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Article

Implications of the Pore Size of Graphitic Carbon Nitride Monolayers on the Selectivity of Dual-Boron Atom Catalysts for the Reduction of N_2 to Urea and Ammonia: A Computational Investigation

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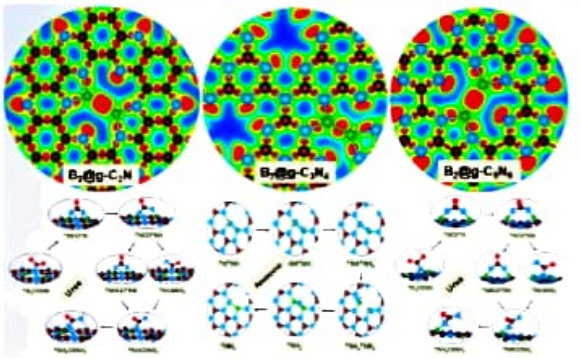
ABSTRACT: The formation of urea by electrocatalytic means remains a great challenge due to the lack of a suitable catalyst that is capable of not only activating inert N_2 and CO_2 molecules but also circumventing the complexity associated with subsequent reaction steps leading to urea formation. Herein, by means of comprehensive density functional theory simulations, we investigate the catalytic activity of highly stable transition-metal-free dual-boron atom-doped graphitic carbon-nitride monolayers with different pore sizes toward urea production under ambient conditions. As per the results, dual boron atoms impregnated in g-C_2N and g-C_6N_6 monolayers with large pore diameters can successfully activate the N_2 molecule and lead to the spontaneous formation of the *NCO*N intermediate, which is the most crucial step for urea formation via direct coupling of N_2 and CO_2. Interestingly, the B_2@g-C_2N and B_2@g-C_6N_6 favor urea production with low limiting potentials of −1.11 and −1.18 V compared to very high limiting potentials of −1.71 and −1.88 V, respectively, for ammonia synthesis, leading to an almost 100% Faradaic efficiency for urea formation over ammonia. The dual-boron doping in g-C_3N_4 with a smaller pore size depicts comparatively weaker N_2 adsorption than g-C_2N and g-C_6N_6 counterparts. Further, B_2@g-C_3N4 prefers ammonia formation at a very low limiting potential of −0.40 V compared to a very high limiting potential of −2.11 V for urea formation. Thus, our findings clearly highlight the critical role played by the pore size of carbon-nitride monolayers in tuning the reactivity and catalytic activity of dual-boron atom catalysts toward urea formation in a selective manner, thereby providing valuable guidance in exploring other highly efficient urea catalysts.



INTRODUCTION

Urea is one of prominent nitrogen-based fertilizers used in agriculture to promote the crop production and sustain the ever-growing human population on earth.[1−3] Apart from fertilizers, urea acts as a starting material for production of resins,[4] dermatological creams,[5] and other valuable chemicals.[6] As per recent reports, the urea market experienced tremendous growth with the demand of urea reaching 190 million tons in 2021, and an expected compound annual growth rate of 4.15% until 2035 poses a serious challenge to meet such elevated demands. Currently, urea synthesis at the industrial level is achieved by coupling NH_3 and CO_2 under extreme conditions of the temperature and pressure, requiring large amounts of energy and sophisticated equipment.[7−10] The NH_3 for urea synthesis is obtained artificially by means of the Haber−Bosch process wherein N_2 is reduced to NH_3 using an iron-based catalyst. However, the NH_3 synthesis via the Haber−Bosch process is still a highly energy-intensive process and leads to the emission of harmful gases such as CO_2, thereby causing the depletion of nonrenewable energy reserves and worsening the environment.[11] Thus, to meet such elevated demands, greener and economically viable routes need to be devised for the sustainable synthesis of urea.

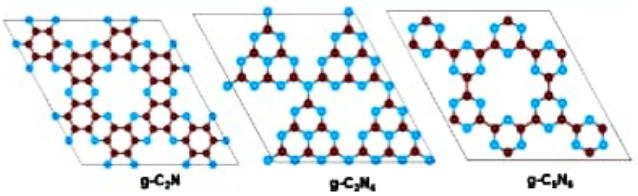


Figure 1. Top view of the optimized 2 × 2 monolayers of g-C_2N, g-C_3N_4, and g-C_6N_6 used for double-boron atom doping.

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