Towards single-atom catalysts to reduce noble metals in catalytic converters

Ceria (CeO₂) is a key component in automotive catalytic converters. It is often used as the top layer on the internal honeycomb structure. It holds the noble metal particles that perform the catalytic reactions (like CO and CH₄ oxidation) that clean the exhaust gases. As noble metals are scarce, we want to use as little of them as possible. This is why a lot of research is done into ‘single-atom’ catalysts. In this study we investigate single noble metal atoms dispersed in ceria. One of the findings is that the often used gold-ceria catalyst is active on much more atomic locations than was previously thought.

The synergy between ceria and dispersed metals can significantly improve the catalytic conversion. Despite many experimental studies, the active sites for CO and CH₄ oxidation at the metal-ceria interface are still under considerable debate. Within this thesis, we have elucidated some of the mechanisms for the CO and CH₄ oxidation at the metal-ceria interface, using the computational quantum mechanical modelling method ‘density functional theory’ (DFT) in conjunction with microkinetic modelling and thermodynamic stability analysis.

Firstly, we investigated the migration of oxygen vacancies (V₀) over the ceria CeO₂ surface. Herein, we identified the several pathways wherein V₀ diffusion is facilitated by polaron transport via phonon-electron coupling, resulting in an extremely low energy barrier of 0.18 eV. These results provide a deeper understanding into the mechanism of carrier drift in metal oxide semiconductors.

We explored the sintering of palladium atoms on CeO₂, which is an unwanted process as it reduces the surface area. We clarified the structure of palladium clusters on the most stable ceria (111) and showed how palladium (Pd) atoms or clusters on CeO₂ are prone to thermal sintering into larger clusters via Ostwald ripening and coalescence involving small clusters.

The most favorable structure of single-Pd atom embedded into CeO₂(111) was determined. Herein, the Pd atom adopts a square-planar coordination over the conventional octahedral coordination. We propose that CO can drive the Pd atoms to the top surface from the subsurface position. Furthermore, we showed that CO oxidation proceeds via a Mars-van Krevelen mechanism over this Pd atom.

The most active sites for CH₄ activation on the Pd-CeO₂ surfaces were studied. Furthermore, we developed a novel model wherein noble metal atoms aren’t merely added, but instead two Pd atoms substitute a single Ce lattice atom. This structure turned out to be both stable and reactive towards CH₄, due to the strong adsorption on the coordinatively unsaturated Pd ion (three-fold) as a σ-complex. This model readily explains the very high activity of Pd-CeO₂ solid solutions towards methane activation.

To elucidate the effect of the local topology on CO oxidation, we investigated the corresponding elementary reaction step at various sites at the Pd-CeO₂ interface. We found that the CO oxidation activity is critically effected by the charge states of the Pd atoms in Pd/PdO clusters supported on CeO₂. As the thermodynamic stability of the states of interest depends on the temperature, the temperature plays an important role as well and a slight change of the temperature can result in a shift of the dominant reaction mechanism.

Finally, we developed a methodology to examine the stability and catalytic activity of single metal atoms dispersed on CeO₂ in the presence of adsorbates such as CO. We found that platinum atoms have a comparable activity for CO oxidation as flat platinum facets. In contrast to the conventional
hypothesis that the corner sites at the Au-CeO₂ interface are the most active for CO oxidation, we found that the edge sites at the Au-CeO₂ interface as well as the single Au atoms on step-edges of CeO₂ are even more active towards CO oxidation.

Our findings provide a detailed insight into the fundamental factors underlying the activity of highly dispersed metals on CeO₂. Such insights are critical for understanding environmental catalysis at the metal-ceria interface in detail, but can also be used in general for the development of novel computational models and methodologies in heterogeneous catalysis.