Vacancy-Mediated Hydrogen Migration in MgH_2: A First-Principles Study of Quantum Tunneling and Isotope Effects

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Magnesium hydride (MgH_2) is one of the most efficient materials for solid-state hydrogen storage (7.6 wt%), but its high thermodynamic stability and slow internal diffusion hinder desorption. Defect engineering offers a way to overcome this limitation by modifying the local environment and creating favorable pathways for hydrogen migration in the lattice. In this work, we present a first-principles study of the effect of a positively charged hydrogen vacancy (V_H^+) on the nearest-neighbor hydrogen hop in MgH_2, comparing protium (H) and deuterium (D) in the thermal and quantum regimes. Using DFT calculations, we determine the migration barrier by coupling the NEB and DIMER methods, characterize the vibrational modes and the zero-point energy (ZPE) differences, and estimate the transmittance and hopping rate using a quantum tunneling model. Our results show that the V_H^+ defect enables a favorable pathway (with a barrier of 0.454 eV) where low-temperature migration is dominated by tunneling, with a pronounced kinetic isotope effect (KIE) favoring H. This study establishes a starting point for investigating the effect of vacancy concentration on the macroscopic desorption kinetics of MgH_2.

References

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