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N_2 Activation and Reduction on Graphdiyne Supported Single, Double, and Triple boron Atom Catalysts: A First Principles Investigation.

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First principles simulations were carried to investigate the activity and selectivity of single, double, and triple boron atom catalysts supported on graphdiyne (GDY) monolayer for N_2 capture and reduction. Our results demonstrate that the double and triple boron atom catalysts bind and activate N_2 molecule effectively with significantly large binding energies of 1.23 and 1.16 eV respectively. In depth density of states analysis revealed that build-up of boron *p* states near the Fermi level promotes the N_2 binding on the double and triple boron atom catalysts leading to strong overlap between boron and nitrogen *p*-states. The free energy pathways for nitrogen reduction indicate very low limiting potentials of −0.41 and −0.58 V for the single and triple boron atom catalysts along the alternating pathways whereas the double boron atom catalyst is found to show a very high limiting potential of −3.29 V along the enzymatic pathway. Moreover, as compared to the single boron atom catalyst, the triple boron atom catalyst is found to be effective in suppressing the competitive hydrogen evolution reaction. Thus, we expect that the current work will lead to more investigation for design of transition-metal free catalysts for N_2 conversion to ammonia.

Introduction

Design of proficient catalysts for the electrochemical synthesis of ammonia from nitrogen and hydrogen under ambient conditions by green means is the need of hour for sustainable development.[1–5] Ammonia, recorded as the second highest synthetic chemical in the world, plays a key role in the synthesis of fertilizers, plastics, explosives, and dyes. Owing to its carbon free nature, high hydrogen storage,[6] high energy density and high transportation, it is considered as a green alternative energy carrier. However, the fixation of nitrogen into ammonia via Haber Bosch process[7,8] is an energy intensive process and is extremely challenging.[9,10] Therefore, it is highly desirable to switch to alternative approaches for sustainable NH_3 production under ambient conditions. Recently, electrochemical nitrogen reduction reaction (NRR) has shown great promise to convert N_2 to NH_3 in a sustainable and environmentally benign manner.[11–12]

Consequently, TM-based catalysts have drawn considerable attention due to their inherent ability to accept lone-pair electrons of N_2 using their empty or unoccupied orbitals, while simultaneously donating d-orbital electrons to the antibonding orbitals of N_2 thereby weakening N_2 bond and facilitating NRR.[13–23] Compared to bulk transition metal catalysts, very recently one to few atom catalysts of transition metals dispersed on suitable supports have opened up a new direction towards catalysing the NRR. For instance, single Fe atom catalysts immobilized on MoS_2 have been experimentally synthesized and explored as catalysts for NRR.[24] Combined experimental and theoretical investigation by Feng and co-workers[25] unveiled that Fe–N_4–C possesses unique electronic structure with localized electronic states near the Fermi level, leading to stronger interaction with N_2 and efficient NRR kinetics compared to other M–N_4–C centers. Many theoretical works have also followed to discern the NRR ability of single atom catalysts (SACs) on different supports. High throughput computational screening by Lui *et al.*[26] successfully aided in building a picture of NRR on transition-metal based SACs leading to an effective strategy for designing highly active and selective catalysts. Similarly, Xue *et al.*[27] screened 24 different single transition metals anchored on C_9N_4 substrate and found W@C_9N_4 as an excellent catalyst bearing extremely low limiting potential of −0.24 V. In addition, several transition-metal based SACs have been shown to possess profound activity in catalysing the NRR.[28–31] Following SACs, double[32–34] and triple atom[35,36] catalysts of transition metals have also been explored for catalysing the NRR. However, the high cost coupled with low selectivity and environmentally hazardous issues of traditional transition-metal catalysis demands alternative approaches to NRR.[29,37]

Towards this direction transition metal-free catalysts based on boron have recently received paramount importance for activation and reduction of small molecules such as N_2 and CO_2.[38–41] Braunschweig and co-workers[42] were the first to investigate the binding and reduction of N_2 by di-coordinate borylene, stimulating significant interest in boron-based catalysis for NRR. Since then, single atom species of boron incorporated in different two-dimensional frameworks have

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