

Tailoring catalytic activity of MoS₂ catalyst through functionalization with Brønsted-acid ligands: A Computational and experimental study for enhanced Hydrogen Evolution Reaction in Alkaline Media

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Significance and Relevance

The hydrogen evolution reaction (HER) conducted in alkaline electrolytes represents a crucial breakthrough for the sustainable development of hydrogen production as a green fuel. In this context, the surface functionalization of chemically exfoliated MoS₂ flakes with strongly Brønsted-acid end-capped aryl fragments, such as sulfonic (Ar-SO₃H) acids,^{1,2} has been found to be surprisingly effective for HER in alkaline environments, where water dissociation typically acts as the bottleneck. DFT calculations, combined with ab initio molecular dynamics simulations (AIMD), reveal the mechanisms behind this unexpected but desirable behavior, demonstrating how this engineering-based functionalization creates an ideal surface microenvironment that efficiently promotes HER, with kinetics surprisingly independent of the acidic or basic nature of the electrolyte.

Preferred and 2nd choice for the topic: Oral Preferred presentation: **Short Oral**

Introduction and Motivations

The HER conducted in alkaline electrolytes could pave the way to produce hydrogen as a green fuel, as it enables the use of cost-effective and abundant transition metal-based catalysts.³ However, the slow water dissociation kinetics in alkaline environments still hinders its development.^{4,5}

Recent advances have highlighted the potential of transition metal dichalcogenides, such as MoS₂, as low-cost, effective alternatives for HER catalysis.⁶ However, molybdenum disulfide still faces challenges, including hydrophobicity and limited performance in alkaline conditions. Surprisingly, chemically exfoliated MoS₂ flakes functionalized with Brønsted-acid end-capped aryl groups, such as carboxylic (Ar-COO⁻) and sulfonic (Ar-SO₃⁻), have shown activity in HER under pH conditions dependent on the acid strength of the pendant group.⁷ With the goal of designing and developing more efficient catalysts for HER in alkaline environments, this unexpected behavior was rationalized through a detailed theoretical study. The electronic and steric properties of these modified surfaces, together with mechanistic insights into the water dissociation process and molecular dynamics simulations, helped define the kinetic framework and clarify the relationship between catalytic performance in alkaline environment and the chemical and electronic nature of the surface modification.

Results and Discussion

This study explores how sulfur vacancies (Vs) and surface functionalization with Brønsted-acid endcapped aryl fragment ligands impact the hydrogen evolution reaction (HER) activity of 1T-MoS₂-based catalysts. Specifically, we focus on the Volmer step in the HER process, which involves water adsorption on the catalyst surface and its subsequent dissociation to form H* and OH* species, a key ratedetermining step in alkaline media.⁸ We computed the adsorption energies of H₂O on both stoichiometric and sulfur-defective 1T-MoS₂ catalysts, including functionalized models (1T-MoS₂@2COO⁻ and 1T-MoS₂@2SO₃⁻). Our results show that water adsorption is thermodynamically unfavorable on stoichiometric 1T-MoS₂ due to repulsive interactions with sulfur atoms. In contrast, sulfur-defective catalysts exhibit significantly stronger water adsorption, especially when



functionalized with ligands that further stabilize the system by enhancing the exposure of molybdenum (Mo) sites, as observed with Ar-SO₃⁻.

Through nudged elastic band (NEB) calculations, we found that the presence and nature of the organic ligands significantly influence the overall reaction kinetics. The aromatic ligands, interacting with hydrogen atoms from the water molecules, guide the water toward the channel formed by neighboring ligands, facilitating its approach to the surface. Notably, the vacancy site interacts more readily with water only in the case of the Ar-SO₃⁻ ligand, which facilitates the subsequent dissociation step, in agreement with experimental data.

Additionally, ab initio molecular dynamics (AIMD) simulations confirmed that the wettability of the catalysts improves in the presence of sulfur vacancies. Specifically, $1T-MoS_2@Vs@2SO_3^-$ exhibited enhanced hydrophilicity, while $1T-MoS_2@Vs@2COO^-$ remained hydrophobic due to interactions between the vacancy and the ligand.

In conclusion, this study demonstrates that sulfur vacancies and surface functionalization with organic ligands significantly influence both water adsorption and dissociation, offering valuable insights for optimizing HER catalysts under alkaline conditions. Our findings suggest that tuning vacancy sites and ligand chemistry can enhance the catalytic efficiency of 1T-MoS₂-based materials, enabling efficient hydrogen production across a broad pH range and advancing the design of HER catalysts.



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