

INVITED REVIEW PAPER

Metal organic frameworks (MOFs): Current trends and challenges in control and management of air quality

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Abstract—Coordination polymers (CPs) are a unique class of polymers characterized by a molecular structure consisting of repeating metal centers linked by organic ligands in an infinite array connected through coordination bonding. In the last two decades, research interest in CPs, such as metal organic frameworks (MOFs), has grown rapidly owing to their exclusive advantageous properties (e.g., exceptionally high surface area, chemical and thermal stability, molecular functionality, porosity, electron mobility, thermal conductivity, and mechanical strength). In this study, we started with a basic question: *Why and how are coordination polymers special and how do they differ from other classes of polymers?* Next, we explored the value of unique and innovative CPs in line with the advent of design and synthesis approaches. We focused on the current trends and challenges of CPs/MOFs for application in the control and management of air quality. The intent of this review is to motivate development of CPs/MOFs that can be ultimately applied towards more efficient and effective technology as remediating and managing of the air quality. Ultimately, this review will help us open a new paradigm to pursue the future progress in polymers and materials science that targets specific applications in environmental engineering.

Keywords: Metal Organic Frameworks, Environmental Applications, Control and Management, Air Quality

INTRODUCTION

In both the 20th and 21st century, economic and industrial growth has been achieved at a rapid pace across the globe. Concurrently, the increasing world population has been accompanied by major environmental challenges, such as global climate change and the depletion and/or contamination of major natural resources, e.g., air, soil, and water [1-5]. There is a growing concern over the increase in air quality degradation (e.g., worsening of the air quality index (AQI)) as reflected in numerous scholarly and media reports. For instance, the Indian national capital area has experienced the worsening of the AQI over the past 20 years [6,7]. According to the AQI in the 2014-2015 (winter), the average number of days with severe pollution levels in Delhi was ~34%, which increased to 68% in the 2015-16 (winter). The PM₁₀ (2002 to 2015) and PM_{2.5} (2011 to 2015) trends, as reported by the Centre for Science and Environment [7], are shown in Fig. 1 [7]. In 2017, the average daily PM_{2.5} levels in Delhi, India (473 µg m⁻³) were more than twice those seen in

Beijing, China (227 µg m⁻³) [6-8]. The daily PM_{2.5} pollution level in New Delhi increased by 44% in 2017 compared to 2016 [6,7].

The key factors contributing to the degradation of air quality are the combined effects of increases in pollutant emissions from anthropogenic sources and atmospheric inversion of air masses. Although the former can be controlled to a varying degree, the latter is a rather uncontrollable component governed by meteorological and natural factors. The control of air quality issues due to increases in emissions of anthropogenic pollutants can be pursued through a strong political or administrative effort for regulation guided by scientific and technical advances. An older, but simple, option to reduce the impact of atmospheric pollutants is to enhance dispersion from their sources. For instance, installation of taller stacks at power stations was one of the foremost choices historically. Nevertheless, to pursue the goals of effective control on air quality, it is important to develop the actual techniques to regulate the emissions of pollutants. In line with such efforts, the United Nations and major OECD environmental protection agencies (e.g., U.S. EPA) have proposed a list of stringent strategies to restrict pollutant emissions from the important sources (e.g., industrial flue stacks and fossil fuel combustion) [6,7].

In response to worsening air quality, the development of inno-

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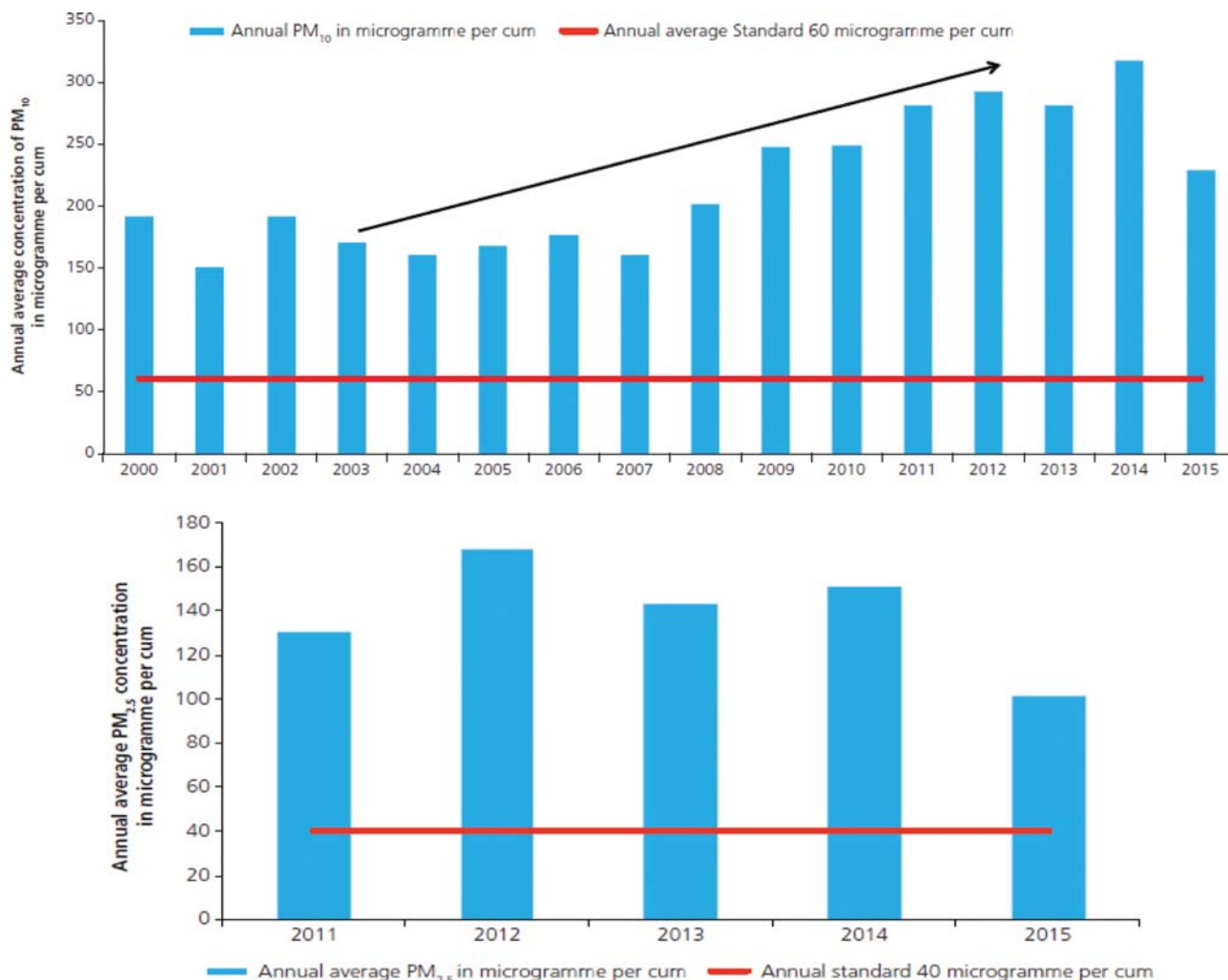


Fig. 1. Average annual concentration levels of PM₁₀ and P_{2.5} in Delhi, India (Central Pollution Control Board and Economic Survey of Delhi, 2014; Delhi Pollution Control Committee report to the Centre for Science and Environment (CSE: Delhi, India) [7].

vative control approaches has gained considerable interest among researchers as well as the general public for items such as filter materials for personal protective equipment (PPE: e.g., face masks) and air purifying systems for indoor environments. Flexible, robust, and readily available filter technology with diverse merits (e.g., broad working temperature range, high robustness, and high PM removal efficiency (especially for fine particle fractions)) has been researched so that advanced filters can be easily retrofitted into existing air quality management (AQM) systems, ship engine exhausts, and flue gas streams. The recent Global and Indian Air Purifier Market report is a detailed analysis of the on-going trends, opportunities/high growth areas, and market drivers for air purifiers to help stakeholders plan and align market strategies according to current and future market dynamics (Fig. 2) [8].

Efforts to resolve major environmental issues have increased the application of advanced functional materials/nanomaterials, such as metal organic frameworks (MOFs) or porous coordination polymers (PCPs) in diverse fields, e.g., storage, removal/separation, catalysis, water treatment, sensors, and waste management production [4,9]. To date, PCPs/MOFs belong to a special category of coordi-

nation polymers (CPs) that are among the most vibrant research directions in materials science domain. CPs were originally reported by Kluiber and Lewis in the 1960s [10-15]. Based on extensive research and development in material engineering, CPs with unique and notably porous natures have become 'special materials' in the 21st century. One of the most popularly used terms to describe 'CPs' in the current literature is MOFs [4,9,16,17]. According to the IUPAC recommendation, MOFs are presently classified as CPs with open framework structures containing potential voids [4,9-18]. Although most of the earlier investigations focused on common properties of MOFs, recent efforts have assessed many other properties that are still poorly understood [4,9-18].

To learn more about the diverse applicability of CPs for control and management of air quality, we first discuss their synthesis and basic properties and then critically review recent developments in CPs/MOFs toward AQM applications. Our review emphasizes how CPs/MOFs and their composite materials can contribute to future technological improvements for the control and management of air quality. Finally, we highlight the main challenges to fully recognize the potential of CPs/MOFs in the diverse fields of AQM applica-

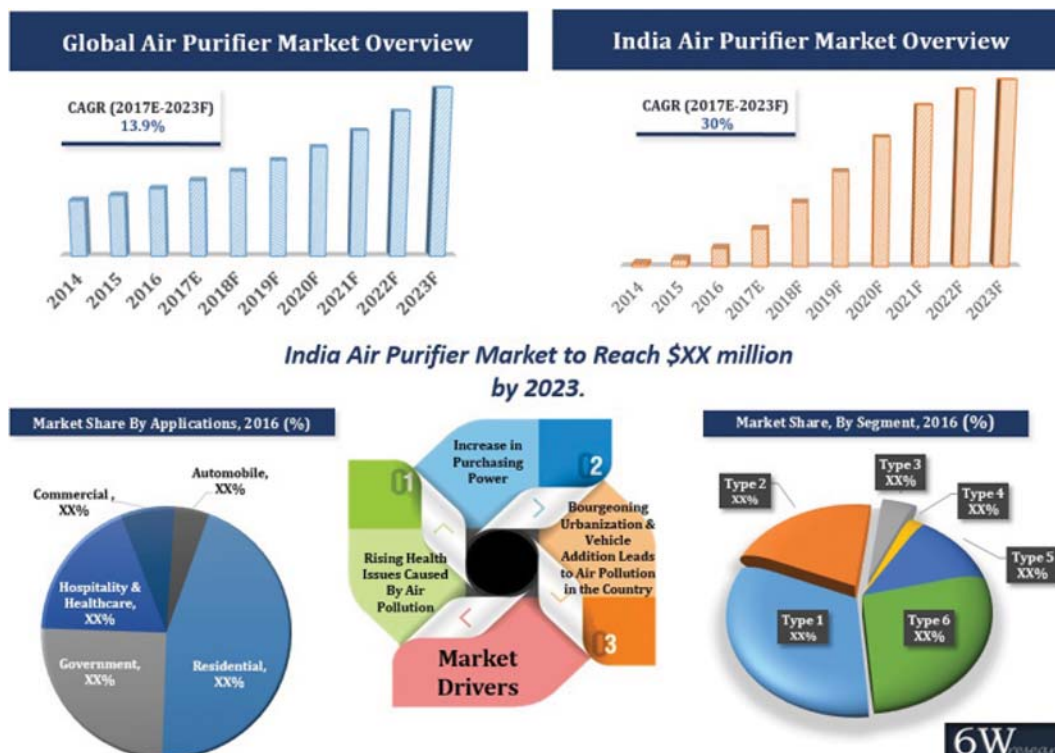


Fig. 2. Summary Report of the India Air Purifier Market: Predicted growth at a compound annual growth rate (CAGR) of 30% during 2017-2023. The market for air purifiers in India is highly cyclic, where the major demand comes around in winters due to the presence of smog. The trend is likely to continue for the next 2-3 years as well [8].

tions from sensing and contaminants removal to catalysis and adsorption.

PREREQUISITES OF MOFs FOR CONTROL AND MANAGEMENT OF AIR QUALITY

1. Synthesis and Structure

The design of PCPs/MOFs is mainly tunable through the choice of metal ions (e.g., alkali salt, alkaline-earth, transition, main group, and rare-earth elements) and the choice of organic linkers (e.g., mono-, di-, tri-, and tetra carboxylic aromatic acids, bipyridines, and polyazaheterocycles (imidazoles, triazoles, tetrazoles, pyrimidines, pyrazines, etc.) and their derivatives [19-24]. Solvothermal/hydrothermal (transformation of electric energy into heat as energy source) and non-solvothermal/hydrothermal synthesis techniques (mechanical, electrochemical, or ultrasound radiation as energy source) serve as the main drivers in the nucleation and crystallization approach [19-27].

Through the arrangements of metal ions and organic linkers, numerous possibilities have been sought in the synthesis/structural evolution of PCPs/MOFs with projected topology and dimensions. PCPs or MOFs are grouped into the fourth generation of polymers. Purposely designed CPs/MOFs technology has excellent features with respect to its crystal structure, topology, structural integrity, flexibility, stability, robustness, dynamics, post synthetic modifications (PSM), and non-permanent porosity in association with inseparable host-guest dependence (e.g., MOFs containing charged frame-

works with pores filled by counter anions) (Fig. 3) [13,28,29]. With the advent of novel PCPs/MOFs, their potential environmental applications have been greatly extended (Fig. 4) [30]. For example, purposely-designed CPs/MOFs technology can be applied in residential and industrial environments for AQM purposes (e.g., pipe filtration, baghouse dust collection, and inlet barrier filtration for vehicle or aircraft engine systems).

2. Properties and Functions of CPs/MOFs

In the past decades, properties of MOFs have been determined by synthesis techniques and modification approaches (e.g., atomic doping or substitution, particle size control, and surface modification within the stability limits of the underlying structures). Research efforts have been directed toward precise control of the structure and associated properties of MOFs, substantially improving the properties of CPs/MOFs and their composite materials. The most important and attractive properties of MOFs include their large surface area (e.g., 100 to $>6,000 \text{ m}^2 \text{ g}^{-1}$), well-defined pore size (e.g., 0.2 to 3.8 nm), low densities (e.g., 1.00 to 0.09 g cm^{-3}), selective uptake of small molecules, and excellent optical/magnetic responses to the inclusion of guest molecules [31-40]. These properties make MOFs excellent material for diverse industrial/environmental applications. In addition, other possibilities for innovative applications have been identified based on a better understanding of the subtleties in the reticulation process [31-40].

Some essential properties of MOFs (including crystallite integrity, large chemical energies, and low carbon content) have already been covered in a comprehensive manner (Fig. 5). Likewise, many

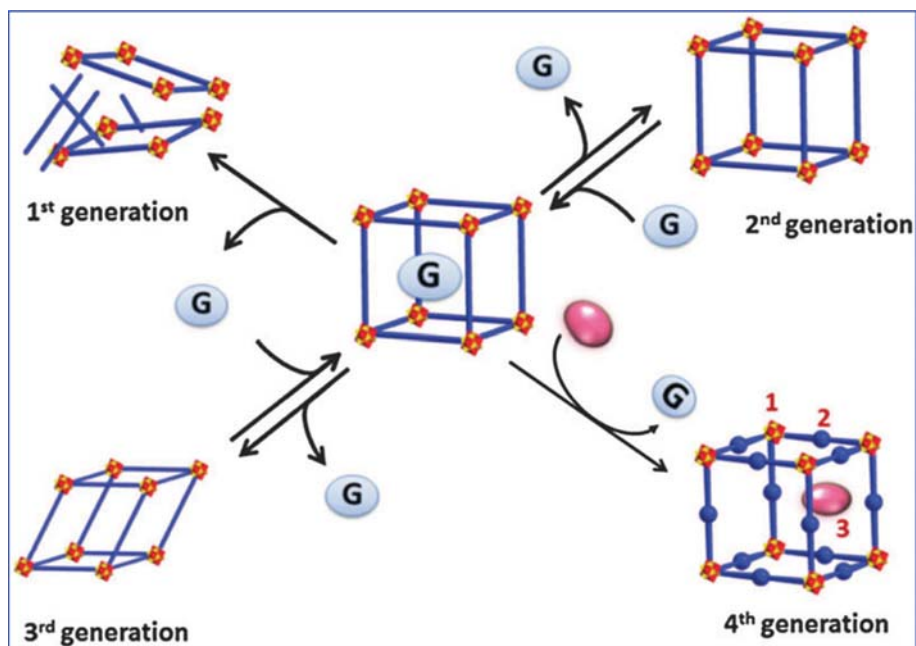


Fig. 3. Classification of MOFs: The 1st generation MOFs collapse on guest removal, the 2nd generation MOFs maintain permanent porosity against guest removal, the 3rd generation MOFs show flexible and dynamic properties, and the 4th generation MOFs can sustain post-processing (modifiable positions: (1) metal/cluster sites, (2) organic linkers, and (3) vacant space) [13,28,29].

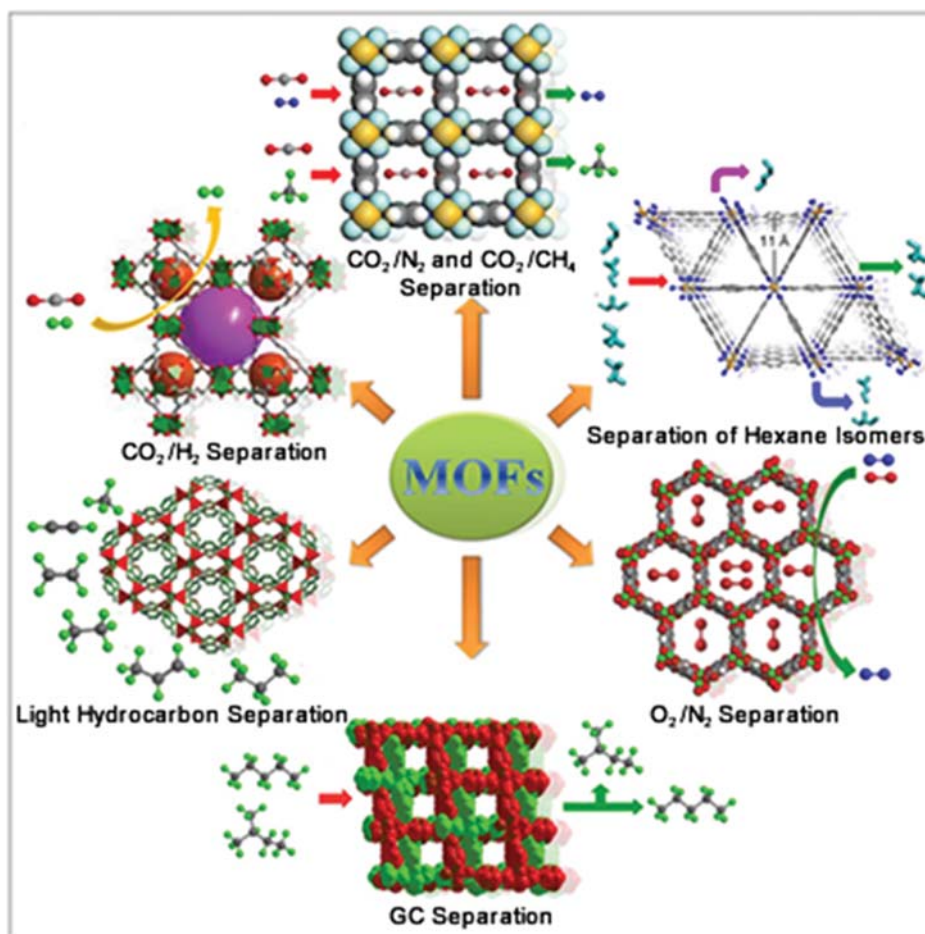


Fig. 4. A broad range of environmental applications for MOFs [30].



Fig. 5. Strategic properties of PCPs/MOFs and their functions for factual energy and environmental applications.

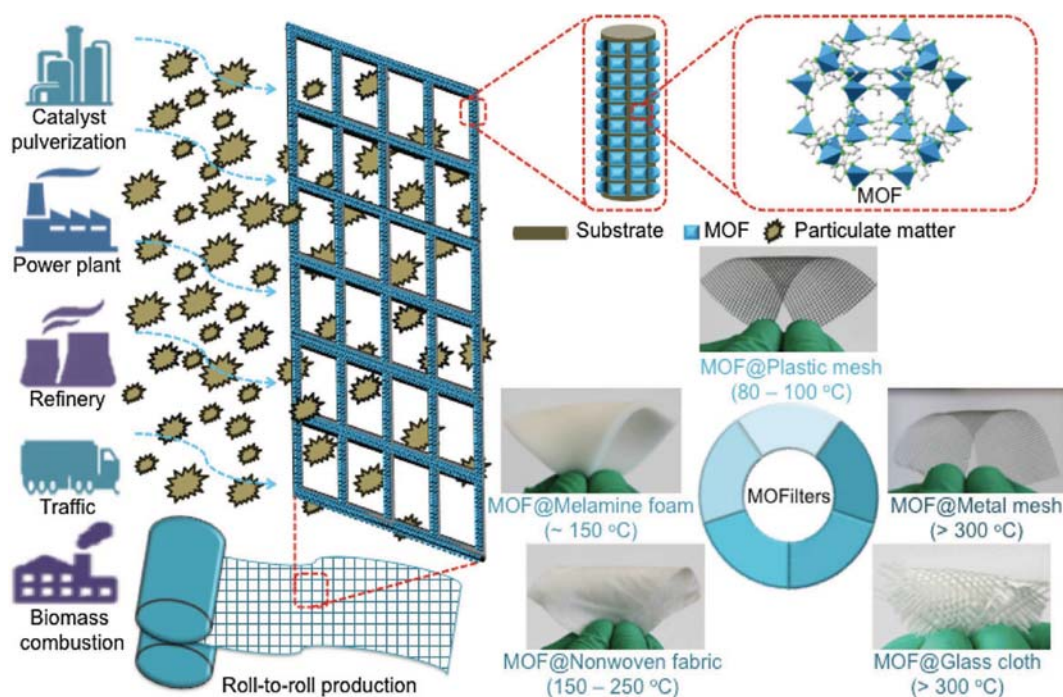


Fig. 6. Roll-to-roll production scheme of MOF-based filters for particulate matter (pm) removal [41].

authors have validated the feasibility of MOFs toward AQM applications. For example, Chen et al. [81] investigated a powerful roll-to-roll hot-pressing strategy for mass production of filter materials composed of CPs [41]. Three types of MOFs consisting of Co, Ni, and Zn were applied individually to substrates including fabric, foam, and plastic using two hot rollers (Fig. 6) [41]. The successfully obtained Zn-based CPs/MOFs filters reduced hazardous airborne particle levels (2.5- (PM_{2.5}) and 10-μm (PM₁₀)) by up to 99.5% at room temperature, with an efficiency loss of only a few percent at 200 °C [41]. Furthermore, the potential of MOFs for

quantitative exchange with a variety of small molecules (e.g., volatile organic compounds (VOCs), pesticides, and other organic/inorganic materials) highly specific towards the nature of guest molecules (e.g., size, shape, and functionality) has been identified [31–40]. Consequently, MOFs can be tailored for use as highly selective devices, including molecular sieves, sensors, catalysts, separation matrices, and highly efficient sorbents. For sensing capacities, the superiority of MOFs has been realized through modification of their optical, electronic, or magnetic properties by interactions with guest molecules. As such, the capacities of MOFs have been demon-

strated extensively in sensing/catalytic/adsorption/removal phenomenon for diverse AQM applications [31–42].

CURRENTS TRENDS AND CHALLENGES IN ENVIRONMENTAL APPLICATIONS OF CPs

CPs have great potential for developing novel materials for the control and management of air quality. Addressing the unique opportunities for implementing CPs/MOFs in real world applications may improve potential AQM applications. In this section, we focus on environmental applications including adsorption, cataly-

sis, removal/separation, and sensing using CPs/MOFs (Table 1) [43–60].

1. Adsorption

Adsorption is an important process for the removal and separation of hazardous compounds and their contaminants from aqueous and non-aqueous media. CPs/MOFs have attracted a great deal of attention in the research and development of adsorption technology, including advanced analytical applications [61,62]. The superior performance of advanced porous materials (e.g., MOFs and graphene) has been acknowledged before [63–66]; however, these materials are expected to vastly improve or upgrade their per-

Table 1. AQM applications using CPs/MOFs with emphasis on adsorption and catalysis

Sr. No.	AQM applications	CPs/MOFs	Synthesis method	Target compound/ Exp. conditions	Partial pressure out (Pa)	Capacity (mmol g ⁻¹)	Capacity at P out (mg g ⁻¹)	PC (mol kg ⁻¹ Pa ⁻¹)	Ref.
1	A. Adsorption	Fe-MIL-101-SO ₃ H	Hydrothermal synthesis	NH ₃ at 1 bar and 298 K	1,900	18.00	0.3325	0.00350	[42]
2		Co ₂ Cl ₂ (BTDD)-(H ₂ O) ₂			36,660	12.00	0.2566	0.00014	[43]
3		Mn ₂ Cl ₂ (BTDD)-(H ₂ O) ₂			36,660	15.47	0.2750	0.00015	
4		Mg-MOF-74			4,690	1.500	0.1066	0.00100	[44]
5		Mg-MOF-74			3,125	5.280	0.1420	0.00200	[45]
6		Mmen-Cu BTTr		CO ₂ at 0.01 bar and 298 K	2,36,835	0.023	0.2153	0.00004	[46]
7		fcu-MOF-1			1,600	0.330	0.0175	0.00048	[47]
8		fcu-MOF-2			1,600	0.620	0.0142	0.00039	
9		[Mg ₂ (dobdc)(N ₂ H ₄)1.8]			100	4.900	0.0909	0.04000	[48]
10		IRMOF-3		CH ₃ SCH ₃ at 448 K	0.0041	0.009	0.0017	25.7000	[49]
11				C ₂ H ₅ SH at 448 K	0.0025	0.013	0.0022	54.0000	
12				H ₂ S at 448 K	0.0066	0.014	0.0133	68.0000	
16		kag-MOF-1		CO ₂ at 298 K	18,749	0.0375	0.0263	0.00005	[51]
17		Cr-soc-MOF-1	Solvothermal synthesis	Water/70% relative humidity at 298 K		1.95 g/g	1950	0.00001	[52]
19		Diamine functionalized MOF-74-Mg		CO ₂ /373 K	6923	-	0.0740	0.00047	[53]
20	B. Catalysis	Cu/Cu ₂ O@C	Hydrothermal method	4-Nitroaniline, 4-nitrobenzaldehyde, and nitrobenzene		0.0248 s ⁻¹			[54]
21		MFM-300(Al)		Nitrogen dioxide		14.1 mmol g ⁻¹			[55]
22		Cu@N-C		4-Nitroaniline, 4-nitrobenzaldehyde, and nitrobenzene		0.01 s ⁻¹			[56]
21		DABCO-Functionalized Zn-MOF1	Stirring method	4-nitrobenzaldehyde with nitroalkanes					[57]
22		Co(2-methylimidazole) ₂ -ZIF-67	One-step pyrolysis	Nitrobenzene					[58]
23		NH ₂ -MIL-125	Solvothermal synthesis	Nitroarenes		99%			[59]
24		Pd ₅ Ag1-N-doped-MOF-C							
25		Ni-MOF@C	Direct thermal treatments			99.40%			[60]

formance (e.g., in terms of adsorption capacity of absorbent polymeric materials (e.g., through composite formation and/or functionalization), selectivity (e.g., highly precise interaction with adsorbates), partition co-efficient at low partial pressure region (PC), recyclability, and regenerability). The sorbents with better removal capacity or extended breakthrough volume can be applied effectively for air quality management (AQM) purposes [67]. In ambient conditions (e.g., indoor environment), the AQM focuses on dealing with air pollution at relatively low concentration levels of pollutants (even in ppb range of some VOCs and odorants) [68]. In contrast, the control on high pressure level (e.g., ~kPa) pollutants is needed to deal with strong emission sources (e.g., plume emission). Therefore, the type of sorbents needed for AQM purposes is determined mainly by source strengths or source types.

To learn more about the sorbent performance for target sources, it is important to learn the versatile performance for a range of source types. To this end, the obtained capacity data of sorbents were converted in terms of PC (in $\text{mol kg}^{-1} \text{Pa}^{-1}$). As the adsorption capacity is determined to reflect the effect of partial pressure under which measurements were made, comparison of such capacity obtained under different pressure range can offer large biases in performance comparison [67] (See Table 1). The PC is considered an important parameter for exploring the interactive phases of solid sorbents and gases. The PC for a two-phase equilibrium (Henry's law is a special case where the PC is essentially invariant over a wide range of pressures) has been reported in previous studies. In addition, the PC has also been used to characterize adsorbent heterogeneity and adsorption affinity against odorants [70]. We used a generic formula $PC=a/(b \cdot c)$ to calculate the partition coefficient at any point using the adsorption capacity and outlet partial pressure of sorbent. Here "a" is adsorption capacity (mg g^{-1}), "b" is molecular mass (g mol^{-1}), and "c" is outlet partial pressure (Pa). For instance, IRMOF-3 sorbent (highest PC values among the data found in Table 1) have PC values of 68, 54, and $25.7 \text{ mol kg}^{-1} \text{Pa}^{-1}$ for the adsorption of H_2S , $\text{C}_2\text{H}_5\text{SH}$, and CH_3SCH_3 , respectively [50]. The corresponding adsorption capacity $<0.014 \text{ mg g}^{-1}$ was noticed under low pressure/Henry's region $\sim 0.007 \text{ Pa}$. In contrast, the capacity $\sim 0.2 \text{ mg g}^{-1}$ was converted into very low PC $\sim 0.0004 \text{ mol kg}^{-1} \text{Pa}^{-1}$ in case of CO_2 adsorption using Mmen Cu BTTr sorbent at 239 kPa. In light of such capacity, such sorbent should also be suitable for high emission sectors. The PC also has a strong relation with breakthrough volume (BTV: L/mass) of sorbents. Normally, the assessment of BTV at 5, 10, and 50% is recommended [67]. In this work, BTV 10% have been selected as a base line for figure of merits of sorbents. The BTV values of 1% (near quantitative VOC capture), 5% (detection limit), and 10% (VOC readily detectable in outlet stream) were previously arbitrarily selected depending on the types of application [70]. For some unknown reasons, isotherm information of $C_{\text{out}}/C_{\text{in}}$ is not commonly reported (same for partial pressure information used for experiment). If provided, such information can help gain the detailed performance metrics of a given sorbent like BTV, PC, and sorption capacity at outlet partial pressure points. Therefore, we attempted to extract the BTV of dimethyl sulfide by IRMOF-3 sorbent at specific BT points: $\text{BTV}_{5\%}$: 50 L g^{-1} , $\text{BTV}_{10\%}$: 58 L g^{-1} , $\text{BTV}_{50\%}$: 68 L g^{-1} , and $\text{BTV}_{100\%}$: 130 L g^{-1} . The relatively large BT (at 5%) shows the

strongest region for sorption (lowest pressure region or retrograde region: 0.0002 Pa) [50]. This phenomenon is some time responsible for an unbelievable pattern of PC increasing with loaded volume called retrograde [70]. Consequently, a low variation in 5 and 50% BT corresponds to the low-pressure region ($0.0004 < P < 0.004 \text{ Pa}$) where low sorption capacity is prevalent. However, from 50% to 100% of BT (or high-pressure region: $P > 0.004 \text{ Pa}$), the capacity is flattened out. This implies that PC patterns change considerably across the pressure regions, i.e., the highest PC at lowest pressure region, moderate PC at low pressure region, and the lowest PC at high pressure region. The evaluation of sorption behavior based on such prominent PC trends may be used as one of the important criteria in the selection of proper sorbents for targeting any pollutant or for any source types.

1-1. Physical Adsorption (or Physisorption)

Physisorption of compounds on surfaces is primarily dependent on van der Waals forces with adsorption energy ranging from 5 to 40 kcal/mol, with no activation energy required. Unlike chemisorption, physisorption preserves the chemical identity of the adsorbate and adsorbent with only a minimal shift in the electronic states between them [71,72]. Although the degree of physisorption increases with gas pressure at moderately high pressures, it decreases with temperature increases [71,72]. Under appropriate temperature and pressure, physisorption of adsorbate occurs as a multi-molecular layer. Hence, the sorption capacity is primarily dependent on the adsorbent's surface area and porosity, MOF's properties to be utilized.

Physisorption plays an important role in the ability of MOFs to selectively separate and/or purify gases for industrial/environmental applications and storage. Whereas, the separation and purification of gases with similar molecular weights cannot be achieved using conventional adsorbents (e.g., zeolite and activated carbon) owing to their non-selective adsorption of target compounds [73]. Furthermore, MOFs have attracted wide scientific attention owing to their ability to exhibit a variety of pore surface properties such as hydrophilicity and chirality (e.g., through the controlled incorporation of organic functional groups into pore walls). For example, Matsuda et al. [73] investigated a $\text{Cu}_2(\text{pzc})_2(\text{pyz})$ MOF to separate and purify C_2H_2 from a mixture of gases containing CO_2 [73]. The C_2H_2 was held at a periodic distance from one another through hydrogen bonding between two non-coordinated oxygen atoms in the nanoscale pore wall of the MOF and the two hydrogen atoms of the C_2H_2 molecule [73].

The physical characteristics (e.g., porosities such as surface area) of an MOF greatly contribute to its adsorption properties. The physical adsorption of gases by MOFs is also affected by temperature and pressure. For instance, at low temperature conditions (77 K) and pressure, Cu-BTC has a higher storage capacity for hydrogen than MOF-5, while MOF-5 has a higher storage capacity for hydrogen at higher pressure. Furthermore, the adsorption capacity of MOF-5 is closely correlated with its specific surface area and porosity [74,75]. The adsorption capacity of hydrogen was compared using eight types of MOFs (IRMOFs, MOF-74 ($\text{Zn}_2(\text{C}_6\text{H}_2\text{O}_6)_2$), and HKUST-1 ($\text{Cu}_2(\text{C}_9\text{H}_3\text{O}_6)_{4/3}$) at the same temperature and pressure conditions, with a large pore capacity seen to exert critical control [75].

In light of their impressive absorptivity, MOFs can be used to remove or denude contaminants (e.g., VOCs), especially in indoor

air environments. Physisorption onto MOFs occurs not only on inorganic compounds but also on organic compounds, depending on the molecular/structural properties of the adsorbate and MOFs. The use of IRMOF-1 (MOF-5, $\text{Zn}_4\text{O}(\text{BDC})_3$) in micro packed capillary columns for inverse gas chromatography (IGC) was successful for adsorption/desorption-based analysis of more than 30 VOCs. The adsorption of nonpolar or weakly polar VOCs differed from polar VOCs, with size exclusion expected to play an important role in adsorption [76]. Hydrogen bonding has been identified as the primary contributor to specific interactions between adsorbates and the IRMOF-1 surface [76]. Likewise, the adsorption of six types of VOCs (n-hexane, toluene, butanone, dichloromethane, methanol, and n-butylamine) on MIL-101 was investigated by Huang and co-workers [77]. Comparing adsorption capacities to conventional adsorbents (e.g., activated carbon), n-butylamine had a strong affinity on MIL-101 while n-hexane had a weak affinity because of being energetically heterogeneous [77]. Additionally, MIL-101 showed higher adsorption capacity for investigated VOCs relative to activated carbon [77].

MOFs can also be applied as an analytical sorbent for air quality monitoring such as VOC analysis. Sorption-based analysis of low molecular weight VOCs like formaldehyde is generally limited because of poor adsorption affinity to sorbents composed of organic polymers (e.g., Tenax TA) and graphitized carbon black (e.g., Carbograph 1TD). Hence, its analysis is commonly by the HPLC method with a lengthy derivatization procedure. However, the enhanced sorption capacity of certain MOFs (e.g., MOF-5) has enabled simple GC-based analysis with a higher recovery rate ($100 \pm 7\%$) in parallel with the TO-11A guidelines of the United States Environmental Protection Agency (U.S. EPA) [57,78].

1-2. Chemical Adsorption or Chemisorption

Chemisorption, the chemical adsorption process, involves novel bonds being generated between the adsorbing moiety and the adsorbing surface. Fundamentally, the unique adsorption/desorption characteristics of CPs (e.g., minimal shrinkage, uniform rigid structure, durability, hardness, insoluble spheres of porosity, high pore volume, and surface area) are highly desirable features for advancement in adsorption applications [79]. Hence, polyaromatic cross-linked adsorbent materials with polar/nonpolar nature are estimated to have significant future growth owing to their advantages described above. For example, diamine-appended $\text{Mg}_2(\text{dobpdc})$ ($\text{dobpdc} = 5,5',4,4'$ -dioxidobiphenyl-3,3'-dicarboxylate) MOFs are 'phase-change' adsorbents with unusual step-shaped CO_2 adsorption isotherms that shift markedly with temperature [53]. In that study, an unprecedented mechanism of CO_2 adsorption was elucidated by the step-shaped isotherms, demonstrating that the replacement of divalent metal ions with Mg^{2+} enabled the adsorption step to be manipulated in accord with the metal-amine bond strength [53]. Similarly, Jin et al. [80] investigated two 3-dimensional high porous PCN-124-stu, namely $[\text{M}_2(\text{PDBAD})(\text{H}_2\text{O})]_n$ ($\text{M} = \text{Cu}, \text{Zn}$, $\text{PDBAD} = (\text{pyridine-3,5-dicarbonyl})\text{bis}(\text{azanediy})\text{diisophthalic acid}$), MOFs for selective adsorption of CO_2 and CH_4 [80]. These Cu- and Zn-based MOFs, with excellent chemical and thermal stability, were investigated intensively for adsorption application of gases due to their recyclability and regenerability. In addition, these MOFs were also used as a host for efficient extraction

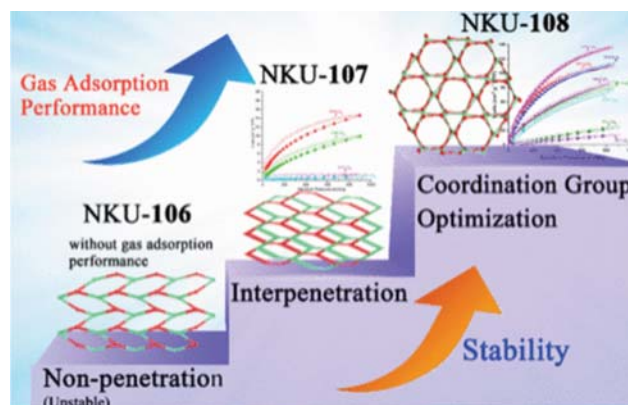


Fig. 7. Graphical presentation of acylamide group functionalized zinc MOFs through optimization of coordination group for adsorption of CO_2 and C_2 hydrocarbons [80].

materials for various organic dyes from water, especially large sized dyes like Coomassie brilliant blue, as well as fluoroquinolones [80]. Accordingly, PCN-124-stu(Cu) was found to be an excellent selective platform for adsorption of CO_2 and CH_4 due to H-bonds between fluoroquinolones molecules and the amide groups within the frameworks [80]. Similarly, the acylamide group functionalized Zn MOFs (NKU-106, NKU-107, and NKU-108) were also reported for enhanced adsorption capacities with respect to CO_2 and C_2 hydrocarbons [80]. As one isophthalate moiety of the tetracarboxylate ligand was replaced with a pyrazole group, the resulting NKU-108 exhibited good adsorption capacities with respect to CO_2 and C_2 hydrocarbons with improved thermal/chemical stability (Fig. 8) [80]. This strategy for incorporating a functional (or chemical) group has provided very valuable information regarding the future design and synthesis of porous MOFs. Likewise, the application of MOFs for adsorbing hazardous chemicals like VOCs has also been investigated.

Novel bipyridinium porous frameworks have also exhibited superior adsorption with a broad spectrum toward organic pollutants [81]. This was ascribed to conjugated pyridyl rings connected by C-C single bonds that can rotate freely to keep twisted or large-conjugated planar configuration during the self-assembly process (Fig. 8) [81]. In addition, the abundance of π - π interaction sites for efficient adsorption of benzene and toluene molecules also facilitated the accommodation of cyclohexane molecules for enhanced adsorption [81]. Recent examples of MOF applications in this direction are briefly summarized in Table 1 [43-53].

2. Catalysis

To remove toxic gases, various physical and chemical approaches have been developed based on polymers or advanced materials. Polymers have been widely used as catalysts or catalyst supports due to their soluble linear structure, large internal surface areas, adoption of functional/pendant groups, and possible acquisition of uniform pore/cavity sizes. Accordingly, catalytic polymers can be categorized into four groups: (a) catalysis by polymers, (b) catalysis by ion exchange resins, (c) polymer-supported 'homogeneous' metal complex catalysts, and (d) polymer-supported phase transfer catalysts [82,83].

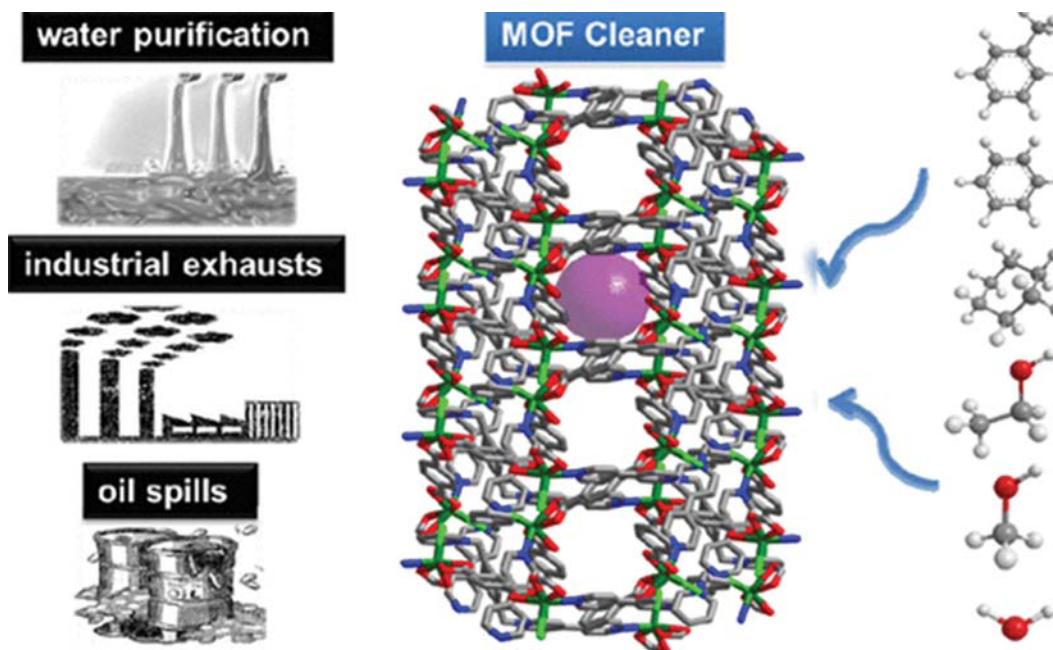


Fig. 8. Graphical presentation of flexible bipyridinium constructed porous frameworks $[\text{Cd}_2(\text{pbpy})(\text{bdc})_2\text{X}_2] \cdot n\text{H}_2\text{O}$ (H_2bdc =1,4-benzenedicarboxylic acid; $\text{pbpy} \cdot 2\text{Cl}$ =1,1'-[1,4-phenylenebis(methylene)]bis(4,4'-bipyridinium) dichloride; $\text{X}=\text{Cl}$, $n=5(1)$; $\text{X}=\text{Br}$, $n=8(2)$; $\text{X}=\text{Cl}/\text{Br}$, $n=9(3)$) bearing 4,4'-bipyridinium functional moieties with superior broad-spectrum adsorption toward benzene, toluene, and cyclohexane molecules [81].

2-1. Homogeneous Catalysis Reaction

MOFs are attractive catalysts because of their advantageous properties. In the catalytic reaction of MOFs, the arrangement of the metal framework with the organic linker shapes catalytic properties of the system [84]. For example, MOF-5 loaded with palladium (Pd/MOF-5) has higher catalytic activity than activated carbon with palladium in the hydrogenation of styrene to ethylbenzene [85]. The palladium loaded MOF-5 forms ethylbenzene from the styrene hydrogenation through catalysis, with 99.7 wt% conversion after 12 hours [85].

Most homogeneous catalysts have a limit to recovery and reuse due to decomposition during the reaction. Thus, methods for heterogenization of homogeneous catalysts have been developed to

overcome this limit [86], making it possible for benefits from both heterogeneous and homogeneous catalysis. For instance, a cation exchange method has been used to form the heterogenization of homogeneous catalysts. Genna et al. [87] exchanged cationic transition-metal complexes in ZJU-28 to endogenous H_2NMe_2^+ like complexes of palladium (Pd), iron (Fe), iridium (Ir), rhodium (Rh), and ruthenium (Ru) [87]. Specifically, the Rh-containing MOF converted 1-octene into n-octane rapidly and can be reused at least four times [87].

In other cases, MOFs have been used to bridge between homogeneous and heterogeneous catalysts. Au-MOFs (IRMOF-3-SI-Au), synthesized with IRMOF-3, 2-aminoterephthalic acid (H_2ATA), and NaAuCl_4 , imitated the characteristics of homogeneous gold

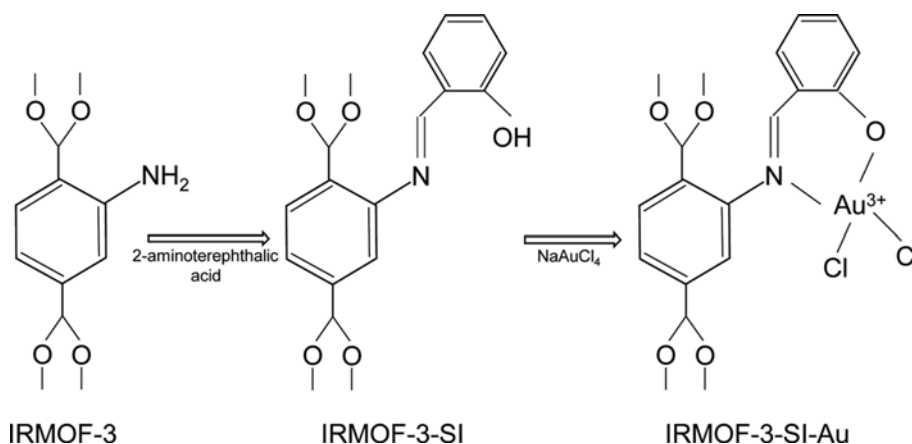


Fig. 9. Synthesis procedure of IRMOF-3-SI-Au from IRMOF-3, H_2ATA , and NaAuCl_4 [88].

catalysis with high performance and selectivity (Fig. 9) [88]. Similarly, copper-containing MOFs (Cu-MOFs) have bridged between homogeneous and heterogeneous catalysis. To learn more about the catalytic potential of Cu-MOFs, MOFs (including Cu(2-pymo)₂, Cu(im)₂, Cu₃(BTC)₂, and Cu(BDC) (2-pymo: 2-hydroxypyrimidinolate; im: imidazolate; BTC: benzene tricarboxylate; BDC: benzene dicarboxylate) were synthesized using indole and imidazopyridines from 2-aminopyridine, benzaldehyde, and phenylacetylene [89]. The Cu-MOFs were efficient and regioselective heterogeneous catalysts for the click reaction between azides and alkynes. In the one-pot two-step domino reaction, azide was formed in situ and reacted immediately with phenylacetylene without the aid of alcohol or water solvents [89]. The activity of the Cu-MOF catalysts (e.g., Cu(2-pymo)₂ (>99%), Cu(im)₂ (>99%), Cu₃(BTC)₂ (37%), and Cu(BDC) (42%)) was comparable to homogeneous Cu catalysts. Hence, the rate-determining step of the reaction was the formation of an adduct between Cu and phenylacetylene [89].

2-2. Heterogeneous Catalysis Reaction

Reaction of a catalyst with reactants existing in different phases is heterogeneous catalysis, while catalysis occurring in a single phase is homogeneous catalysis. Recently, the most prominent role of MOFs as heterogeneous catalysts was explored based on several criteria, including metal nodes, metal-free organic struts (or cavity modifiers), designed framework nodes/struts, functionality, encapsulated molecular species/clusters, large internal surface areas, and uniform pore/cavity sizes [90]. Heterogeneous catalysts of CPs/MOFs are superior to homogeneous catalysts due to their facile separation after reaction and recyclability.

Heterogeneous catalysts of CPs/MOFs, as well as their composites/derivatives, are newly emerging for various applications [83]. For example, a titanium-based porous coordination polymer (Ti-PCP) was synthesized through the reaction of a 1,3-diol-substituted shape-persistent arylene-ethynylene macrocycle with Ti(OⁱPr)₄ [91]. Ti-PCP works as a cyclocarbonate through the cycloaddition reaction with epoxides under mild conditions for chemical fixation of CO₂ (Fig. 10) [91]. The catalytic activities of Ti-PCP may be ascribed to high surface area (1,029 m² g⁻¹) and good adsorption selectivity for CO₂ over N₂. The enhanced capacity for CO₂ uptake and improved catalysis for the conversion of CO₂ into use-

ful chemicals might be helpful to solve environmental problems regarding post-combustion capture and conversion of CO₂ [91]. As such, Zn-based CPs have been synthesized using linker 5-(benzylamino)isophthalic acid (H₂L) to form a robust 2D Zn(II)-coordination polymer, {[Zn₃(L)₆(μ₃-OH)₄(H₂O)₆](DMF)·(H₂O)_{2.5}]_n·(1_{Zn})} consisting of [Zn₄(μ₃-OH)₂]⁶⁺SBUs. The two-dimensional porous Zn(II)-coordination polymer exhibited SC-SC transmetalation with Cu(II) as an efficient heterogeneous catalysis in the Henry reaction [92]. Likewise, there are numerous advantages to using CPs/MOFs as catalysts (Table 1) [54-60]. In particular, the attractive structural features and catalytic performance of CPs/MOFs in various organic reactions are fundamental reasons for the notable progress in this exciting research area.

3. Applications of MOFs in Miscellaneous Fields

Novel materials including CPs/MOFs, graphene, and polymeric composites have been extensively employed in various miscellaneous techniques such as sensors and filtration. Future development of MOFs can be helpful to improve their performance in terms of sensitivity, reliability, rapid processing of multiple samples, real-time detection, and broad applicability [93-96].

3-1. Sensing Applications

Air pollution has worsened in some regions owing to substantial emissions of hazardous substances into the environment from industrial and anthropogenic sources. Therefore, continuous monitoring of key hazardous air pollutants is vital to safeguard environmental resources. In this regard, the development of sensitive, selective, low maintenance, portable, and convenient to use sensing devices for onsite detection of airborne pollutants is imperative to overcome practical limitations encountered in conventional methodologies [97]. A typical sensor (e.g., electrochemical) is comprised of two main components: (1) a recognition element that selectively binds or reacts with the target molecule, and (2) a transduction element that transduces the signal correlating to the selective binding or reaction (e.g., via the extent of concentration of the target analyte) to the signal that can be physically measured (e.g., potential or current) [98]. Among various detection methods, optical sensors have gained much attention owing to their high sensitivity, selectivity, lower limit of detections, rapid response, operating in real-time, and being ease for deployment [99].

Nonetheless, numerous CP sensing techniques (e.g., surface-enhanced Raman spectroscopy (SERS) based sensing, application of imprinted polymers in electrochemical, optical, and biosensing methods) are available for environmental monitoring applications toward various pollutants including VOCs, polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), odor, herbicides, and pesticides [93-96]. Most of these techniques are sensitive, reliable, handy, and portable, countering the challenges and requirements of conventional methods (e.g., large set-ups, expensive instrumentation, and highly skilled manpower). In general, the sensing mechanisms of a target through a sensor are divided into two categories: (1) mechanisms involving direct coordination of the analyte to the central metal atom of CPs (e.g., detection via displacement of coordinated water molecules or coordinated antenna molecule), and (2) mechanisms that do not require direct coordination of the analyte to the metal center of CPs (i.e., detection via electrostatic interaction, π - π stacking interaction, and nucleophilic

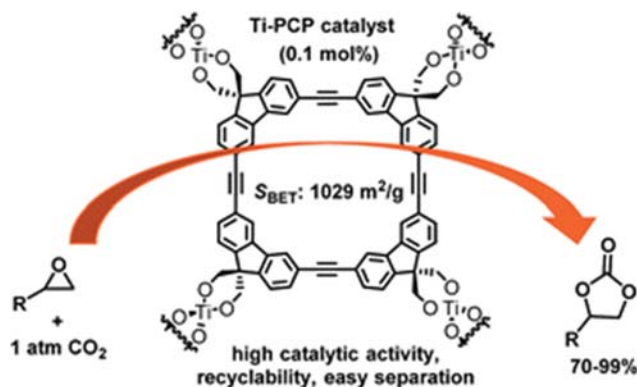


Fig. 10. Ti-PCP based catalyst reaction to convert CO₂ into cyclocarbonates through the cycloaddition reaction with epoxides under mild conditions [91].

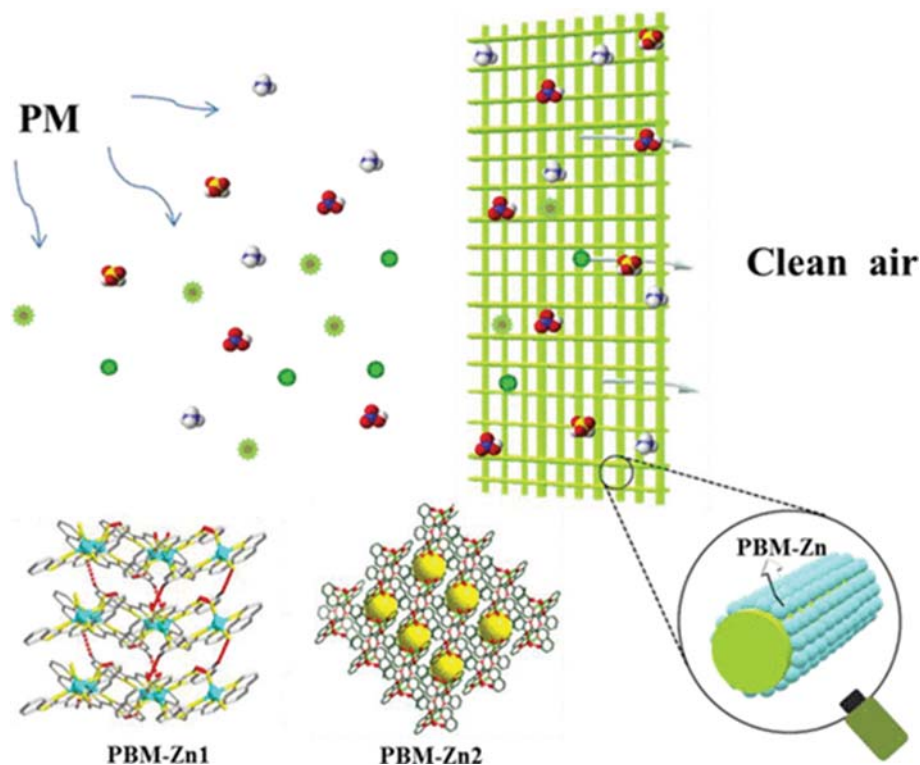


Fig. 11. Graphical presentation of hot-pressing method to prepare imidazole-based Zn(II) metal-organic complexes coatings for highly efficient air filtration [104].

reaction) [99].

Numerous types of CPs have been employed for the detection of various target components involving anions, cations, and neutral species (e.g., I_2 and nitrobenzene). For example, 3D MOFs with diverse structures have been constructed by a solvothermal reaction of Zn or Cd ions with linear thiophene-functionalized dicarboxylic acid (benzo-(1,2,4,5)-bis(thiophene-2'-carboxylic acid, H_2L) [100]. These MOFs were found to exhibit efficient luminescent sensory characteristics required for highly selective and sensitive determinations of environmental contaminants in the presence of other coexisting species, especially for salicylaldehyde or metallic species like Hg(II), Cu(II), and Cr(VI). The luminescent sensing mechanism for selective detection of salicylaldehyde in the presence of other aldehydes (e.g., formaldehyde and acetaldehyde) was ascribed to the high electron affinity of the former relative to the latter. The observed phenomenon may also be explained by electron transfers from the HOMO (highest occupied molecular orbital) of MOFs to the LUMO (lowest occupied molecular orbital) of the salicylaldehyde upon excitation. Such aldehyde selective properties of MOFs are indeed very useful for AQM applications [43].

Thin CP films have been extensively investigated for environmental sensing applications [93-95,101]. For example, Troyano et al. [102] utilized two Cu(I)-thiophenolate-based CPs (e.g., $[CuCT]_n$ (1) (CT=4-carboxy-thiophenolate) and $[CuMCT]_n$ (2) (MCT=4-methoxycarbonyl-thiophenolate)) reversible thermochromic polymeric thin films for 2D imaging sensor films [101]. These films were thermal stimuli-responsive, freestanding, free of macroscopic defects, and robust under mechanical bending stress [101]. These

types of advancements in sensing technique-based polymeric materials will accelerate the creation and commercialization of advanced sensor devices for environmental applications.

3-2. Filtration

Research and development in filter materials based on novel materials (including CPs) has recently become an interesting approach in materials science, albeit with much hyperbole and without in-depth consideration of actual real-world applications [41, 103]. For example, Wang et al. [104] investigated metal-organic complexes PBM-Zn1 and PBM-Zn2 coatings (PBM-Zn-filter) produced by the hot-pressing method on various substrates (e.g., glass, melamine, foam-4, plastic, and carbon fiber cloth-4) (Fig. 11) [104]. The obtained PBM-Zn filters had excellent $PM_{2.5}$ and PM_{10} removal performance ($99.6\% \pm 0.5\%$ and $99.4\% \pm 0.8\%$, respectively). These products further exhibited acceptable air resistance after 24 hour tests. The PBM-Zn2@melamine foam-4 gave the highest removal rates of $PM_{2.5}$ ($99.5\% \pm 1.2\%$) and PM_{10} ($99.3\% \pm 1.1\%$). Its removal efficiency, when tested for $PM_{2.5}$ and PM_{10} particles in cigarette smoke, was high ($>95.5\%$) due to its larger conjugation system, micropore structure, lower pressure drops, higher electrostatic potential ζ , and electron cloud exposed metal center (DFT calculations) [104]. Likewise, Gholami et al. [105] investigated TMU-5 MOFs as novel nanofillers for flux increment and fouling mitigation in PES ultrafiltration membranes [105]. A novel hydrophilic polyethersulfone (PES) ultrafiltration membrane was synthesized through blending TMU-5 CPs via the phase inversion method. Importantly, the antifouling properties of the 0.1 wt% MOF NPs-PES membrane had high flux recovery ratio (FRR) (98.74%) and low irreversible

fouling resistance (R_{ir}) (1.25%) [105]. While rarely reported in the literature, complete life cycle analysis (LCA) and cost analysis of MOF-based PM filter materials, including end-of-life disposal/recycling and toxicity appraisal, are urgently needed before implementation of mass-scale production. While MOFs are costly for small lots (e.g., $>10 \text{ USD} \cdot \text{g}^{-1}$), they are projected to be as low as $10 \text{ USD} \cdot \text{kg}^{-1}$ in the near future [103], providing hope for real-world MOF applications including filter materials.

PRACTICAL PERFORMANCE ASSESSMENT OF MOFs

Practical performance of MOFs can be useful to improve air quality through their applications toward innovative efficient adsorbents, catalysts, and sensing materials. The assessment of PC and adsorption capacity at both low (Henry's region) and high-pressure region is ideal for proper evaluation of sorbent performance, as explained above. For instance, in Table 1 [50], the highest PC ($68.0 \text{ mol kg}^{-1} \text{ Pa}^{-1}$) and lowest adsorption capacity (0.013 mg g^{-1}) for H_2S were simultaneously observed from IRMOF-3. These high values of PC may be more relevant for the low outlet pressure areas like ambient conditions, while the ones with low sorption capacity should be less effective for applications for control on emission sources (high outlet pressure areas). The level of air purification achievable by CPs/MOFs should ultimately comply with international guidelines (e.g., OSHA/NIOSH) [42]. Some recent review articles and the key remarks are summarized for AQM using CPs/MOFs [9, 42, 90, 96, 106–108].

To properly evaluate the performance and related properties of MOFs, it is necessary to understand the design and synthesis of MOFs from fundamental perspectives. MOF performance can be assessed with respect to (a) the positional isomerism, substituents, and spacers of organic ligands; (b) the coordination mode of metal centers; (c) the architecture topology, dimensionality, and structural transformation; (d) secondary building units (SBUs); (e) solvents; (f) linking defects; and (g) hierarchical porosity generation. In our literature review, the functional tailorability of MOFs was recognized as a great merit for improving performance of capturing and storage of gaseous pollutants over conventional materials. However, the precise chemistry of MOFs requirements needs to be specified for AQM applications [42]. The success of an adsorbent depends on the development of materials that, under flue gas temperature conditions, will have high sorption capacity and selectivity with the aid of high tunability of chemistry and structure.

As aforementioned, successful dynamic adsorption mediums should possess some reactive functionalities, often in the form of a coordinatively unsaturated metal sites. While many MOFs with reactive functionalities in the pores have been recognized, immense potential exists for the development of unknown novel MOFs with unique functionalities. Furthermore, the performance of any MOF is expected to improve dramatically once impregnated with reactive species such as ions and compounds. Nevertheless, the direct and indirect cost of MOF production is still a major hurdle impeding large-scale industrial applications. Apart from capital investment in infrastructures, the cost of MOF production is largely dependent on raw materials (e.g., metal salts, organic ligands, and organic solvents) and processing (e.g., activation). The catalytic per-

formance of CPs/MOFs is superior due to their excellent structure stability, large internal surface areas, adoption of functional/pendant groups, and possible acquisition of uniform pore/cavity sizes. Heterogeneous and homogeneous catalytic activity of MOFs may also be enhanced through easier post-reaction separation and recyclability [82, 83].

In sensing applications of gaseous targets (e.g., breath analysis and indoor air quality monitoring), precise detection of trace-level species in complex gas mixtures is a major challenge [109–112]. Nevertheless, modern sensors can be extremely compact, inexpensive, and highly sensitive, although their practical success is still limited by selectivity. To counter such major challenges, MOFs have been recently investigated as chemo resistive sensors where their engineered surface reactivity offers not only high selectivity but also excellent capability (e.g., molecular size selection and chemical separation based on adsorption). The diffusion properties of CPs/MOFs have imparted greater flexibility for the optimization of selectivity for gas sensing applications. For example, a zeolite MFI/ Al_2O_3 microporous membrane was investigated for chemo resistive gas sensors for highly selective sensing of formaldehyde [113]. The membrane exhibited exceptional selectivity (>100) for formaldehyde (down to 30 ppb) at 90% relative humidity, outperforming most state-of-the-art detectors by more than an order of magnitude. The high sensitivity of these sensors should aid formaldehyde detection, even down to 30 ppb at relative humidity of 50 and 90%. This system is especially appealing for expanded applications including breath analysis and indoor air quality monitoring [113]. Additional forms of novel materials with widely tunable separation properties should be available in the future. Such development will facilitate a new generation of portable breath analyzers or indoor air monitors with unprecedented sensitivity and selectivity for sensor applications [109–113].

CONCLUSION AND FUTURE PROSPECTIVE

Over the past several years, significant progress in MOFs has been achieved not only in air purification but also in many other areas (e.g., storage, separation/removal, biomedical, catalysis, and sensors). MOFs have excellent potential for AQM applications due to their significant advantages over other materials. Accordingly, several approaches have been developed to help evaluate CPs/MOFs for AQM-related applications through single- or multiple-component selective features for adsorption/permeation/catalysis/sensors. The advent of such MOFs will provide an opportunity for their practical implementation to fulfill various AQM demands, both at urban as well as industrial scale. Some key parameters for AQM applications based on CPs/MOFs have been pointed out for researcher/readers in Fig. 12. Hopefully, these points are helpful for finding systematic, designed and useful sorbent materials for commercial deployment with considering the cost-effective AQM technology. In addition, it would provide a direct critical information about their performance.

Purposely-designed MOFs can be applied to air purification and AQM tasks for residential and industrial environments, including flue-pipe filtration, baghouse dust collection, and air intake filtration for vehicle or aircraft engines. Nonetheless, it is highly desir-

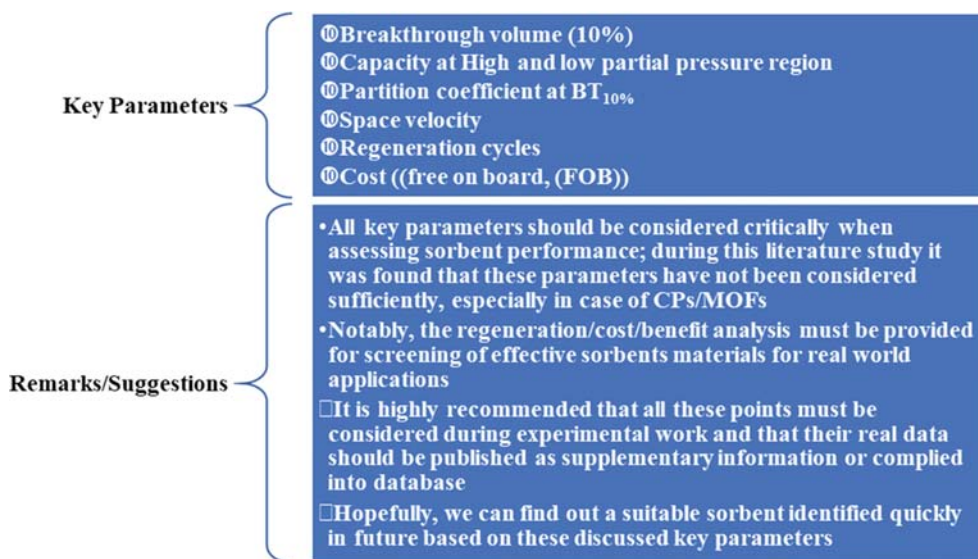


Fig. 12. Some key parameters for AQM applications based on CPs/MOFs.

able for researchers to provide MOFs potential (but unproven) performance metrics (including high breakthrough volume, long-term reusability, excellent permeability with low pressure drop, and high PM removal efficiency) for proper performance assessment. To this end, it is recommended that materials scientists should also focus on natural materials or bioinspired materials (BMs) MOFs, which are one of the most attractive candidates for future air purification technology. While BMs are not free from the current challenges in materials for AQM applications (as discussed in section 4), they offer some excellent features (e.g., porosity, high surface area, flexibility, tunable porosity, and functionality) while maintaining chemical and thermal stability.

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