

TiN based Single-Atom Catalyst in Aqueous Environment: a Step Towards the Experimental Complexity

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Significance and Relevance

This work shows that solvation significantly influences the interfacial behavior of TiN-based Single Atom Catalysts (SACs). Using ab initio molecular dynamics, we show that water strongly adsorbs on bare TiN, forming a structured interface. Introducing platinum into nitrogen or Titanium vacancies enhances water dissociation and alters interfacial charge distributions. These findings highlight the dynamic solvent effects on SAC reactivity, providing novel insights into Pt@TiN's catalytic potential and advancing the understanding of aqueous-phase SAC behavior in real-world applications.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; Multiscale modeling and advanced simulation aspects.

Preferred presentation: Poster

Introduction and Motivations

Catalysis has a key role in the green transition, it is fundamental in most of the industrial processes that we need to redefine in order to invert the trends in climate change. Single atom catalysts(1) are now emerging as a hot topic. They bridge homogeneous and heterogeneous catalysis by unifying their advantages, providing higher yield with lower metal loading. The basic problem related with these systems is that one needs simulation to approach their atomistic nature. In the modeling phase, many aspects are left behind, such as the role of unconventional intermediate and the impact of solvation.(2–5) In this work we present a study on solvation of TiN bare surface and the corresponding two Single Atom Catalysts one can form introducing Pt in either N vacancy or Ti vacancy. Platinum supported on TiN is a promising system. It is important to evaluate the dynamic effect of the solvent because its presence can change the shape and the structure of the active site and therefore its reactivity. To access this information we used ab-initio molecular dynamics.(4,6) This can lead to a deeper understanding of the Pt@TiN SACs in aqueous environment which can be explained by the interactions between the catalyst's surface and the solvent. With this work we are not only aiming at describing the behavior of a novel catalyst in aqueous environment, but we are also attempting to make a further step towards the experimental complexity.

Results and Discussion

Ab-initio molecular dynamics (AIMD) simulations of the TiN-water interface reveal significant differences in interfacial behavior depending on surface modifications. Starting from bare TiN, water molecules exhibit strong adsorption to surface titanium atoms, forming a stable hydration layer, as one can see in *Figure 1*. The effect of the Nitrogen comes into play when one considers dissociated water on the surface, we can see that a water molecule close to the surface can donate a proton to an exposed nitrogen generating an hydroxyl group. This interaction significantly affects the surface electronic properties by inducing local charge redistribution. When a Platinum atom is introduced into either a Nitrogen or Titanium vacancy, the interfacial chemistry changes. For the Pt@N-vacancy, platinum acts as a catalytic site, enhancing water dissociation and increasing the formation of hydroxyl species at the interface. Similarly, for the Pt@Ti-vacancy, the platinum atom promotes stronger interactions with water molecules, but the vacancy influences the charge distribution differently, affecting the dynamics of water reorientation and dissociation. These findings highlight the potential of Pt@TiN surfaces for applications in catalysis and electrochemical systems, as the introduction of Pt significantly modifies the interfacial structure and reactivity compared to bare TiN.





Figure 1: a) Snapshot of water/ Ti_xN_x interface during AIMD calculation; b) Snapshot of water/ $Pt@Ti_{x-1}N_x$ interface during AIMD calculation; c) Snapshot of water/ $Pt@Ti_xN_{x-1}$ interface during AIMD calculation.

References

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