Structure−Activity Relationships that Identify Metal−Organic Framework Catalysts for Methane Activation

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Introduction

Recently, metal−organic frameworks (MOFs) have been extensively investigated for the catalytic upgrading of natural gas-derived light alkanes, due in part to their inherent ability to support well-defined, spatially isolated metal-oxo complexes [1]. The high degree of chemical and topological tunability of MOFs, enabled by the vast library of potential inorganic nodes and organic linkers, also makes them particularly well-suited for high-throughput computational screening studies. Despite the promise of computationally guided catalyst design via high-throughput density functional theory (DFT), modeling of MOFs for the partial oxidation of light alkanes has traditionally relied on small-scale, system-specific studies involving finite cluster models. Given the many thousands of MOFs that can be experimentally synthesized and the computational cost associated with modeling the large unit cells of most MOFs, there exists a significant need for robust design principles that would greatly accelerate the process of discovering MOF catalysts for the oxidation of strong C−H bonds.

Materials and Methods

Due to the spatially isolated nature of the transition metal active sites in the MOFs screened in this work, we consider the radical rebound mechanism shown in Figure 1a. In this mechanism, the overall reactivity is dictated by the ease of forming the metal-oxo active site and the reactivity of the metal-oxo species toward H-abstraction (steps 1 and 3 in Figure 1a). The thermodynamic favorability of forming the metal-oxo active site, ΔE_O, is defined as

$$\Delta E_O = E_{MOF-O} - E_{MOF} - \frac{1}{2} E_{O_2} \qquad (1)$$

and the energetic barrier for activating the C−H bond of methane, $E_{a,C-H}$, is computed using the universal H-affinity scaling relationship [2]. All DFT calculations are performed with the Vienna *ab initio* Simulation Package (VASP) via a publicly available high-throughput workflow that we developed [3]. The electron exchange-correlation is described by the PBE functional with Grimme's D3 dispersion correction scheme and Becke-Johnson damping. For all MOFs, a 520 eV plane-wave kinetic energy cutoff, a k-point grid consisting of 1000 k-points per atom, and a maximum force convergence criterion of 0.03 eV/Å are implemented.

Results and Discussion

In this work [4], we leverage advances in high-throughput periodic DFT to efficiently screen a diverse set of 60 MOFs with accessible metal sites for the catalytic conversion of methane to methanol. As a result of this screening study, we show that a single parameter – the active site formation energy – can be used to predict the reactivity toward oxidative C−H bond activation in addition to the thermodynamic stability of the metal-oxo active site (Figure 1b). We find this relationship to hold across all of the MOFs screened in this work, regardless of coordination environment, metal type, and degree of charge delocalization, so long as the bond orders of the remaining framework atoms are conserved. The need to conserve bond orders is an important constraint on the correlations but also demonstrates a route to intentionally break the scaling relationship to generate novel catalytic reactivity. Periodic trends with regards to active site stability and reactivity are observed, with later transition metals forming less thermodynamically favored but more reactive metal-oxo active sites for C−H activation. As a result of this screening study, the binding strength of the oxo species appears to be a powerful descriptor for assessing the ability of isolated metal sites in MOFs to oxidatively activate strong C−H bonds, especially for the purposes of rapidly identifying promising MOF candidates for further investigation.
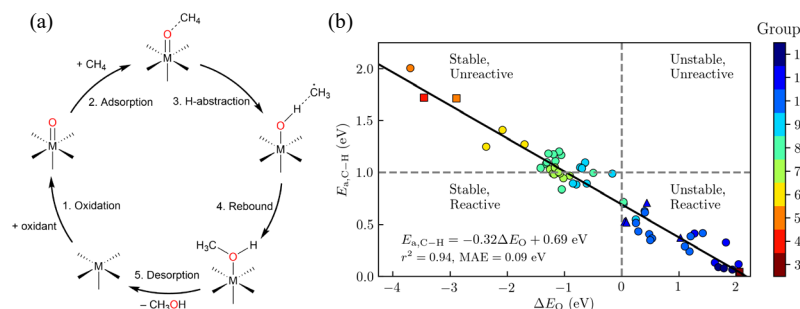

Figure 1. (a) Radical-rebound mechanism for the catalytic partial oxidation of methane to methanol. (b) Barrier for methane C−H activation, $E_{a,C-H}$, as a function of the active site formation energy, ΔE_O, for the screened MOFs. Symbol color refers to the metal group number. Symbol shape indicates the formal oxidation state of the metal site prior to oxidation as 1+ (▲), 2+ (●), or 3+ (■).

Significance

The current method to convert methane, the main component of natural gas, into methanol, a liquid fuel and feedstock for valuable chemical derivatives, is via a multi-step industrial process that involves the intermediate production of synthesis gas and requires harsh operating conditions. The discovery of a catalyst that can directly convert methane into methanol at moderate temperatures and pressures is therefore extremely desirable, although such a catalyst has yet to be fully realized. We anticipate that the structure−activity relationships reported in this work will enable greatly accelerated computational screening of MOFs that can activate methane at moderate reaction conditions. Such relationships will provide a set of promising criteria to determine which MOFs are worth investigating both computationally and experimentally.

References

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