

How does structural disorder impact heterogeneous catalysts?

Ammonia decomposition on ionic crystals

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Ammonia (NH_3) has recently attracted attention due to its potential as a hydrogen vector in a low-carbon economy. While hydrogen (H_2) has a low density and its transport and storage pose hard challenges, its conversion into NH_3 alleviates these limitations. The feasibility of H_2 production from NH_3 crucially hinges on the development of efficient catalysts. To this end, experiments on lithium imide (Li_2NH) and, later, on the imide-amide non stoichiometric compounds $\text{Li}_{2-x}(\text{NH}_2)_x(\text{NH})_{1-x}$ have evidenced highly promising catalytic properties. Progress in building machine learning-based reactive potentials with near-quantum accuracy and the use of enhanced sampling techniques to accelerate the occurrence of reactive events have recently enabled us to simulate the NH_3 decomposition on Li_2NH first, and then on $\text{Li}_{2-x}(\text{NH}_2)_x(\text{NH})_{1-x}$. We show here how Molecular Dynamics allows to elucidate the origin of the reported enhanced catalytic efficiency, providing atomic-scale insights into the mechanism and an estimate of the free energy profile for the rate limiting step (i.e. the formation of an N-N bond). We highlight the role played by enhanced fluctuations of the surface layers, with NH_2 groups featuring a larger mobility: catalytic reactions are favored, making the system flexible enough to accommodate and stabilize reactive intermediates. These results are also compared with latest developments concerning $\text{Li}_{14}\text{Cr}_2\text{N}_8\text{O}$, a new catalyst still under experimental characterization. While some fine details are different, due to the presence of metal atoms which influence charge transfers during the chemical reactions, also this Li-based catalyst can be understood within the larger framework of a new vision of heterogeneous catalysts. In such materials, reactive events are not just triggered in proximity of specific active sites, but it rather occurs a collective promotion of the chemical reaction due to the catalyst's disordered surface.