Unraveling the catalytic activity of FeCo alloys for ammonia decomposition via molecular dynamic simulations

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Significance and Relevance

This study establishes a robust, data-efficient framework for simulating catalytic processes under realistic conditions. This allowed us to study for the first time ammonia decomposition on FeCo via molecular dynamic (MD) simulations, revealing its reaction mechanism on the atomistic scale. Our simulations provide a rational explanation of the promoter effect of alloying, laying the foundation for a knowledge-based design of sustainable catalysts for H_2 production from ammonia.

Preferred and 2nd choice for the topic: H2 storage and transportation, hydrogen vectors
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

Ammonia is considered a potential hydrogen vector due to its high hydrogen content and ease of transportation and storage. However, on-site carbon-free hydrogen production requires the development of efficient methods of hydrogen extraction from ammonia. To this end, iron-based catalysts are widely employed in the thermocatalytic cracking of ammonia. Despite more than a century of studies, the cracking reaction steps are still not well characterized due to the operative temperature conditions (700-800 K).[1] Several DFT-based theoretical studies have elucidated the process at T=0 K. However, the resulting reaction profiles do not reflect the operando conditions and do not consider the dynamic behavior of the surface catalyst. In fact, surface dynamics play a critical role in heterogenous catalysis, explaining activity and long-term stability.[2] Our recent studies on ammonia decomposition on Fe at the operando temperature via machine learning (ML) based MD reveal the complexity of this process and the non-trivial effects of finite temperature description. For the dehydrogenation steps, we found a unique reaction mechanism over an ensemble of reaction pathways[3]. Furthermore, in combination with experiments, we rationalized the early stage of Fe(110) nitridation under ammonia decomposition[4]. In this study, we focus on FeCo alloy, which has recently been proposed as an alternative to Fe as a catalyst for ammonia decomposition, given its superior activity and stability[5]. Catalytic cracking of NH_3 on FeCo has never been studied at the atomistic level, even with static methods, given the combination of complexity and high computational cost. To do so, we developed a new protocol to construct potential MLs in a data-efficient manner, in addition to the use of advanced dynamics simulations. This allowed us to study the complete reaction at operating temperatures at a fraction of the cost, revealing the microscopic origin of the promoter effect of alloying iron with cobalt.

Materials and Methods

To build our interatomic ML-potential we employed a two-stage protocol to achieve data efficiency while delivering high accuracy along the reaction pathways. In the exploratory phase, uncertainty-aware flooding simulations were conducted using Gaussian Processes (GPs) to identify reactive configurations. Enhanced sampling techniques, such as On-the-Fly Probability Enhanced Sampling (OPES), facilitated the efficient exploration of transition states and metastable configurations under high-temperature conditions. The convergence phase utilized equivariant graph neural networks (GNNs) to consolidate the dataset and provide a uniformly accurate potential. A novel Data-Efficient Active Learning (DEAL) algorithm was developed to refine the training dataset further. DEAL integrates query-by-committee uncertainty estimates from GNNs with the assessment of local environment similarity via GPs to systematically select a subset of relevant configurations to be recalculated at the DFT level. This ensures accurate modeling of the potential energy surface with minimal demand for QM calculations.

Results and Discussion

Our workflow required approximately 1,000 DFT calculations per reaction step; a reduction of more than 20-fold compared to previous studies[3,4,6,7]. The DEAL approach systematically identified non-redundant configurations, ensuring uniform accuracy along reactive pathways while limiting the training set size.

Enhanced sampling simulations revealed complex, multi-channel reaction mechanisms for ammonia dehydrogenation, including $NH_3 \rightarrow NH_2 + H$, $NH_2 \rightarrow NH + H$, and $NH \rightarrow N + H$ steps. Free energy profiles were reconstructed with a sampling error of less than 20 meV, revealing an ensemble of transition states and reaction pathways for each with similar barriers but distinct geometric configurations. These simulations captured the dynamic evolution of FeCo active sites under operando conditions, offering microscopic insights into surface-catalyzed reactions.

More importantly, the ML-based simulations revealed the microscopic origin of the higher catalytic activity of the alloy with respect to the pure Fe catalyst, which is both a lowering in the activation energy of the rate-limiting step (nitrogen recombination) and a higher resistance to nitridation (Fig 1). The latter is originated from a combination of multiple aspects, revealing the necessity of a full dynamic description. The theoretical results were validated by experimental evidence of no bulk nitride formations in FeCo during ammonia decomposition, contrary to what was observed for Fe.

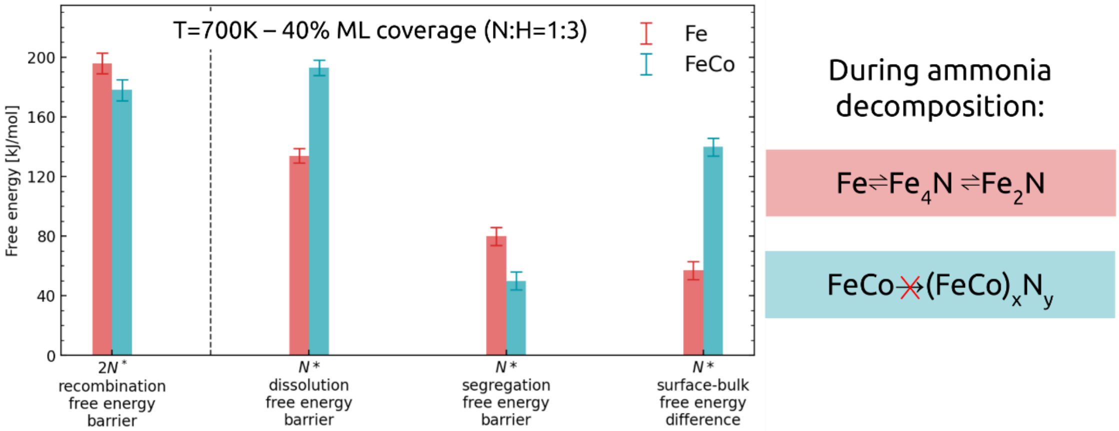

Figure 1 Free energies of the most relevant process on Fe and FeCo, obtained from MD simulations at 700K with a surface coverage of 40% (monolayer coverage, N to H ratio 1:3). On the left of the dotted line, the free energy barrier of the rate-limiting step while and on the right the free energy nitridation related process. These explain both the superior catalytic activity of FeCo with respect to Fe and its greater stability against nitridation.

References

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