Molecular dynamics simulation of water dynamics at the water/solid interface of ceria-supported Pt clusters

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Abstract: The present work is a theoretical analysis based on density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations investigating the physical and chemical properties of $H_2O/Pt_6/CeO_2$ material. Water-ceria interface exhibits increased H_2O dissociation and partial surface hydroxylation of the CeO_2 surface. The hydroxylated surface allows for fast proton diffusion along the water-ceria interface which promotes a transfer of OH molecules towards adsorbed Pt nanoparticle. The presence of water solvent induces charge reorganization at the Pt-ceria material creating new active centers for OH adsorption.

Keywords: Heterogeneous catalysis, Cerium Oxide, DFT+U.

1. Introduction

Ceria-based materials have important applications in heterogeneous catalysis as well as for renewable energy technologies such as fuel cells. Their catalytic ability is connected to their oxidation state and is significantly enhanced by contact with metal. For example metal-ceria-based catalysts are highly active in CO oxidation, NO reduction, water gas shift (WGS) reaction or methanol steam reforming.

Reactions important for heterogeneous catalysis as well as electrochemical reactions in fuel cells proceed in wet conditions, therefore understanding the mechanisms of water interaction with metal-ceria systems is essential. Water is, in fact, regularly present in ambient reaction conditions. Moreover, water-based approaches to heterogeneous catalysis in industrial chemistry are cheap and sustainable alternatives to expensive and toxic solvents. In all these cases, the structure and dynamics of the first water layers in contact with the solid surface profoundly impact on heterogeneous catalysis: The effects of moisture at the active sites range from increasing the catalytic activity by orders of magnitude, as for CO oxidation on oxide-supported Au nanoparticles, to deactivating the catalyst, as for methane combustion on metal−oxide catalysts.

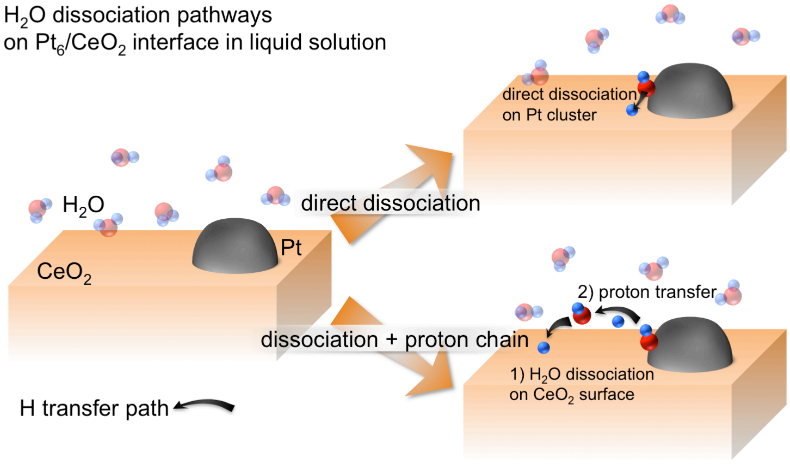
2. Theoretical

Our calculations are based on density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations. In order to correctly describe electronic state of reduced and oxidized forms of cerium oxides we employ DFT+U method, with Hubbard U applied to Ce f states in agreement with previous studies[1,2]. We focus our calculations on both gas phase (Pt_6/CeO_2) structure as well as the ceria supported Pt cluster in liquid solution ($H_2O/Pt_6/CeO_2$). We employ periodic boundary conditions on supercells consisting of three monolayers of ceria, Pt_6 cluster and 15 Å of vacuum empty or filled with 66 water molecules. We analyze the ground state properties, structures and H_2O adsorption and dissociation properties on ceria supported Pt cluster in gas and liquid phases as well as up to 60 ps of AIMD trajectories at 350 K.

3. Results and discussion

At the water-ceria interface, the H_2O molecules dissociate and form surface OH groups until equilibrium concentration is reached. The hydroxylated surface aids to the fast proton diffusion along the water-ceria interface similar to the Grotthus mechanism [3]. This effectively promotes a transfer of OH molecules towards adsorbed Pt nanoparticle, resulting in adsorption structures different from those in gas phase. In particular OH adsorption on top Pt atom is favored in the gas phase, while liquid phase prefers OH at the Pt-ceria interface. Water solvent and the polarization effects further promote charge transfer from the Pt cluster to ceria support upon water dissociation and OH adsorption on Pt cluster, causing the reduction of the ceria surface. Similar reduction was not observed in the gas phase.

Figure 1. Two distinct dissociation pathways of water molecules on $H_2O/Pt_6/CeO_2$ interface.



4. Conclusions

In this work we show that the Grotthus-like mechanism for H/OH transfer along ceria surface observed on H_2O/CeO_2 interface has importance for ceria supported Pt clusters. It allows for faster transport of OH molecules towards the active sites on the Pt cluster. The presence of water solvent induces charge reorganization at Pt-ceria material unlocking new stable active centers available for water adsorption/dissociation as well as promotes spillover of ad-species between the metal and oxide sites during wet catalysis.

References

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