Research Project #14

Simulating Catalytic Interfaces for Chemical Hydrogen Storage (IET-3 & INW-1)

Background. Hydrogen plays a pivotal role as an energy carrier in the transition towards sustainable energy and industry systems [1]. Storage of hydrogen in either gas or liquid form is challenging and associated with high costs due to special requirements in container materials and storage conditions [2]. Liquid organic hydrogen carriers (LOHCs) are an attractive alternative to store hydrogen via chemical bonding in organic molecular structures, providing safe and economically feasible options for infrastructure compatibility [2,3]. During charging (hydrogenation), or discharging (dehydrogenation), hydrogen is incorporated into, or released from, the LOHC molecules via changes in process temperature and pressure at the surface of a catalyst material that is needed to achieve feasible hydrogenation/dehydrogenation rates. **New results show that the hydrogen turnover can be enhanced by applying an electrochemical potential at the catalyst surface**. It is assumed that the electrochemical environment modifies the interaction between catalyst and LOHC molecules and induces structural dynamics at the solid–liquid interface that facilitate the release of hydrogen. While the electrochemical LOHC activation has been demonstrated in experiments [4,5,6], fundamental understanding of the physicochemical interactions between LOHC molecules and electrified catalyst surfaces is still limited and systematic studies including theory and computation are required.

Goals. This Ph.D. project will model and simulate the interfacial interactions and phenomena between electrified platinum catalyst surfaces and liquid organic hydrogen carrier (LOHC) molecules, such as benzyltoluene. Using density functional theory (DFT) simulations, the hydrogenation and dehydrogenation mechanisms of LOHC molecules at the catalytic interface will be elucidated and the influence of the electrochemical environment on activation and degradation of LOHC molecules assessed. The theoretical investigations of this project at the *Institute of Energy Technologies: Theory and Computation of Energy Materials (IET-3)* will be closely aligned with experimental studies conducted simultaneously at the *Institute for a Sustainable Hydrogen Economy: Catalytic Interfaces for Chemical Hydrogen Storage (INW-1)*. Through combined theoretical and experimental assessment, fundamental understanding of the electric modulation effect in catalytic LOHC (de)hydrogenation will be achieved. The results of this project are expected to be of immediate relevance in chemical hydrogen storage by defining conditions for optimal process efficiency, selectivity, and durability.

Computational methods. Applying an electrochemical potential can tune the catalytic turnover during (de)hydrogenation of LOHC molecules in thermal catalytic processes [7]. We aim to reveal the fundamental principles underlying this effect using quantum-chemical DFT simulations for studying reaction pathways, intermediate molecular structures, and associated reaction barriers for the hydrogenation and dehydrogenation of LOHC molecules at electrified solid–liquid interfaces. The electrochemical environment will be simulated with the use of hybrid explicit/implicit solvation models in combination with advanced grand-canonical DFT schemes [8]. Concepts from chemical reactivity theory, such as frontier orbital analysis, will be used to identify descriptors for interfacial reactivity of LOHCs under electrochemical control and estimate the stability windows of LOHC molecules [9,10]. This workflow will not only provide essential insights for the design of optimized catalytic processes for hydrogen storage but also enable accelerated search for new LOHC candidates.

Tentative Work Plan. The Ph.D. student to be hired will first construct atomistic models of catalytic interfaces between a platinum catalyst surface and a liquid phase comprising LOHC molecules. The DFT framework will be used to predict the thermodynamic properties of the LOHC system. After validation of the simulation framework, the interfacial structures and transition states during LOHC (de)hydrogenation will be explored to gain insights into critical reaction steps and kinetic barriers. As an important advancement, the influence of the electrochemical reaction environment will be included by grand-canonical DFT and solvation methods and the impact of interface polarization on the catalytic reaction barriers will be analyzed. Finally, the stability properties of LOHC molecules at the charged catalyst surface will be determined, examining various possible decomposition pathways. The results from DFT simulations will be used to construct kinetic

rate models for the catalytic LOHC (de)hydrogenation on Pt as a function of external control variables. The Ph.D. student will engage in a close collaboration with experimentalists at INW-1 to validate and leverage results from simulation and modelling in real-world experiments and applications. To conduct the theoretical studies, the Ph.D. student will access and utilize the cutting-edge supercomputers installed on the campus of Forschungszentrum Jülich.

Outcomes. This Ph.D. project will deliver a simulation and modelling workflow to describe the processes of (de)hydrogenation of LOHC molecules at electrified catalytic interfaces. The project results will be disseminated through presentation at international conferences and publication in recognized scientific journals. The resultant understanding will set the theoretical foundation of utilizing electrochemical control for tuning molecular interactions at catalytic interfaces for hydrogen storage technologies. Forschungszentrum Jülich provides an ideal environment for this project with a strong integration of theoretical and experimental research for driving the energy transition.

Location of the HITEC Fellow	Forschungszentrum Jülich, Institute of Energy Technologies - Theory and Computation of Energy Materials (IET-3), Director: Prof. Dr. Michael Eikerling https://www.fz-juelich.de/en/iet/iet-3
Partners of the HITEC Project	Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy - Catalytic Interfaces for Chemical Hydrogen Storage (INW-1), Director: Prof. Dr. Hans-Georg Steinrück https://www.fz-juelich.de/de/inw/unsere-bereiche/inw-1
Specific **requirements**	M.Sc. in computational chemistry or physics. Knowledge in physical chemistry and prior experience with first principles-based simulation approaches.
For **project specific** questions please **contact**	Dr. Tobias Binninger, IET-3, t.binninger@fz-juelich.de Dr. JiMun Yoo, INW-1, j.yoo@fz-juelich.de

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