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Understanding the activity of single atom catalysts for CO₂ reduction to C₂ products: A high throughput computational screening†

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The tunable electronic structure of the central metal atoms in single-atom catalysts (SACs) helps to control the adsorption energy of reactants and different reaction intermediates involved in multistep chemical processes. Although SACs have been recently proposed to be effective for electrochemical CO₂ reduction to C₁ products such as HCOOH, CH₃OH and CH₄, their role in catalysing CO₂ reduction to C₂ products involving more complex reaction pathways is largely unknown. Herein, by means of systematic first-principles simulations, we thoroughly evaluate a total of 27 transition metal-based SACs supported on a g-C₃N₄ monolayer for CO₂ reduction to C₂ products such as ethene and ethanol. Our results demonstrate that the SACs reveal limiting potential values ranging from −1.50 to −2.70 V and are capable of effectively suppressing the competitive hydrogen evolution reaction. The most effective candidates capable of reducing CO₂ to C₂ products were found to be Cu@C₃N₄, Cr@C₃N₄, and Fe@C₃N₄ exhibiting limiting potential values of −1.50, −2.23, and −2.27 V, respectively. We further find that the catalytic activities of all the SACs can be correlated with the adsorption free energy of one of the intermediate species (*COCH₂O) making it a suitable descriptor for evaluating their CO₂ reduction activity. Hence, this study provides key inputs regarding CO₂ conversion to C₂ products on SACs and is expected to lead to further explorations for future design of SACs for the formation of multicarbon products.

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Introduction

CO₂ reduction to valuable chemicals is highly appealing due to its potential for mitigating the dependence of mankind on non-renewable fossil resources in a much greener manner.^{1–3} CO₂ as a member of the carbon pool is expected to have great potential for becoming a suitable feedstock for generating C₁, C₂ and C₂₊ hydrocarbons.^{4,5} Despite recent advancements, the poor product selectivity coupled with a competing hydrogen evolution reaction (HER) makes the electrochemical CO₂RR highly challenging for practical applications on an industrial scale.⁶ These challenges necessitate a better understanding of the CO₂RR reaction mechanism as well as new design concepts for more effective electrocatalysis. Recently generation of C₁ products such as formic acid and carbon dioxide, which

involves transfer of 2 electrons and is kinetically more feasible has been the focus of electrocatalytic CO₂ reduction.⁷ However, from an application standpoint, the conversion of CO₂ to C₂ hydrocarbons is highly imperative because of the versatility of C₂ products in the chemical industry^{8–11} as well as their higher economic value per unit mass compared with C₁ counterparts.^{12,13} Also it is well known that the catalyst surface and operating circumstances such as temperature, pressure, and CO₂ concentration have a determining impact on the reaction pathways leading to the formation of C₂ hydrocarbons.¹⁴ Electrocatalytic reduction of CO₂ to C₂ hydrocarbons holds great promise and is expected to bring down the energy requirements for the all-important step of C-C coupling with the help of suitable catalysts in the presence of water using renewable energy under ambient conditions.^{15–18}

Despite holding great promise, the electrocatalytic conversion of CO₂ to C₂ hydrocarbons still remains highly challenging due to the non-availability of suitable catalysts^{19,20} which can catalyse C-C coupling under ordinary conditions in a cost effective manner. Thus, the design of new and out of the box catalysts with suitable electronic structure and enhanced performance for CO₂ reduction to C₂ hydrocarbons is of paramount importance and occupies top priority among

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† Electronic supplementary information (ESI) available: Reaction pathways for CO₂ reduction to C₂H₄ and C₂H₅OH, adsorption free energies of CO₂ reduction intermediates on SACs supported on the g-C₃N₄ monolayer, the linear correlation between adsorption free energy of intermediate species and that of *COCH₂O and predicted limiting potential values for Cr, Mn, Fe, Co, Cu, Tc, Rh, Pd, Re, Os and Ir-based SACs. See DOI: <https://doi.org/10.1039/d3nj00247k>