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Optimizing the NRR activity of single and double boron atom catalysts using a suitable support: a first principles investigation[†]

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Designing cost effective transition-metal free electrocatalysts for nitrogen fixation under ambient conditions is highly appealing from an industrial point of view. Using density functional theory calculations in combination with the computational hydrogen electrode model, we investigate the N₂ activation and reduction activity of ten different model catalysts obtained by supporting single and double boron atoms on five different substrates (viz. GaN, graphene, graphyne, MoS₂ and g-C₃N₄). Our results demonstrate that the single/double boron atom catalysts bind favourably on these substrates, leading to a considerable change in the electronic structure of these materials. The N₂ binding and activation results reveal that the substrate plays an important role by promoting the charge transfer from the single/double boron atom catalysts to the antibonding orbitals of *N2 to form strong B-N bonds and subsequently activate the inert $N \equiv N$ bond. Double boron atom catalysts supported on graphene, MoS₂ and g-C₃N₄ reveal very high binding energies of -2.38, -2.11 and -1.71 eV respectively, whereas single boron atom catalysts supported on graphene and $g-C_3N_4$ monolayers bind N₂ with very high binding energies of -1.45 and -2.38 eV, respectively. The N₂ binding on these catalysts is further explained by means of orbital projected density of states plots which reflect greater overlap between the N₂ and B states for the catalysts, which bind N₂ strongly. The simulated reaction pathways reveal that the single and double boron atom catalysts supported on g-C₃N₄ exhibit excellent catalytic activity with very low limiting potentials of -0.67 and -0.36 V, respectively, while simultaneously suppressing the HER. Thus, the current work provides important insights to advance the design of transition-metal free catalysts for electrochemical nitrogen fixation from an electronic structure point of view.

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1. Introduction

Ammonia is one of the most recurrently produced chemicals industrially with an annual production of almost 200 million tons.¹⁻³ About 80% of the ammonia produced is utilized in

the synthesis of nitrogen-based fertilizers and 20% for pharmaceuticals, explosives and other types of materials.4 In addition to these attributes, ammonia is also a profitable and ecofriendly hydrogen carrier bearing 17.6 w% hydrogen content in the liquid state in contrast to 12.5 w% in methanol.5-7 Conventionally, the demand for ammonia production on an industrial scale is achieved by the well-known Haber-Bosch process, which requires high temperature and pressure (300-500 °C and 150-300 atm).8 It is reported that the Haber-Bosch process utilizes ~2% of global energy and produces ~2% of CO2 annually at a global level. The energy intensive nature of the Haber-Bosch process and its adverse environmental impact necessities alternatives and sustainable approaches for ammonia synthesis. Among various approaches, electrocatalytic reduction of N2 into NH3 utilizing renewable energy sources has picked up pace. However, the rate of ammonia production via electrocatalytic processes is still relatively low mainly due to the scarcity of desirable electrocatalysts.9,10 To date, numerous electrocatalysts at different size regimes have been investigated for the NRR, which

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[†] Electronic supplementary information (ESI) available: Free energy profile for NRR on single and double atom catalysts along possible pathways (alternating, distal, enzymatic, and consecutive). Truncated side views of the optimized NRR intermediates on designed single and double boron atom catalysts along possible pathways (alternating, distal, enzymatic and consecutive). Calculation dissociation barrier and the AIMD simulation results for the $B_2\oplus g$ - C_3N_4 catalyst. Calculated adsorption free energies of the N_2 molecule and H atom on the single and double boron atoms adsorbed on GaN, graphene, g- C_3N_4 , MoS₂ and graphyne supports. Dissociation barrier for the double boron atom catalysts supported on the g- C_3N_4 monolayer as obtained from nudged elastic band calculations. Energy, ZPE, TS, G and ΔG of reaction steps of the NRR on single and double boron atom atalysts along alternating, distal, enzymatic and consecutive pathways. See DOI: https://doi.org/10.1039/d3cp02358c