Single atom-alloy Ni-based catalysts design for bio-oil upgrading

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Biofuels production from biomass has been a worldwide interest in the hunt for sustainable fuels. A substantial hurdle in commercializing the conversion of biomass-derived feedstocks to *drop-in* hydrocarbons, or hydrogen, is designing a catalyst with high dehydrogenation activity, economic viability, long-term stability, and coke resistance. Attempting to refine the active-sites properties, single-atom alloy (SAA) catalysts have emerged as a pioneer class of heterogeneous catalysts with tuned surface properties. Herein, we employ descriptor-based density functional theory (DFT) calculations, combined with Microkinetic (MK) modelling and *ab initio* molecular dynamics (AIMD) simulations, to elucidate their role in upgrading modelled bio-oil compounds. The deoxygenation upgrading of phenolic O-moieties has been systematically explored on a wide range of SAA M-Ni-based catalysts (i.e., M=Pd, Pt, Cu, Co, Fe, Ru, Re, Rh, V, W, and Mo). Results reveal that the OH*-induced surface improve the SAA catalysts stability, designating their applicability under experimental deoxyeganton conditions. Moreover, the V-Ni catalyst showed the strongest adsorption energy (E_{Ads}) for all modelled O-moieties (**Figure1(a)**). This high E_{Ads} was elucidated to originate from the induced-electronic effect, evaluated by the lessened *d*-band shift (-0.84eV) in the partial density of states (PDOS) of V-Ni, relative to monometallic Ni at -1.3 eV (**Figure1(b)**). Linking the DFT Gibbs-free energy to MK analysis, the Mo-Ni site was shown to be the most active, both at low and high reaction temperatures. We then processed our investigation to conduct a DFT-screening of 26-doped SAA *bimetallic* and *trimetallic* Ni-based catalysts, combined with AIMD simulations, to access the dehydrogenation of acetic acid bio-oil towards green hydrogen (**Figure1(c)**). Results identified 3 *bimetallic* SAA M-Ni combinations, i.e., Cu-Ni, Zn-Ni, and Ag-Ni, with promising costing, stability, and dehydrogenation activity. Moreover, *trimetallic* dopants outperformed the *bimetallic* candidates, signifying 6 stable SAA catalysts with balanced adsorption and reduced coking susceptibility. The findings of this work enable the design of affordable, stable, and active SAA catalysts for multifunctional bio-oils upgrading reactions.

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References

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Figures

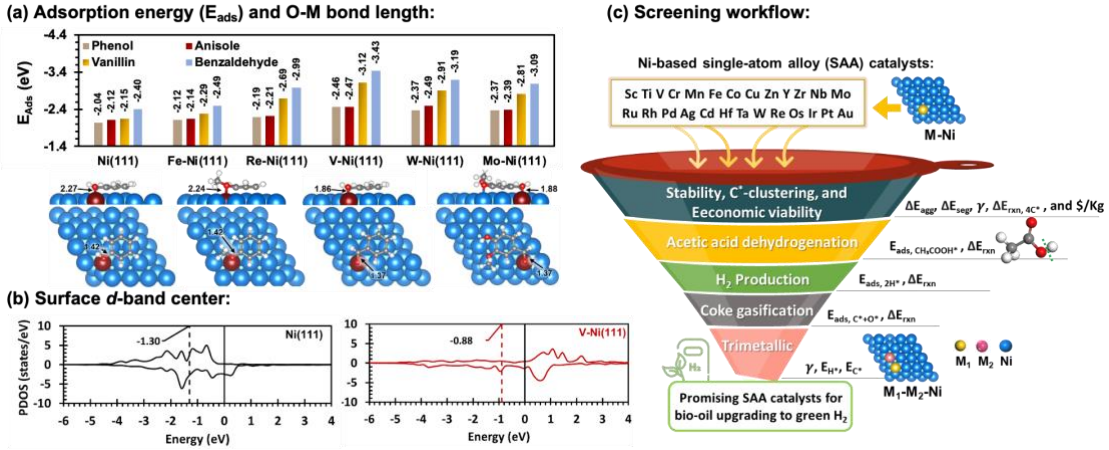

Figure 1: Adsorption energy (E_{ads}) of bio-oils on the M-Ni(111)-based surfaces and their configurations on V–Ni(111). Distances in Angstroms (Å). (b) Projected density of states (PDOS) of *d*-states for the Ni-M-Ni site. Solid black line: Fermi level. Dashed line: *d*-band center. (c) Hierarchical DFT descriptor-based assessment criteria for the discovery of promising SAA Ni-based catalysts for bio-oil upgrading to hydrogen.