Inverted Brønsted−Evans−Polanyi relation of N_2 dissociation originated from a bonding-dependent dynamic adsorption mechanism

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The search for efficient Haber-Bosch catalysts toward ammonia production under mild conditions is never ending, which is greatly limited by the Brønsted−Evans−Polanyi (BEP) relationship. Great efforts have been put into optimizing the BEP relations and achieving the Sabatier optimum, which requires the balance between the dissociation and hydrogenation of nitrogen. But challenges in this field inspire us that completely breaking the linear BEP relations is indeed the final target while out of sight in such a holy grail reaction. Here, based on the first-principles calculations, we discover a unique inverted BEP relation of N_2 dissociation to approach the kinetic optimum of ammonia synthesis on Fe-based single atom alloys. It is found that the adsorption characteristic of N-N transition states follows the ten-electron count rule, while that of the final states mimics the d-band model, which accounts for the inversion. Crystal Orbital Hamilton Populations (COHP) and Bader charge analysis further corroborate that a bonding-dependent adsorption mechanism lies at the root of the reverse BEP relation. Our finding not only paves the way for the milder Haber-Bosch process, but also promotes the explorations on breaking the linear BEP relations of the critical steps in various chemical reactions.