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Nickel single atom catalyst supported on the gallium nitride monolayer: first principles investigations on the decisive role of support in the electrocatalytic reduction of CO_2†

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Designing efficient and low cost electrocatalysts for the reduction of CO_2 to valuable chemicals is a sustainable way of mitigating and balancing its concentrations in the atmosphere which is essential for avoiding effects like climate change and global warming. Herein by means of systematic density functional theory simulations, we investigate the effect of support on the activity/selectivity of Ni based single atom catalyst (SAC) supported on GaN, MoS_2, Mo_2C, g-C_2N and graphyne monolayers towards CO_2 activation and reduction to different C_1 products. Our results reveal that the Ni SAC strongly binds on all the monolayer supports forming highly stable catalysts. The type of support plays a strong role in tuning the binding and activation of CO_2 with Ni SAC supported on GaN and MoS_2 monolayers showing the highest CO_2 binding energies. Rigorous and in-depth electronic structure analysis reveals that the CO_2 binding energy on these catalysts can be successfully rationalized in terms of electronic properties such as the d-band centre and integrated crystal orbital Hamilton populations. Moreover, the computed reaction pathways using the computational hydrogen electrode model indicate that the Ni SAC supported on the GaN monolayer can catalyse the CO_2 reduction to CH_3OH at a record low limiting potential of −0.28 V whereas the Ni SAC supported on the MoS_2 monolayer catalyses CO_2 reduction to HCOOH at a limiting potential of −0.42 V. Thus, our results show that the nature and type of support plays critical role in modulating the CO_2 reduction activity/selectivity on these catalysts and provide insightful guidance for effective catalyst design for CO_2 conversion to value added chemicals.

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Introduction

Excessive consumption of fossil fuels has resulted in accumulation of higher concentrations of CO_2 in the atmosphere, posing a serious challenge to sustainable development on earth.[1,2] The global estimates of CO_2 are expected to shoot up to 600 ppm by the end of this century, leading to serious environmental and health issues. Thus, mitigating the concentrations of CO_2 and converting it into useful chemicals has become an important research topic. Among the different approaches, electrocatalytic reduction of CO_2 utilizing renewable sources of energy holds great promise to solve the environmental issues related to large CO_2 emissions.[3] Towards this direction electrocatalysts based on elemental metals[4,5] have been tested already for CO_2 reduction.[6] However, the poor selectivity and low activity due to sluggish and complex reaction kinetics act as bottlenecks for reduction of CO_2 in these systems. To surmount these challenges and to attain improved CO_2 reduction, novel strategies must be developed for the design of modern electrocatalysts.

Recently, single metal atoms dispersed on suitable two-dimensional materials due to their intriguing electronic structure and geometric features have been found to be a promising ground for catalysing several electrocatalytic reactions.[7–11] This has motivated many researchers to investigate single atom catalysts (SACs) particularly based on Cu[12] and Ni[13] for CO_2 reduction to different value added chemicals.[14,15]

Ni-based single atom catalysts have recently garnered considerable interest for the CO_2RR due to their high catalytic efficiency, good selectivity and low overpotentials.[16,17] To this end, Ni single atoms dispersed over graphene were synthesised by Jiang *et al.*[18] and explored for CO_2RR activity. It was found that these Ni SACs are highly active for CO_2 conversion to CO

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† Electronic supplementary information (ESI) available: Calculated dissolution potentials, spin polarized orbital projected density of states (oPDOS) of Ni SACs supported on different monolayers, top view of CO_2 adsorbed on Ni SACs supported on g-C_2N, GaN, graphyne, Mo_2C and MoS_2, charge density difference plot of CO_2 adsorbed on Ni SACs supported on GaN, MoS_2, and Mo_2C monolayers, d-band center results and optimized structures of CO_2RR intermediates on Ni SACs supported on GaN, MoS_2 and Mo_2C, AIMD simulation of Ni SACs supported on GaN and energy, ZPE, TS and G of reaction steps of the CO_2RR on nickel SACs supported on GaN, MoS_2 and Mo_2C catalysts. See DOI: https://doi.org/10.1039/d3se00830d