaction, but this calls for further computational studies.

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