Tailoring Labile Species in Metal-Organic Frameworks

Dr. Kentaro Kadota

Tailoring labile species in solid materials enables unique structures and functionalities. Robust metal oxides accommodate highly labile species, e.g. hydride (H^-), affording unprecedented reactivity. In contrast, incorporating labile species into molecular-based solids, including metal-organic frameworks (MOFs), has remained largely unexplored because MOF design has traditionally relied on stable components. Meanwhile, the structural tunability of MOFs offers an attractive platform for controlling the reactivity of labile species. Here, we have developed synthetic strategies to incorporate highly labile ions, metal clusters, and molecules into MOF lattices, enabling reactivity and functionality inaccessible to conventional materials.

1. Moisture-labile hydride-based ions

Borohydride (BH_4^-)-based solids, e.g. metal borohydrides, exhibit unique reactivity including hydrogen release and reducing ability. However, incorporating BH_4^- into MOFs has been challenging due to its moisture lability. By controlling polarization of BH_4^- through coordination interactions, we achieved the systematic synthesis of ten BH_4^--based MOFs. Dihydrogen bonding with linkers regulates BH_4^- reactivity, overcoming the conventional trade-off between moisture stability and high reactivity observed in metal borohydrides. Close spatial arrangement of BH_4^- allowed hydrogen release under milder conditions (*Chem. Sci.*, **2019**). Introducing accessible porous structures near BH_4^- enhanced solid-state CO_2 reduction reactivity by improving molecular diffusion (*Chem. Commun.*, **2020**). These results demonstrate precise control of BH_4^- reactivity through coordination-driven design.

2. Redox-labile iron clusters/ions

The cuboidal Fe_4S_4 cluster is a ubiquitous cofactor for electron transport in biological systems, yet its incorporation into artificial electroactive materials has been limited by redox lability. We addressed this challenge by synthesizing electrically conductive MOFs in which Fe_4S_4 clusters are covalently bridged through robust metal-carbon bonds, enabling efficient intercluster electronic communication within the MOF lattice (*Chem. Sci.,* **2023**). We further demonstrated that local redox lability induces redox-responsive assembly behavior of MOF lattices in solution. Fe^{2+}-based MOF nanosheets showed reversible aggregation and dispersion response to redox stimuli in colloidal suspensions (*Adv. Mater.*, **2024**). These results demonstrate MOFs as a platform for stabilizing and dynamically controlling redox-labile species across solid and solution phases.

3. Thermally-labile CO_2-derived molecules

Amines react with CO_2 to form carbamates that are thermally labile and readily release CO_2 upon heating, which has hindered their use as material building units. We synthesized thermally stable, porous carbamate-based MOFs as the first example of CO_2-derived MOFs (*J. Am. Chem. Soc.,* **2021**), in which carbamates are stabilized through coordination interactions. Direct conversion of diluted atmospheric CO_2 into MOFs was also achieved. This strategy was extended to other CO_2-derived molecules such as formate, enabling the synthesis of twenty CO_2-derived MOFs (*Acc. Chem. Res.*, **2024**; *J. Mater. Chem. A*, **2025**).

More recently, we adopted the opposite strategy of deliberately destabilizing otherwise stable species. Metal carbonates are reversible CO_2 carriers but require high temperatures for CO_2 release due to strong ionic bonding. By modulating the coordination environment of carbonate ions, we enabled CO_2 fixation and release at milder temperatures by carbonate-based MOFs (*J. Am. Chem. Soc.*, **2025**). Coexisting linkers reduce the coordination number of carbonate ions, thermally destabilizing them and enabling energy-efficient CO_2 circulation.

In summary, this work establishes a material design concept by developing synthetic strategies in which MOFs function as programmable coordination environments for controlling the reactivity and electronic states of labile species.