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CO2 Activation on Single-Atom Catalysts: Importance of the Supporting Matrix

CO2 Activation on Single-Atom Catalysts: Importance of the Supporting Matrix

Single-Atom Catalysts (SACs) are emerging as a new frontier in heterogeneous catalysis.1,2 They are made of metal atoms atomically dispersed on a supporting matrix. Computational chemistry offers the ability to study catalytic processes with atomic-level precision, enabling the rationalization and even prediction of system properties. Among various chemical processes of interest, the reduction of CO2 (CO2RR) into valuable chemicals has attracted considerable attention.3 The analogy between SACs and coordination chemistry compounds has highlighted the importance of the supporting matrix.4 In this work, we rationalize CO2 activation on SACs using Density Functional Theory (DFT) calculations. Our analysis focuses on nine transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) and three distinct support materials: nitrogen-doped graphene (4N-Gr), a gold surface (Au(111)), and titanium nitride (TiN), an emerging material with unique properties.5,6 Our findings show that CO2 activation on SACs is generally challenging, often requiring dual active centers. SACs based on 4N-Gr and Au(111) show limited ability to bind CO2 molecules. In contrast, TiN emerges as a highly promising support, effectively promoting CO2 activation. This capability stems from the formation of bidentate adducts involving both the dopant and a surface titanium atom of the matrix. Furthermore, TiN-based SACs demonstrate the ability to favour *CO*OH adduct formation (*indicates an adsorbed species) over*COOH or *OCHO during the first electrochemical reduction step, showcasing enhanced reactivity. These results underscore TiN as a robust support material for SACs in CO_2RR, offering new perspectives for efficient CO2 conversion.

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