

Electronic effects on nanoparticles encapsulated by MOFs: implications on catalyst modeling

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Introduction

To reduce the energy expenditures in chemical processes, it is necessary to develop artificial catalysts that can accelerate reactions very selectively. An emerging enzyme-inspired approach to achieve this is to enshroud catalytically active nanoparticles in metal-organic frameworks (MOFs) [1]. The MOF shell can in principle be tuned to force orientation of reactants in a particular way to make certain reaction pathways more favorable. However, optimizing the MOF and NP compositions for a desired reaction is a daunting task for experimentalists given the overwhelming number of possible combinations and the amount of work needed to synthesize any particular combination. Thus, high throughput computational screening (HTCS) is key for accelerated evaluation of possible MOF-NP combinations.

For HTCS, however, it is needed to first understand what the most crucial effects that need to be considered during screening are. Previous studies have decoupled steric effects in NP@MOFs systems from other factors [2-4] and provided insights on how these effects can affect reactivity. However, partly due to a then unknown NP/MOF interface structure, the role of electronic effects due to NP-MOF interactions on catalysts activity have yet to be studied. Leveraging recent insights on the interface structure [5], we study how the interaction between NP and ligands affects the NP electronic structure and, in turn, the formation energies of small chemical species relative to changes in NP composition. Further, via scaling relationships, we examine the uncertainty in the activities and selectivities associated with an encapsulated NP when disregarding MOF-driven electronic effects during computational screening.

Materials and Methods

Density functional theory (DFT) calculations were run in VASP-5.3.1. The PBE functional, PAW formalism and the D2 method were used to describe exchange correlation, core electrons and dispersion interactions, respectively. Charge transfer was analyzed using the Bader method. Descriptor-based microkinetic modeling was done using CATMAP.

Results and Discussion

The interaction of MOF ligands with catalytic surfaces was modeled in consistency with the recently postulated MOF/NP interface model [5] (Figure 1). We found that the interaction led to d-band center shifts away from the Fermi level of pure metals in the range 0.0-0.4. However, these shifts were less pronounced than those observed due to alloying. The formation energies of small chemical species that are regularly used as catalytic descriptors (C*, H₃C*, CO*, O*, HO*, N*, H*) on ligand-covered surfaces were generally found to be within 10 kJ/mol of the values found on bare surfaces. Exceptions due to electronic effects were encountered for C* on Au surfaces and OH* in Pt surfaces, where deviations around 50 kJ/mol were encountered due to the ligand-surface interaction.

The functionalization of the linker with electron donating (-CH₃ and -NH₂) or withdrawing (-F and -NO₂) groups was generally not found to have a major effect on formation energies of the studied species. When exceptions occurred, they were not due to changes in the catalyst electronic structure, but due to direct interactions of the species with the ligand functionality (e.g. hydrogen bonding of OH* with NH₂, which led to changes around 70 kJ/mol). Since such deviations were not found for O*, this shows that i) encapsulation of catalysts in MOFs may provide a way to break scaling relationships, ii) the chemistry of the pore needs to be included in high throughput screening procedures, even if the ligand-NP binding is not considered.

To quantify the effect of electronic effects on reaction rates, we considered the n-butanol oxidation microkinetic model developed in ref [4]. This model includes 26 reactions and is based on OH* and C* descriptors. The uncertainty was quantified by the region of activities and selectivities that are spanned by descriptor values with and without the presence of the ligand (boxes in Figure 1). For this reaction, we found that electronic effects can affect activities and selectivities by several orders of magnitude, but *general trends* identifying what NP compositions are more promising (and which ones are not at all) for encapsulation to engender catalysts that are active and/or selective for n-butanol formation seem to hold.

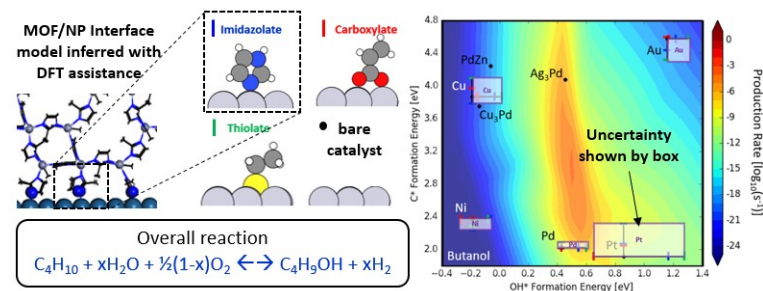


Figure 1. Microkinetic model results for 1-butanol formation activity in bare and encapsulated catalysts based on the model in ref [4].

Significance

The provided understanding of how electronic effects alter trends in high throughput screening will guide computational discovery procedures for MOF-encapsulated catalysts.

References

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