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Local coordination effects on stability and reactivity of single-atom catalysts supported on graphene: Insights and implications

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Single-atom catalysts (SACs) are rapidly advancing across various application domains, particularly in electrocatalysis of diverse reactions, often occurring under challenging pH and electrode potential conditions [1]. Therefore, there is a critical need for a comprehensive atomic-level comprehension of the active sites under realistic electrochemical environments, recognizing that the state of SACs' active centres may be modified by the adsorption of spectator species. In this study, Density Functional Theory (DFT) is utilized to perform a thermodynamic analysis of SACs comprising metal atoms (Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, or Au) incorporated into N_4 moieties within graphene [2]. Various surface electrochemical processes on such SACs are examined, their Pourbaix diagrams are generated, and their activity, selectivity, and stability under operational conditions are deliberated. The DFT outcomes showcased in this research validate that the characteristics of metal sites in $M@N_4$-graphene SACs (M = Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, or Au) evolve depending on the operational electrode potential and pH. Concerning the impact of electrode potential, the investigated SACs demonstrate heightened thermodynamic stability of metal centres against dissolution compared to bulk metal phases. Stability rises along the periods of transition elements and decreases for coinage metals (Cu, Ag, Au). Regarding the influence of pH, while some metal centres (Mn, Co, Ni) are prone to dissolution in acidic media, others (Ru, Rh, Ir, Pd, Pt) are anticipated to remain stable across all pH levels. The localization of the primary catalytic activity of SACs is contingent upon the electronic configuration of the utilized metal via preferential adsorption of electrolyte species. Metals with an electron configuration of $d^{n\leq 8}$ are identified as the reactivity centres in $M@N_4$-graphene, serving as the preferred sites for all investigated adsorbates. The affinity of $M@N_4$-graphene SACs towards H_{ads} and their oxophilicity diminishes along the period as H_{ads} formation initiates at more negative potentials, while the potentials for OH_{ads} and O_{ads} deposition shift to higher potentials. Depending on the electrode potential, the examined metals can exist either bare or covered by H_{ads}, O_{ads}, or OH_{ads}. These afore mentioned spectator species can obstruct metal sites and prompt alterations in the SACs' electronic structure. The potential occurrence of such changes must be acknowledged when dealing with SACs, both in theoretical modelling and in interpreting the outcomes of their ex-situ characterization. Moreover, we conducted systematic replacements of nitrogen atoms with oxygen or sulphur atoms to achieve $M@O_xN_Y$-graphene and $M@S_xN_Y$-graphene SACs (x + y = 4) [3]. Our findings reveal that the local coordination significantly influences the electronic structure and reactivity towards hydrogen and oxygen species. However, stability is notably more impacted. By employing the concept of Pourbaix diagrams, we demonstrate that substituting nitrogen atoms in metal coordinating centres with O or S destabilizes the SACs against dissolution, while the metal centres become readily covered by O and OH, serving as additional ligands at high anodic potentials and elevated pH values. Therefore, it is imperative not only to consider local coordination concerning the SACs' activity but also to account for its effects on the speciation of SAC active centres under diverse potentials and pH conditions.

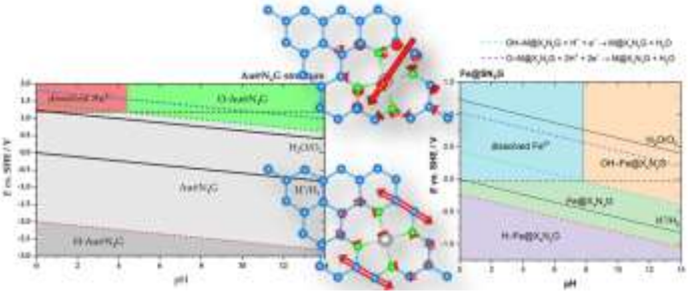

Figure 1. Pourbaix diagram for chosen $M@X_4G$ systems.

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