A path towards improved stereoselectivity

Aminoacids-Functionalized Platinum Nanoparticles as Asymmetric Heterogeneous Catalysts

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In Short

- The demand of chiral chemical products and drugs is increasing.
- We aim at an asymmetric catalyst that is heterogeneous, highly active, stereoselective.
- Aminoacids-functionalized platinum nanoparticles have been demostrated as promising candidates for the role.
- In these systems, stereoselectivity is governed by the interactions between ligand and reactant at the surface.
- This project will sample, both with static and dynamic approaches, the complex configurational landscape of this interaction.

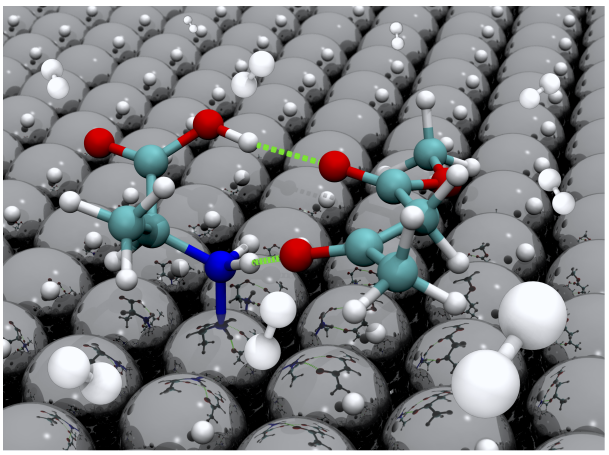

Figure 1: *Pictorial representation of a stereoselective hydrogenation reaction catalyzed by an Alanine-functionalized Platinum nanoparticle*

Since the discovery of the fatal effect of one of thalidomide enantiomers on embryos, the demand of chiral chemical products and drugs has continuously increased. Today more than 80% of all drugs are brought to market as enantiopure compounds. However, the majority is still produced by synthesis of the corresponding racemate (1:1 mixture of the two stereoisomers) followed by separation of the two enantiomers. This leads to the need for new and improved stereoselective catalytic routes in order to operate at low temperatures with high reaction rates.[1]

The development of novel efficient stereoselective heterogeneous catalysts represents a very desirable but rather challenging goal. This sets the goal for the design of a "dream catalyst", that should be heterogeneous, highly active, stereoselective and takes advantage of a simple preparation.

One approach is to functionalize metal nanoparticles with ligands that could bear chiral information. This approach has been followed by the group of Dr. Sebastian Kunz at the University of Bremen, by functionalizing platinum (Pt) nanoparticles with aminoacids, such as L-proline and L-alanine.[2–4] For the first time, an enantiomeric excess above 80% was reported for supported ligand-functionalized nanoparticles, demonstrating the potential of these materials as a novel type of asymmetric heterogeneous catalyst.[4]

The high stereoselectivity can be explained via a ligand-reactant interaction model, that predicts the final stereochemistry of the reaction, based on the energy difference between competing interaction configurations between the reactant and the ligand, with different prochiralities (Figure 1).[4]

The aim of this project is to use quantum mechanical simulations of the experimental system to verify and further refine this introduced interaction model. We plan to test several aminoacid-reactant pairs, looking for confirmation of the experimentally measured dependency with respect to the chemical nature of the involved molecules. We will sample, both with static and dynamic approaches, the complex configurational landscape of the interaction. We will finally study the effect of surface hydrogenation, revealing if the stereoselectivity is dependent on the reaction conditions.

While the individual planned simulations do not explicitly require an HPC infrastructure on their own, the large amount of them, due to the inherent complexity of the interaction configurational space, characterizes this project as "high throughput", possible only on the computational resources provided by HLRN.

We believe that this study will not only afford new insights into ligand-functionalized NP catalysts, but the results will also more generally help the development of a novel approach to control the selectivity of reactions in heterogeneous catalysis. This can open up yet unexplored possibilities for manipulating

reactions on catalytic surfaces to control selectivity.

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More Information

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