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Grand-canonical DFT investigation of transition-metal sulfide nanoalloys for electrochemical nitrogen reduction

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Ammonia is essential for agriculture and chemical manufacturing, but its industrial production via the Haber–Bosch process is highly energy-intensive and carbon demanding. The electrochemical nitrogen reduction reaction (NRR) provides a sustainable alternative under mild conditions but remains challenging due to the strong stability of the N≡N bond and competition from hydrogen evolution. Among potential catalysts, transition-metal sulfide nanoalloys are attractive thanks to their tunable electronic properties and surface reactivity.[1]
To explore their activity, we performed spin-polarized density functional theory (DFT) calculations using the PBE-dDsC functional with dispersion corrections to investigate stability, adsorption and reaction energetics. Electrochemical effects were included through grand-canonical DFT combined with an implicit solvation model (VASPsol) based on the linearized Poisson–Boltzmann equation.[2] A systematic screening of Co, Ni, and Fe sulfide hosts and their substitutional nanoalloys identified the most stable composition. We then analyzed its dominant (111) surface, mapping gas-phase adsorption and reaction pathways before incorporating potential-dependent energetics via GC-DFT.
The Fe-Co sulfide nanoalloy exhibits strong N_2 adsorption (-0.65 eV) at the Fe–Co bridge site, leading to clear N≡N bond elongation and efficient activation. Free-energy profiles reveal an associative-to-dissociative hybrid mechanism: the first protonation ($N_2 \rightarrow N_2H$) is mildly endergonic (0.31 eV), subsequent hydrogenations are exergonic, and NH_3 desorption is the potential-determining step (0.88 eV), which decreases by around 0.2 eV with explicit water coadsorption. Hydrogen adsorption is weak on the most active Fe sites (0.01 eV), indicating low HER activity and enhanced NRR selectivity. Including the applied potential through GC-DFT captures its effect on adsorption and reaction energetics, allowing us to define the operating potential window where NRR is thermodynamically favored over HER.
This work establishes the connection between nanoalloy composition, active sites, and reaction mechanism, providing detailed insights into N_2 activation and NH_3 formation and offering clear design guidelines for developing efficient and selective transition-metal sulfide electrocatalysts for sustainable ammonia synthesis.

References

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