Adsorption kinetics of small molecules on FePt metallic electrode by classical molecular dynamics simulation

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This study presents a time-resolved analysis of molecular adsorption at the FePt electrode-electrolyte interface during the methanol oxidation reaction (MOR) by using all-atom classical molecular dynamics simulations. While previous studies have mainly discussed adsorption behavior in terms of adsorption energy or static interfacial structures, the key innovation of this work is the introduction of **adsorption time** as a quantitative kinetic descriptor. This approach makes it possible to evaluate not only whether molecules adsorb on the catalyst surface, but also **how long they remain there** , thereby providing a dynamic perspective that is directly relevant to catalytic reactivity and surface poisoning.

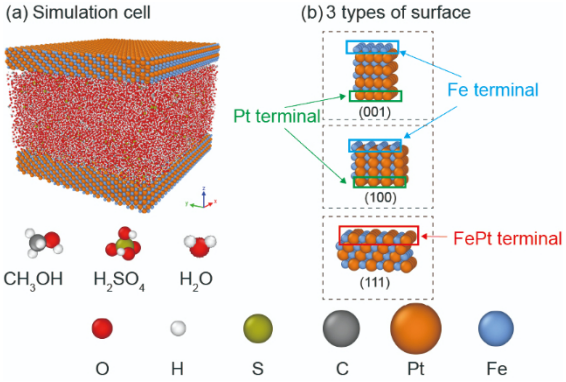
The simulations were performed for FePt surfaces with the (001), (100), and (111) facets in a mixed electrolyte containing methanol, sulfuric acid, and water. By statistically tracking the residence of molecules near the catalyst surface, the adsorption times of each species were quantitatively determined. The results show that methanol has the longest adsorption time, followed by sulfuric acid and then water. This trend reflects their different functional roles in MOR: methanol must remain at the interface long enough to undergo oxidation, sulfuric acid stabilizes the acidic interfacial environment, and water participates more dynamically in transport processes.

A major finding of this work is that adsorption behavior should be understood not only as a static structural property but also as a **time-dependent interfacial phenomenon** . In particular, the FePt(111) surface exhibits the strongest adsorption capacity for methanol, with an adsorption time about 18 ps longer than that on the FePt(001) surface. This result demonstrates that surface atomic arrangement strongly influences the kinetic residence of reactants, and suggests that adsorption time can serve as an effective descriptor for comparing catalytic interfaces with different facet structures.

In addition to the time-scale analysis, molecular orientation near the surface was examined to clarify how adsorption proceeds at the atomic level. The simulations reveal a two-layer interfacial mechanism. In the outer region, approximately 5 Å from the surface, methanol molecules preferentially approach the surface in a C-down configuration. In the inner region, within about 3 Å of the surface, the molecules tend to reorient into a nearly surface-parallel geometry. These two regions can be interpreted as a guiding layer and a reaction layer, respectively. This finding indicates that adsorption is not a single static event, but a dynamic process involving both residence time and structural reorganization.

The significance of this study lies in establishing a framework that connects **surface structure, adsorption time, and molecular orientation** in a unified manner. In particular, the time-resolved characterization of adsorption provides a new viewpoint beyond conventional energy-based discussions and offers a direct way to evaluate interfacial kinetics in complex electrochemical reactions. This work therefore provides a new design concept for FePt-based electrocatalysts and demonstrates the broader potential of adsorption-time analysis for understanding and optimizing catalytic interfaces.

Keywords:
Methanol oxidation reaction; Adsorption time; FePt; Molecular dynamics simulation; Interfacial adsorption



(a) MD model of the FePt electrode-electrolyte interface: a FePt slab at the bottom contacts a mixed methanol, sulfuric acid, and water electrolyte under periodic boundary conditions. (b) FePt (001), (100), and (111) surfaces show Pt-, Fe-, or mixed Fe-Pt terminations.