Revealing the role of surface disorder in H_2 desorption from metal surfaces via machine learning enhanced simulation

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Abstract

Understanding interactions between hydrogen and metal surfaces as well as the desorption of hydrogen is essential for hydrogen storage and heterogenous catalysis. Conventional computational methods such as the nudged elastic band together with the harmonic approximation are limited in capturing the dynamical behavior of surface atoms, especially at high coverages. With the assistance of machine learning interatomic potentials, we investigate the thermodynamic and kinetic aspects of associative desorption of H_2 from metal surfaces including Pt(111), Cu(111), and Fe(110) at different coverages. By employing enhanced sampling simulations, we have identified intrinsically different desorption kinetics on various metal surfaces, in which the significant entropic effect is observed on Pt(111) and Fe(110) at high coverages, while the desorption is enthalpically driven on Cu(111). The underlying mechanism is ascribed to entropy induced by the diffusion of surface hydrogen atoms. Characterized by the mean position variance, a profound entropy increase is identified, contributing to the decrease of the desorption free energy. Our results not only highlight the limitations of conventional static methods but also provide a new protocol to obtain accurate hydrogen desorption kinetics from metal surfaces.

Figures

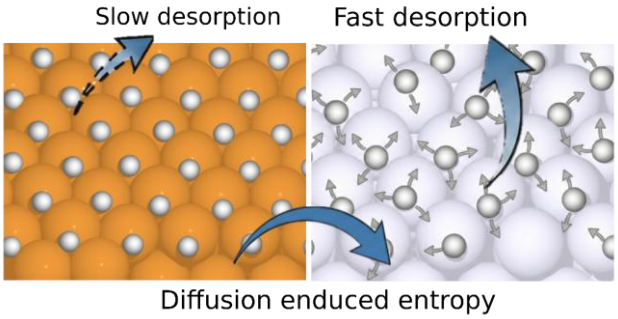

Figure 1. Schematic illustration of the desorption kinetics accelerated by diffusion induced entropy. More diffusive hydrogen atoms on Pt(111) promote the desorption at high coverage, while hydrogen atoms are more constrained on Cu(111). The brown, white, and grey circles represent Cu, Pt and H atoms, respectively.