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Previews

Robust metal-organic framework catalysts for important reactions of industrial interest

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The stability of metal-organic frameworks remains a concern in catalysis under harsh conditions. In the December 2023 issue of *Matter*, Cao and coworkers developed a robust metal-borate-organic network stable up to 560°C that drives the selective oxidative dehydrogenation of propane to light olefins.

Propylene, ranked as the second most substantial petrochemical after ethylene, serves as a crucial upstream feedstock in the production of plastics, rubbers, and fibers. Propylene demand in 2022 was estimated at $104.05 billion and is anticipated to reach $150.54 billion by 2032.[1] Presently, propylene production predominantly relies on non-renewable chemical intermediates and energy-intensive processes, such as light naphtha steam cracking. However, these conventional procedures significantly depend on petroleum-based resources and contribute to serious carbon emissions and environmental problems. The oxidative dehydrogenation of propane (ODHP) arises as a viable alternative.[2] Propane, a primary component of natural gas, represents a more sustainable feedstock option. Compared to traditional techniques, ODHP has been recognized to be an important catalytic process of industrial interest and offers several advantages, such as potential reductions in carbon emissions, diminished energy consumption, and less reliance on oil-based resources. Nevertheless, the issue of poor selectivity caused by overoxidation of propane to CO_x remains a significant obstacle to the widespread application of ODHP.

Boron-based catalysts, such as hexagonal boron nitride (h-BN), have been adopted as effective catalysts for ODHP, demonstrating high selectivity toward light olefins (propylene and ethylene).[3,4] The development of catalysts with abundant boron sites is crucial for high ODHP activity. Meanwhile, the active sites responsible for ODHP often originate from the surface reconstruction of B-based catalysts, particularly involving B–O–O–B oligomers or B–O rings. The development of high-performance catalysts with well-defined structures is not only important for ODHP but also highly desirable for deciphering related catalytic mechanisms involved in this process.

Metal-organic frameworks (MOFs), composed of metal nodes and organic linkers through coordination bonds, exhibit great potential in catalysis.[5,6] MOFs with atomically precise and tailorable structures provide an ideal platform to elucidate the structure-performance relationship in catalysis.[7,8] Unfortunately, most of the MOF catalysts were employed for probe reactions under mild conditions in past years, partially due to the stability limitations. For the important reactions of industrial interest, such as Fischer-Tropsch synthesis, direct dehydrogenation of propane (DDHP), and ODHP, they are typically driven in a reduction/oxidation atmosphere at high temperatures. It is generally considered to be challenging for MOFs with relatively weak coordination bonds to catalyze these reactions;[9] related reports remain rare.

In the December 2023 issue of *Matter*, Cao and co-workers have presented the synthesis and characterization of a new MOF with a metal-borate-organic network named MBON-2.[10] MBON-2 was synthesized by zinc ions, imidazole, and boric acid in a water reaction medium. The resulting structure of MBON-2 features a pillared layered structure in which the layers consist of Zn nodes coordinated with BO_3 groups and exhibit a graphene-like six-membered ring. The layers are interconnected by imidazole linkers, thus forming a robust three-dimensional network (Figure 1A). This architecture ensures the exposure of high-density boron sites for ODHP. Furthermore, the magic angle spinning ^{11}B nuclear magnetic resonance (NMR) spectrum suggests that the boron sites exist in the form of trigonal planar BO_3 sites, which are considered the key active sites for ODHP. Apart from abundant catalytic sites, unexpectedly, MBON-2 possesses remarkable oxidation resistance under high temperatures with exceptional stability up to 560°C in an oxygen-rich atmosphere. The presence of rich boron sites and superior stability enables MBON-2's notable performance in ODHP, exhibiting a remarkable olefin selectivity of ~87.0% (C_3H_6 = 76.4%; C_2H_4 = 10.6%) while maintaining a propane conversion of 14.4% at 490°C.[10]

The ODHP experiments were performed in a fixed-bed microreactor. The conversion of propane began at

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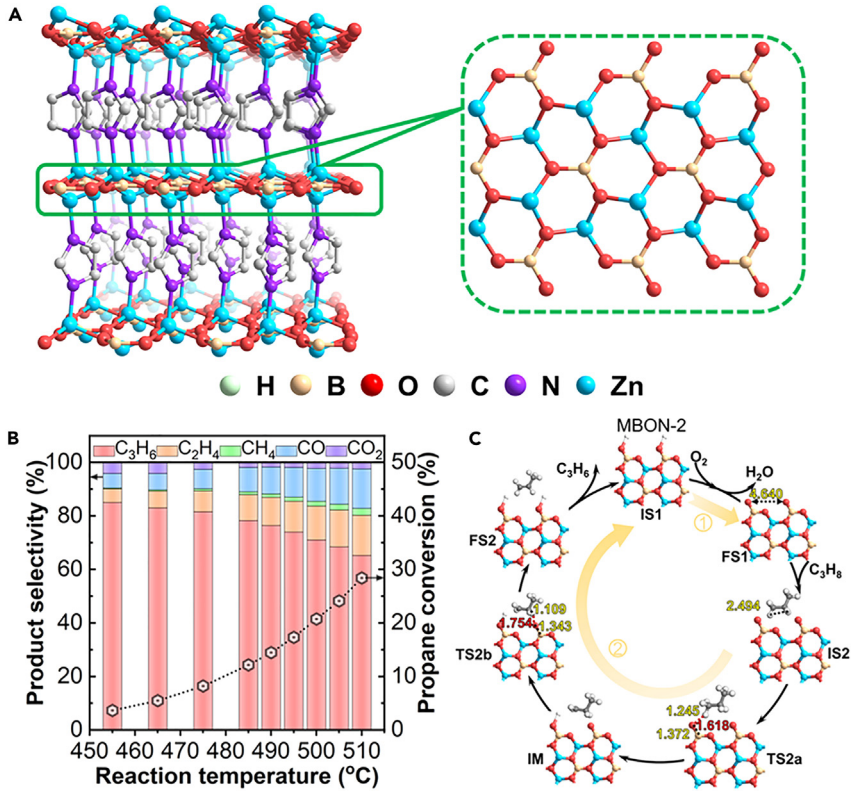

Figure 1. The structure of MBON-2, its catalytic performance, and involved mechanisms in the oxidative dehydrogenation of propane

(A) The pillared layered structure of MBON-2.[10]

(B) The catalytic performance of ODHP at different temperatures.

(C) Schematic reaction cycle of the ODHP reaction over MBON-2.

455°C. By increasing the temperature, the conversion of propane reached 28.4% at 510°C with the yield of light olefins exceeding 20% (Figure 1B). The selectivity in the conversion of propane to light olefins is comparable to that of commercial h-BN and significantly surpasses that of traditional V/SiO_2. Furthermore, the catalytic stability of MBON-2 for ODHP was assessed at 490°C. During 48 h of continuous operation, the conversion of propane remained at 14.5% ± 2% with selectivity for light olefins being ~87%. The carbon balance remained steady at 100% ± 3%, manifesting the absence of coke formation or MBON-2 decomposition. Further comprehensive characterizations suggested that MBON-2 held high crystallinity with largely preserved BO_3 sites despite minor generation of adverse BO_4 sites due to surface reconstruction.

Based on the *ex situ* and *in situ* results, MBON-2 possesses remarkable oxidation resistance under high temperatures and further proves that the dynamic switching between B–OH and B–O species is the key to driving the extraction of H atoms from C_3H_8. To elucidate the catalytic mechanism of MBON-2 for ODHP, the reaction pathways have been further investigated by density functional theory (DFT) calculations. Firstly, two adjacent B–OH sites in MBON-2 undergo dehydrogenation with the aid of oxygen to form active B–O sites, which is identified as the rate-determining step. Subsequently, each B–O site chemically adsorbs a propane molecule, accompanied by C–H activation, to generate a C_3H_7• intermediate. During this stage, the B–O site abstracts an H atom from propane and is converted to the initial B–OH state. Then, the C_3H_7• intermediate is captured by another neighboring B–O site, releasing a second H atom and forming an adsorbed propylene molecule. Ultimately, the desorption of the propylene molecule from the catalyst surface completes a reaction cycle (Figure 1C).

In summary, in the December 2023 issue of *Matter*, the authors have meticulously constructed a borate-coordinated framework, MBON-2, which exhibits exceptional stability and resistance to oxidation. The high density of boron sites within MBON-2 confers a notable advantage in ODHP for the production of light olefins. Through comprehensive characterization methodologies alongside theoretical calculations, the study elucidates the dynamic switch mechanism between B–OH and B–O sites within MBON-2 during propane conversion. This work offers valuable insights into the catalytic mechanism involved in ODHP, and more importantly, this is a highly worthwhile attempt and breakthrough by adopting MOFs for reactions of industrial interest under harsh conditions, in comparison with common MOF catalysis that has generally been performed below 300°C.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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Janus textile imparts unidirectional flow for the improved design of hygiene products

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Davidson and co-authors recently published a study wherein they develop a superhydrophobic Janus membrane by coating one side of a polyester mesh with ZnO tetrapods. They use the membrane to create a multi-layered menstrual hygiene prototype that effectively wicks fluids.

The incorporation of nanostructures in designing superhydrophobic surfaces has revolutionized the field of materials science and surface engineering. These nanostructures, often inspired by natural phenomena like the lotus leaf and water striders, create a unique surface topography, rendering them highly water-repellent.[1] The use of nanostructures provides a versatile platform for tailoring the wetting properties of surfaces, allowing for applications ranging from anti-icing, self-cleaning, and anti-fouling coatings to efficient water harvesting (Figure 1).[2] Using nanostructures in designing superhydrophobic surfaces represents a promising avenue for advancements in diverse fields, including aerospace, medical devices, and everyday consumer products, where water-repellent surfaces can significantly enhance performance and functionality.

Fabricating superhydrophobic nanostructured surfaces can range from the simple to the sophisticated, such as generating soot on a glass surface, etching and lithographic processes, phase separation, nanocrystal crystal growth on surfaces, chemical vapor deposition, and electrospinning, to name a few.[2–4] In a paper recently published in *iScience*, Davidson and his colleagues employ the electrospraying technique to coat one side of a polyester fabric with ZnO tetrapods, which results in a hierarchical micro- and nanoscale texture that conferred superhydrophobic properties to one side of the fabric while keeping the other side unfunctionalized and hydrophilic.[5] The researchers also use polydimethylsiloxane, which is chemically hydrophobic, to adhere the nanostructures to the mesh fabric. Although the crystal growth method has been successful in coating ZnO nanomaterials onto fabrics, ZnO nanostructures are generally hydrophilic and require further surface modification to exhibit superhydrophobicity.[3,4] Therefore, polydimethylsiloxane serves a dual purpose of adhering the ZnO tetrapods to the fabric and providing chemical hydrophobicity.

The authors explore using these polyester membranes with engineered wettability as a lining for traditional menstrual hygiene products. Surface modification

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