Issue 31, 2023

From the journal
Physical Chemistry Chemical Physics

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

Anjumun Rasool,[a] Insha Anis,[a] Sajad Ahmad Bhat[a] and Manzoor Ahmad Dar[*a]

Author affiliations

Abstract

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 N_2 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, MoS_2 and $g\text{-}C_3N_4$). 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 N_2 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 $^*N_2$ to form strong B–N bonds and subsequently activate the inert $N\equiv N$ bond. Double boron atom catalysts supported on graphene, MoS_2 and $g\text{-}C_3N_4$ reveal very high binding energies of −1.26, −1.11 and −1.72 eV respectively, whereas single boron atom catalysts supported on graphene and $g\text{-}C_3N_4$ monolayers bind N_2 with very high binding energies of −1.45 and −1.38 eV, respectively. The N_2 binding on these catalysts is further explained by means of orbital projected density of states plots which reflect greater overlap between the N_2 and B states for the catalysts, which bind N_2 strongly. The simulated reaction pathways reveal that the single and double boron atom catalysts supported on $g\text{-}C_3N_4$ exhibit excellent catalytic activity with very low limiting potentials of −0.67 and −0.26 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.