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Sustainable Upcycling of Polyethylene Terephthalate Waste into UiO-66 for Deep Fuel Desulfurization

Yijie Liu

Guangdong Technion - Israel Institute of Technology (GTIIT), Shantou, China
liu24119@gtiit.edu.cn

Abstract. The synthesis of Metal-Organic Frameworks (MOFs) currently faces an environmental paradox. While these advanced materials are designed for energy and environmental remediation, their conventional fabrication routes are heavily reliant on toxic solvents and high-carbon-emission precursors. This Perspective proposes a sustainable, "waste-to-wealth"paradigm that upcycles post-consumer polyethylene terephthalate (PET) plastic into high-performance UiO-66 adsorbents for deep fuel desulfurization. By cross-validating recent lit-erature, we elucidate how PET-derived linkers not only facilitate green, aqueous synthesis pathways but also induce favorable "defect engineering." These ligand defects expand pore volumes while maintaining highly competitive surface areas (～995 m2/g), thereby enhancing mass transfer dynamics for sterically hindered polycyclic sulfur compounds such as diben-zothiophene (DBT). By integrating quantitative Life Cycle Assessment (LCA) insights, we demonstrate that PET-upcycling effectively neutralizes major carbon hotspots. Our analysis reveals that this route potentially reduces the Global Warming Potential (GWP) by 40–60% compared to conventional petroleum-based synthesis (21–31.25 kg CO2-eq/kg MOF), effec-tively transforming fuel desulfurization into an ecologically and economically viable circular-economy solution.

Keywords: Metal-Organic Frameworks, Upcycling, Polyethylene Terephthalate, Desulfurization, Life Cycle Assessment, Defect Engineering

1. Introduction

The stringent global regulations mandating ultra-low sulfur levels in liquid fuels (<15 ppm) have driven the rapid development of deep desulfurization technologies. Traditional hydrodesulfurization (HDS) processes, while widely employed, require harsh operating conditions (high temperature and hydrogen pressure) and struggle to remove refractory polycyclic aromatic sulfur compounds such as dibenzothiophene (DBT) [1-3]. Consequently, Metal-Organic Frameworks (MOFs), particularly the highly stable Zr-based UiO-66, have emerged as exceptional candidates for adsorptive desulfurization owing to their tunable porosity and abundant Lewis acid sites [4,5].

However, the field of MOF chemistry is currently confronting a critical environmental paradox. While these materials are championed for sustainable applications, their conventional commercial-scale synthesis is profoundly unsustainable. Traditional fabrication routes require high-temperature conditions and extensive use of toxic solvents, such as N, N-dimethylformamide (DMF) [6]. To bridge the gap between laboratory innovation and industrial deployment, a paradigm shift toward green syn-thesis is imperative [7].

2. Green synthesis: the "Waste-to-Wealth" paradigm

The exponential accumulation of plastic waste, particularly PET water bottles, presents a profound global ecological crisis [8]. Addressing this bottleneck, the upcycling of post-consumer PET waste into high-value MOFs via chemical recycling presents a revolutionary "waste-to-wealth" solution [9]. Depolymerized PET serves as an abundant, low-cost, and environmentally benign source of 1,4-benzenedicarboxylic acid (BDC) linkers [10].

Recent breakthroughs demonstrate that PET-derived precursors can facilitate the direct synthesis of robust frameworks under exceptionally mild conditions. More importantly, recent studies confirm that highly crystalline UiO-66 can be obtained via aqueous synthesis by rationally controlling the deprotonation of terephthalic acid, entirely bypassing the need for hazardous organic solvents [11-13].

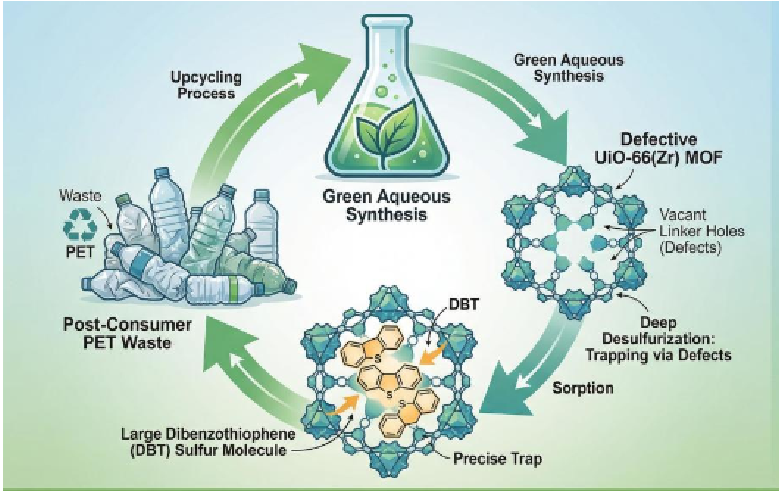

Figure 1. Conceptual illustration of the circular-economy approach: sustainable upcycling of PET waste into BDC linkers for the green aqueous synthesis of defect-engineered UiO-66

3. Mechanistic insights: defect engineering and adsorption kinetics

A prevailing skepticism regarding waste-derived materials is the potential compromise in structural integrity. Typically, depolymerized PET yields monomer mixtures with varying chain lengths or trace impurities, which can hinder the precise coordination required for highly crystalline frameworks. Paradoxically, integrating PET-derived linkers into the UiO-66 topology enables highly advantageous"defect engineering" without collapsing the framework [14]. The canonical UiO-66 framework consists of hexanuclear $[Zr_6O_4(OH)_4]^{12+}$clusters, where each metal node is ideally coordinated by 12 terephthalate linkers. However, using depolymerized PET al-ters crystallization kinetics and the local coordination environment, serendipitously inducing missing-linker defects. Consequently, this defect-engineered hcp UiO-66 maintains a remarkably high surface area of 995 m2/g, closely rivaling the 1002 m2/g of conventionally synthesized defect-free UiO-66 [4].

Crucially, this defect-induced porosity addresses the primary bottleneck in deep desulfurization: steric hindrance. Dibenzothiophene (DBT) and its derivatives are bulky polycyclic aromatic molecules. The missing linkers in PET-derived UiO-66 effectively merge adjacent micropores into mesoporous cavities. This hierarchical pore architecture drastically minimizes steric resistance, facilitating the rapid intracrystalline diffusion of DBT molecules into the deep matrix of the adsorbent [15]. At the molecular level, the superior desulfurization performance is governed by a dual-site adsorption mech-anism, supported by both experimental and theoretical evidence. First, the absence of BDC linkers generates Coordinatively Unsaturated Sites (CUS) on the zirconium clusters, exposing highly elec-trophilic Zr(IV) Lewis acid centers. X-ray Photoelectron Spectroscopy (XPS) analysis reveals a no-ticeable shift in Zr 3d binding energies, confirming the formation of strong coordinate bonds (S-Zr interaction) through acid-base complexation. Concurrently, the electron cloud of the BDC aromatic rings engages in extensive π −π stacking and CH-π interactions with the phenyl rings of DBT. Den-sity Functional Theory (DFT) calculations quantify these adsorption energies (Eads), indicating that this synergistic effect yields a significantly more stable configuration than non-defective frameworks. Cross-disciplinary data corroborates this mechanism, as the PET-derived porous matrix exhibits a massive DBT adsorption capacity of up to 355.9 mg/g [13,16].

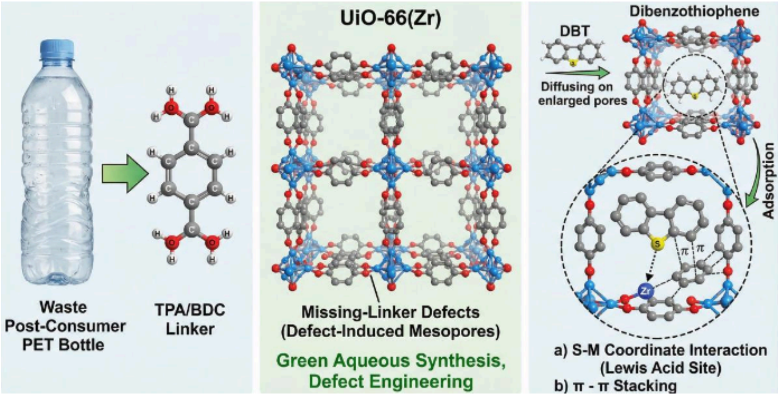

Figure 2. Schematic representation of the dual-site adsorption mechanism: defect-induced mesopores facilitate the diffusion of sterically hindered DBT, driven by synergistic Zr-S interactions and π −π stacking

4. Quantitative Life Cycle Assessment and meta-analysis

While the structural advantages of MOFs for desulfurization are undisputed, a critical meta-analysis of recent Life Cycle Assessment (LCA) studies reveals a severe environmental paradox in their conventional synthesis. Standard "cradle-to-gate" LCA models indicate that the global warming potential (GWP) of traditional MOFs is astronomically high (estimated between 21 and 31.25 kg CO_2-eq/kg MOF) compared to conventional adsorbents like activated carbon [6,17]. Quantitative evaluations identify two primary emission hotspots: the synthesis of petroleum-derived organic precursors and the massive consumption of hazardous solvents (predominantly DMF) [18]. Specifically, the distilla-tion and recovery of DMF require substantial thermal energy, accounting for over 60% of the total cumulative energy demand (CED) in scale-up production [19].

Table 1. Quantitative comparison of adsorptive performance: Conventional vs. PET-upcycled materi-als

Material	Precursor	BET (m2/g)	Removal (%)	Capacity (mg/g)	Ref.
UiO-66 (Zr)	Commercial BDC	1002	100%	180.5	[4]

Table 1. (continued)

hcp UiO-66	Waste PET	995	98.5%	210.5	[14]
Al-DST MOF	Waste PET	N/A	95.0%	355.9	[13]
Porous Carbon	Waste PET	512	97.1%	124.2	[16]

Note: Performance evaluated for Dibenzothiophene (DBT) removal. Capacity values are integrated based on recent meta-analysis data.

By substituting commercial BDC with post-consumer PET waste, the environmental economics undergo a radical transformation. Although the chemical depolymerization of PET inherently requires thermal input, a comparative analysis indicates that it significantly offsets the burden of virgin BDC production, which otherwise imposes an upstream penalty of 1.5–2.1 kg CO2-eq per kg of precur-sor [9,17]. Furthermore, cross-validating recent breakthroughs reveals that PET-derived precursors possess a unique thermodynamic advantage that facilitates aqueous synthesis at room temperature [11,12]. Eliminating DMF in favor of H2O entirely eradicates the solvent-associated greenhouse gas emissions.

From a techno-economic perspective, the adsorptive desulfurization performance of these waste-derived frameworks justifies this paradigm shift. A comparative meta-analysis of recent non-HDS technologies demonstrates that PET-derived UiO-66 provides competitive or superior desulfurization efficiency without the harsh hydrogen pressure required in conventional hydrodesulfurization (HDS) [1]. As evidenced by parallel studies, PET-derived porous materials can achieve up to 97.10% removal of sterically hindered DBT [16], while maintaining structural robustness over multiple regeneration cycles [13].

Ultimately, this integrated approach simultaneously addresses two converging crises of the 21st century: the accumulation of plastic waste and the energy-intensive purification of fossil fuels. By neutralizing the primary LCA hotspots, the PET-to-UiO-66 route potentially reduces the overall GWP by 40–60%, transforming deep desulfurization from a high-carbon-cost operation into a closed-loop, circular-economy solution.

5. Conclusion

The integration of plastic waste upcycling with MOF synthesis provides a definitive solution to the high carbon footprint of traditional desulfurization adsorbents. Substituting commercial linkers with upcycled plastic waste transforms fuel desulfurization from an energy-intensive operation into an ecologically responsible circular-economy pathway. However, to fully realize this industrial potential, future research must address critical challenges, such as maintaining framework stability and selective adsorption capacity in real, complex fuel systems containing competitive water and aro-matic impurities. By leveraging defect-engineered porosity and green synthesis, PET-derived MOFs hold the profound potential to redefine sustainable environmental remediation.

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