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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

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.1 However, the slow water dissociation kinetics in alkaline environments still hinders its development.2,3 Recent advances have highlighted the potential of transition metal dichalcogenides, such as MoS2, as low-cost, effective alternatives for HER catalysis.4 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 and sulfonic, have shown activity in HER under pH conditions dependent on the acid strength of the pendant group. 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. This study explores how sulfur vacancies (Vs) and surface functionalization with Brønsted-acid end- capped 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 rate- determining step in alkaline media. We computed the adsorption energies of H2O on both stoichiometric and sulfur-defective 1T-MoS2 catalysts, including functionalized models. 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. 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. 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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Primary author(s) : RITACCO, ida (Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy); Mr. SANTORIELLO, giuseppe (university of salerno); Dr. TUCI, giulia (Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 - 50019, Sesto F.no, Florence, Italy); Prof. GIAMBASTIANI, giuliano (Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 - 50019, Sesto F.no, Florence, Italy); Dr. FARNESI CAMELLONE, matteo (Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali (CNR-IOM), 34136 Trieste, Italy); Prof. CAPORASO , lucia (Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy)

Presenter(s) : RITACCO, ida (Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni

Paolo II 132, 84084 Fisciano, Salerno, Italy)