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From Single MOFs to Synergistic Systems: A Review on Flame-Retardant Applications

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Abstract. Metal-organic frameworks (MOFs) are porous crystalline materials whose metal nodes, organic linkers, and pore environments can be adjusted for a particular use. These features make them useful candidates for polymer flame retardancy. In a burning polymer, an MOF may contribute through more than one route: it can promote char in the condensed phase, adsorb volatile products, and help interrupt radical reactions in the gas phase. This review first outlines the structural features that control those effects. It then compares the reported performance of individual MOFs with that of MOF-based composite systems, including phosphorus-containing and nanomaterial-assisted formulations. The remaining limits, especially thermal stability, synthesis efficiency, and scale-up, are also considered. The aim is to connect MOF structure with the practical design of halogen-free polymer flame retardants.

Keywords: Metal-organic frameworks, Flame retardancy, Polymer, Synergistic modification, Char formation

1. Introduction

Metal-organic frameworks are assembled when metal ions or clusters coordinate with organic ligands to form an ordered porous solid. Their value in flame-retardant design comes from the fact that the metal node, ligand chemistry, and pore geometry can be varied together. The resulting materials may provide a physical barrier, catalyze carbonization, or capture smoke-forming species during polymer decomposition [1]. These functions are relevant to the search for halogen-free flame retardants, where the formulation must slow burning while limiting toxic or corrosive products [2].

Work on MOFs for polymer flame retardancy has moved from describing isolated material effects toward designing coordinated multi-component systems. The reported mechanisms include char-layer formation, gas-phase radical interception, adsorption, and cooperation between different fillers [3]. Metal centers can catalyze the conversion of polymer or ligand fragments into a protective residue, while the porous framework controls the passage of volatile products [4]. The usefulness of an MOF therefore depends on how these functions survive the temperature history and interact with the polymer matrix.

This review organizes the available evidence around three questions. What structural features give an MOF flame-retardant activity? How do single MOF fillers compare with phosphorus-, nitrogen-, or nanomaterial-assisted systems? Which material and process limits still prevent wider

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application? The discussion follows the mechanisms first, then the material classes and synergistic designs, and finally the challenges that must be solved for high-performance polymer formulations.

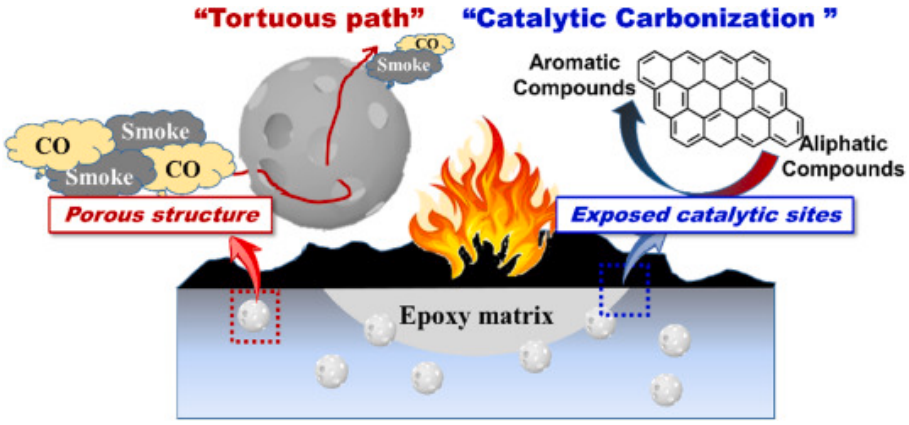

Figure 1. Proposed flame-retardant mechanism of an MOF-derived porous transition-metal oxide in epoxy resin (EP/C-ZrO2 sample) [3]

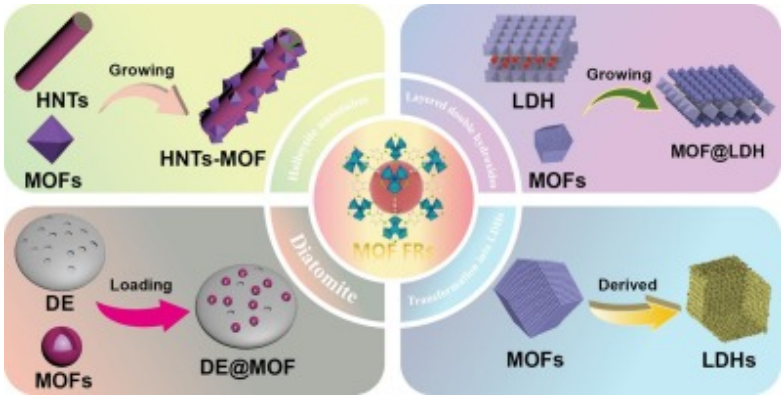

Figure 2. Synthesis routes for MOF-clay flame retardants: (a) halloysite nanotubes; (b) layered double hydroxide; (c) diatomite; (d) MOF-derived layered double hydroxide [5]

2. Basic characteristics and flame retardant mechanisms of MOFs

2.1. Basic characteristics

2.1.1. Structure and diversity

MOFs are built from repeating inorganic nodes and organic linkers, but the available choices for both components are unusually broad. Changing the metal identity or its coordination state changes the connectivity of the framework; changing the linker changes the pore shape, chemical environment, and thermal response. The same design freedom can therefore produce materials with very different flame-retardant behavior. Their ordered lattices are not only a structural motif: they determine which catalytic sites and transport pathways remain accessible during heating [6].

2.1.2. Porosity

Pore size and pore chemistry can be tuned through the choice of metal, linker, solvent, reaction time, and temperature [5]. This tunability matters because the pores must allow small molecules to move

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or be captured while the polymer is decomposing. Many MOFs also provide very large internal surface areas, sometimes reaching several thousand square meters per gram [7]. The combination of accessible surface and adjustable apertures creates sites for adsorption and for contact between volatile fragments and catalytic centers.

2.1.3. Thermal stability

The thermal stability of an MOF is controlled by both coordination chemistry and framework packing. Strong metal-ligand bonds can delay structural breakdown, while a regular network reduces the chance that hot gases will rapidly erode the solid [8]. Stability is not absolute, however. The linker may decompose before the inorganic skeleton, and the final behavior depends on the heating rate and the surrounding polymer. These details are important when a material is expected to protect a matrix throughout combustion.

2.2. Flame retardant mechanisms

2.2.1. Gas-phase mechanism

Gas-phase flame retardancy acts on the chain reactions that keep a flame alive. A filler may release non-combustible gases that dilute oxygen and fuel, or it may generate species that remove active radicals such as ·OH and H·. Either route reduces the probability that the combustion sequence will continue. The actual balance between dilution and radical quenching depends on the decomposition chemistry of the MOF and the polymer matrix.

For MOFs containing phosphorus or nitrogen, thermal decomposition can produce phosphorus radicals such as PO·. These species react with ·OH and H· and interrupt the radical cycle in the flame [9]. Ligand fragments may also rearrange into relatively inert gaseous products. Those products dilute the combustible atmosphere, although their contribution is governed by the ligand structure and the temperature at which it breaks down.

2.2.2. Condensed-phase mechanism

In the condensed phase, the flame retardant leaves a residue that separates the polymer from heat and oxygen. MOFs can contribute to this barrier in several ways. Heating may oxidize the metal node and create a metal-oxide layer. Ligand fragments can react with polymer intermediates and reduce the formation of small combustible molecules [9]. Phosphonic or nitrogen-containing ligands can additionally promote carbonization, with the metal or its oxide acting as a catalytic site. A continuous, thermally stable char layer is the practical result when these processes remain compatible with the polymer.

2.2.3. Synergistic mechanism

Synergy appears when the different functions of an MOF and a second flame-retardant component reinforce one another. Nitrogen-containing additives may release ammonia or other inert gases, which lower the concentration of oxygen and flammable volatiles. At the same time, their decomposition products can interact with MOF ligands and promote a more continuous char network. The metal nodes can catalyze carbonization, while the resulting residue slows heat transfer and mass transport. The combined system therefore couples gas dilution, radical control, barrier formation, and thermal insulation rather than relying on one mechanism alone [10].

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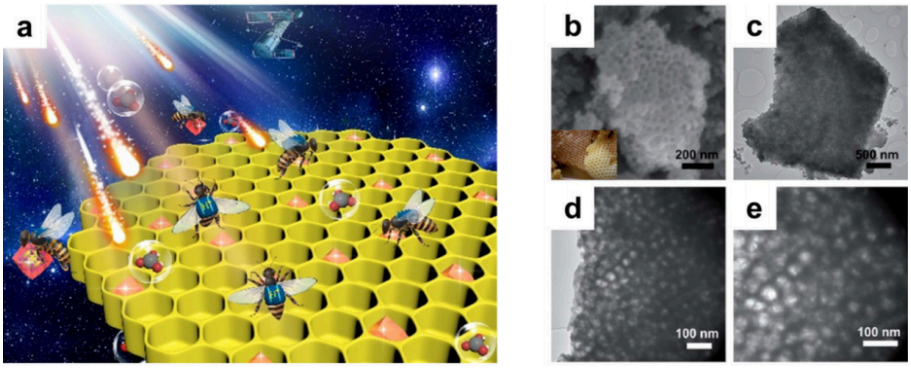

Figure 3. (a) Schematic porous structure of MOFs; (b-e) microscopic morphologies of MOFs

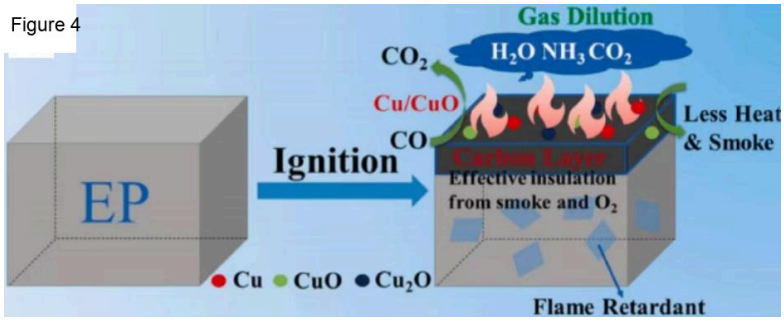

Figure 4. Schematic flame-retardant mechanism of a copper-based MOF in epoxy resin (EP)

3. Research progress on flame retardancy of MOFs

Research on polymer flame retardancy has gradually shifted from single-function MOFs to formulations that coordinate several mechanisms. The main strategies are to tune the structure of an individual MOF, to combine it with a phosphorus-based retardant, or to grow the MOF on another nanomaterial. The choice of route affects dispersion, thermal stability, char quality, and the amount of filler required. The following sections compare these routes through representative material families and reported performance.

3.1. Research on flame retardant modification of single MOFs materials

A single MOF can retard a flame through the joint action of its metal centers, organic ligands, and pores. Because those features vary substantially across frameworks, the resulting performance is material-specific. MIL, ZIF, and UiO families illustrate three different combinations of catalytic activity, pore structure, and thermal robustness.

3.1.1. MILs

Materials of the Institute Lavoisier (MILs) commonly use trivalent metal ions such as Fe^{3+}, Cr^{3+}, or Al^{3+} and carboxylic-acid ligands to build three-dimensional porous frameworks [11]. They combine high surface area with adjustable pores and good hydrothermal stability. MIL-53 is also known for a breathing response: its framework can contract or expand when temperature, pressure, or adsorption conditions change [12]. Such a response may alter how volatile products are retained during burning.

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The flame-retardant contribution of MILs can be viewed as a condensed-phase effect supported by adsorption. Metal centers promote polymer crosslinking and the formation of a compact char layer. Meanwhile, the pores can retain small combustible molecules, including alkanes and aromatic hydrocarbons, as the framework responds to heating. By slowing both residue breakdown and volatile transport, the material reduces the heat released to the gas phase.

Qian et al. [13] reported that MIL-53(Al) improved the flame resistance of polycarbonate without sacrificing tensile strength. The composite showed a 49.4% lower peak heat release rate and a 19.3% lower total heat release; its limiting oxygen index reached 30.5%, and the vertical burning test reached UL-94 V-0. These results support the value of MIL-based fillers, while the breathing behavior offers a structural explanation for the observed adsorption and barrier effects.

3.1.2. ZIFs

Zeolitic imidazolate frameworks (ZIFs) use imidazole linkers with transition-metal centers, most commonly Zn^{2+} or Co^{2+}. Their narrow pore distributions and zeolite-like topologies give them a large accessible surface area [14]. During burning, decomposition of the imidazole ligand can release N_2 and CO_2, which dilute flammable volatiles. A Zn-containing framework may also form ZnO in situ; the oxide can catalyze CO oxidation and thereby reduce toxic gas release [15].

The performance of pristine ZIFs is linked to their thermal resistance and their ability to catalyze carbonization. Wang et al. [16] combined epitaxial growth with phytic-acid treatment to modify a ZIF for epoxy resin. The resulting composite reduced heat release, total CO yield, and smoke emission. As the ZIF decomposed, the metal oxides promoted a dense char layer on the epoxy surface, which limited contact with heat and oxygen.

3.1.3. UiOs

UiO frameworks use Zr^{4+} nodes and dicarboxylic-acid ligands. Their high connectivity and defect tolerance allow the framework to retain much of its structure even after partial ligand loss. With decomposition temperatures above 400 °C, UiOs are attractive for flame-retardant systems that need a relatively stable inorganic scaffold [17].

UiO-66 is especially stable because of its high coordination number. Chen et al. [18] examined it as a single-component flame retardant in polystyrene and found the best performance at 5 wt%. At that loading, peak heat release rate fell by 26.8%, total heat release by 14.7%, and total smoke production by 35%. The char residue at 800 °C increased from 0.21% for neat PS to 4.16% for the composite. The data indicate that UiO-66 can improve fire safety while retaining the basic mechanical integrity of the matrix.

3.2. Synergistic flame retardancy of MOFs

The limitations of single-MOF fillers are equally clear. A relatively high loading may be needed, and one material rarely provides strong gas-phase and condensed-phase protection at the same time. Synergistic designs address this problem by pairing MOFs with phosphorus-based retardants, nanomaterials, or ligands that carry several flame-retardant elements.

3.2.1. Compounding with phosphorus-based retardants

Phosphorus-based retardants are widely used because they can promote char and intercept flame radicals. Used alone, however, they may produce a fragile residue or lose efficiency at high

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temperature. An MOF can provide catalytic metal sites for phosphorus-driven charring and pores that help retain reactive fragments. The combination is useful only when the two components are well dispersed and decompose over compatible temperature ranges.

Nie et al. [19] combined MOF-derived K-doped nickel phyllosilicate (K-NiPS) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) in epoxy resin. Decomposed DOPO generated phosphorus-containing radicals, including PO·, PO2·, and HPO·, which captured active ·H and ·OH species in the gas phase. K-NiPS slowed DOPO decomposition and extended the release of those radicals. In the condensed phase, reactions between K-NiPS and the phosphoric acids formed from DOPO produced a compact protective char. The formulation reached an LOI of 29.8% and a UL-94 V-0 rating.

3.2.2. Synergy with nanomaterials

Nanomaterial-assisted systems address two practical problems of MOF powders: agglomeration and loss of ligand stability at high temperature. Yu et al. [20] grew Ni-MOF nanosheets vertically on transition-metal carbide MXene to produce an MX@MOF-B hybrid (Figure 5). The layered MXene offered distributed nucleation sites and improved MOF dispersion. Interactions between the MOF ligands and MXene surface also protected the substrate against oxidation. At a loading of 2 wt%, the hybrid reduced pHRR by 42.5%, increased char residue by 787.1%, and improved the graphitization of the residue.

The MX@MOF-B example does not completely solve gas-phase radical capture or inert-gas release. Layered and core-shell architectures have therefore been explored as a second design route. Two-dimensional fillers can confine MOF nanocrystals on a surface or between layers, limiting self-agglomeration. Their physical barrier then works alongside MOF catalysis and gas-phase suppression, which explains why hybrid nanocomposites remain promising for polymer modification [21].

3.2.3. Multi-element integrated MOFs

Multi-element integrated MOFs place phosphorus, nitrogen, silicon, or related flame-retardant elements inside the framework or on its surface. A single integrated filler can consequently combine several mechanisms and avoid some of the dispersion problems associated with a loose multi-filler mixture.

Ligand functionalization introduces the relevant elements through the organic part of the framework. Elashker et al. [22] characterized MOF-71(Co) in nitrile rubber and found that 10 phr of the filler produced a more stable char and strong thermal insulation. The material also changed elongation, tensile strength, and hardness, and reduced the linear and mass ablation rates by 41% and 47.9%, respectively. Between 2 and 10 phr, the breathing framework improved flexibility and interfacial compatibility through van der Waals forces and hydrogen bonding. Non-combustible decomposition gases and cobalt-oxide-catalyzed char acted together to lower the ablation rate.

The attraction of an integrated framework is that structure and function are combined in one filler. Because the flame-retardant elements are linked to the MOF, migration is less likely to erase the benefit during long-term service. The trade-off is that synthesis and scale-up become more demanding, so the integrated design must be judged against its processing cost.

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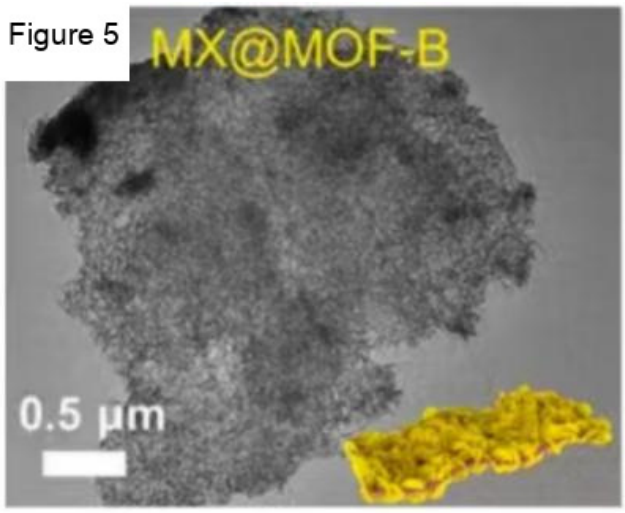

Figure 5. TEM morphology of the MX@MOF-B composite flame retardant

4. Challenges, trends and prospects of flame retardant MOFs

Industrial use still depends on two unresolved constraints. Many MOFs begin to decompose near 400 °C, below the temperature of an actual flame, and the framework may collapse before the protective effect is exhausted. Conventional synthesis can also require large solvent volumes, long reaction times, modest yields, and costly purification. These issues make a laboratory formulation difficult to reproduce at production scale.

Future work should improve both the molecular scaffold and the preparation route. Nitrogen-rich heterocyclic ligands and rigid backbones may raise the high-temperature stability of the framework. Solvent-free and microwave-assisted processes could reduce energy and solvent demand while shortening synthesis. The useful direction is not simply a more active MOF; it is a material whose performance, preparation, and environmental burden can be balanced.

5. Conclusion

MOFs offer a flexible platform for halogen-free polymer flame retardancy because their metal nodes, ligands, and pores can be designed together. Single frameworks can catalyze char, adsorb volatile products, or support gas-phase radical control. Composite systems extend these functions by pairing MOFs with phosphorus-based retardants, nanomaterials, or integrated multi-element ligands. The main barriers remain thermal durability, synthesis complexity, and scale-up. Progress will therefore depend on connecting framework design with green preparation and realistic processing conditions, rather than optimizing flame-retardant efficiency in isolation.

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