

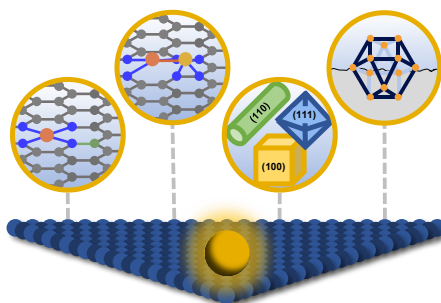
Summary

Controlling Second Coordination Sphere Effects in Heterogeneous Catalysis

A Molecular Approach

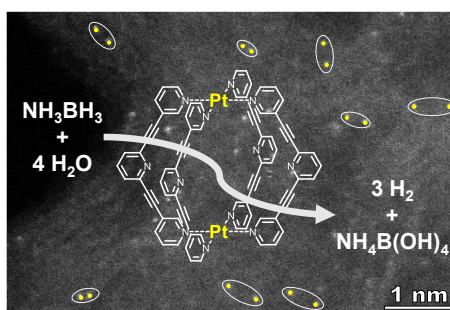
A critical step towards a carbon-neutral society is minimizing the ecological footprint of the energy and chemical sectors. The speed of this transition is dependent on the development of better catalysts to lower the energy input and increase selectivity of catalytic processes, for example. Taking from all catalysis disciplines, heterogeneous, homogeneous, and biocatalysis, my dissertation focuses on implementing and understanding of second coordination sphere effects around supported single-atom catalysts (SACs).

Chapter 1 discusses how second coordination sphere effects are currently implemented in single-atom catalysis based on illustrative examples from literature. There are four main approaches: i) surface doping of SACs by heteroatoms, ii) surface doping of SACs



by metal atoms to create a bi-atomic active site, iii) controlling the surface facet on which the SACs are supported and iv) surface immobilization of supramolecular cages. We show various ways in which controlling the reaction pocket around these single-atom sites resulted in improved activity, selectivity, and stability. However, a clear explanation for the observed effect(s), *i.e.* a structure-performance relationship, is generally missing. By using well-defined catalysts, advanced characterization techniques and suitable probe reactions, we aim to understand this relation between the exact structure of the active site and its catalytic performance.

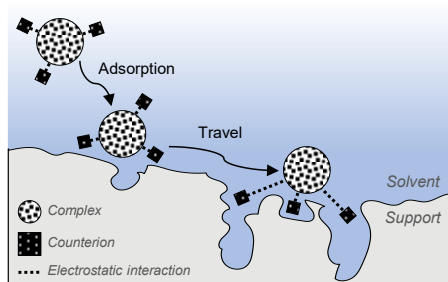
In **Chapter 2**, we describe the synthesis, characterization and catalytic application of Vulcan-supported supramolecular Pt₂L₄ cages. These cages are used to control the first- and second- coordination sphere of the catalysts by design of the organic ligands (L). Immobilization resulted in a



homogeneous distribution of the molecular species, having thus all the metal sites available for catalysis. Next, we studied the hydrolysis of ammonia borane at various temperatures by detailed kinetics. We found that having a second Pt-atom in the

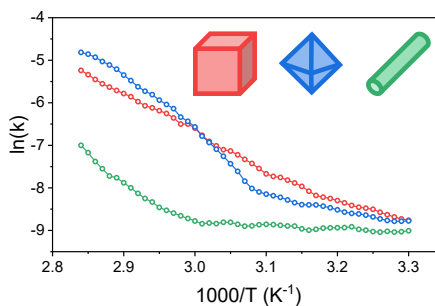
catalysis second coordination sphere, like in Pt₂L₄ cages, caused a different reaction mechanism with a ten-time enhancement in rate compared to the single-atom analogue. Incorporating pyridine functionalities in the second coordination sphere increased the catalytic activity further as a result of substrate binding. Moreover, the pyridine can abstract a proton from water generating locally OH⁻ which is known to stabilize the transition state of the reaction, resulting in near-perfect reaction kinetics. This shows the importance of careful design of the reaction pocket, and provides a framework to do this with hitherto unachievable precision.

In **Chapter 3**, we study the surface binding mechanism of supramolecular cages to the carbonous support Vulcan by using three different platinum cages that vary vastly in size yet share the same counterion. In all cases, nitrogen sorption studies showed the same decrease in one



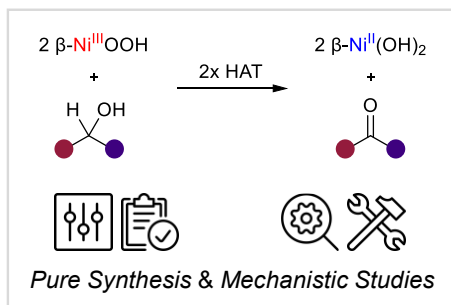
specific size of micropore. The counterions of the cages perfectly fit into these pores in which they are stabilized by anion- π interactions. Further studies showed that the binding process starts with surface adsorption by van der Waals forces and is followed by surface travel to a suitable binding spot prior to surface binding by counterion confinement. In line with the hypothesis of counterion confinement in the surface micropores, we observed a quadratic increase in surface-adsorbate binding constant with the number of counterions per complex. With this, we developed a general and simple strategy to graft molecular species on charge-neutral surfaces with a high binding affinity and good surface distribution.

In **Chapter 4**, we examine facet effects of Pt SACs by synthesizing them on cerium dioxide cubes, octahedra and rods which all have a different, well-structured terminal crystal facet. We show that electronic structure of the Pt atoms is not facet dependent, but that the surface oxygen vacancy density is. Significant differences were observed when applying them in



the catalytic hydrolysis of ammonia borane between 30 and 80 °C. These differences were mainly caused by the facet, *i.e.* the second coordination sphere of the catalyst. We inferred that the oxygen vacancies played a role in stabilization of the Pt sites, substrate diffusion to the Pt sites and stabilization of reaction intermediates. This work provides understanding on how nano-structuring of the support could be used to finetune the catalytic performance of SACs.

In **Chapter 5**, we show a generic way to understand the behaviour of NiOOH electrodes in oxidation reactions. Normally, the crystal phase and surroundings are controlled by the potential and the chemical environment and β -Ni(OH)₂, β -NiOOH and γ -NiOOH



co-exist at the surface. To study the reactivity of each component, we synthesized these nickel(oxy)hydroxides in a pure form and let them react individually with three typical alcohols. These simple stoichiometric reactions showed no reactivity for β -Ni(OH)₂, selective conversion to the corresponding aldehydes by using β -NiOOH, and overoxidation in the case of γ -NiOOH. In-depth mechanistic studies revealed that benzyl alcohol is oxidatively dehydrogenated to benzaldehyde by β -NiOOH via two consecutive hydrogen atom transfer steps via a carbon-centered benzyl alcohol radical.

Overall, this dissertation shows the importance of controlling second coordination sphere effects in single-atom catalysis, and several strategies to achieve this are described. By synthesizing well-defined catalysts and performing detailed catalytic studies, a thorough understanding of the structure-performance relationships was provided. I hope that this motivates others to pursue in this direction focussing on the critical steps towards a carbon-neutral society.