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2   **Metal organic frameworks for the control and management of air quality:**

3   **Advances and future direction**

4

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10   **Abstract**

11   Recently, the potential role of metal organic framework (MOFs) and porous coordination polymers

12   (PCPs) has been recognized in the field of air quality management (AQM) due to their intrinsically

13   tunable chemical structure and multifunctional properties which afforded significant enhancements in

14   adsorption capacities, catalytic degradation, and removal of diverse airborne pollutants and other

15   vapors. A diverse range of MOFs was investigated for separation, capture, and storage of greenhouse

16   gases and other pollutants (including volatile organic compounds (VOCs), sulfur compounds, and

17   chemical warfare agents (CWAs)). Also, we discuss their main drawbacks such as poor selectivity,

18   high energy and fiscal cost, low capacity, and difficulties in regeneration. Here, we provide an up-to-

19   date review on the promising role of MOFs in the field of AQM in relation to the diverse available

20   synthesis methods. As such, we hope to provide a meaningful direction for success in our efforts on

21   air quality control that MOFs/PCPs can offer for a bright future.

22

23   **Keywords:** Metal organic frameworks, toxic gases and chemicals, adsorption, removal

Introduction

25   A wide array of anthropogenic hazardous pollutants including NO_x, SO_x, CO, H_2S, NH_3,

26   hydrogen cyanide, volatile organic compounds (VOCs), and polycyclic aromatic compounds

27   (PAHs) are released from both static and mobile sources (e.g., industrial, transport, household,

28   fossil fuels use, and many other sources). They are emitted into the atmosphere, taken up by

29   plants, and ingested by animals to be bio accumulated along the food chain up to the apex

30   predator. Most of these pollutants are classified as being toxic/carcinogenic by varying degrees

31   and pose a worldwide risk to the environment and human health.[1-4]

32   Exposure (through different exposure pathways i.e., inhalation, dermal absorption, ingestion,

33   and etc.) to those hazardous pollutants can damage the immune, neurological, reproductive (e.g.,

34   reduced fertility), developmental, and respiratory systems of humans and animals.[4-7] As

35   summarized in recent articles, the toxicity levels of hazardous pollutants are established by

36   different agencies on the basis of their metabolic impacts and physico-chemical properties.[8-9] In

37   summary, clean air is one of the most daunting challenges to improve the quality for life on

38   Earth.

39   For more eco-friendlier and economical air quality management (AQM), much research has

40   been done over the last 60 years.[8-9] More recently, the practical applications of porous metal

41   organic framework (MOFs)/porous coordination polymers (PCPs) is being recognized for AQM

42   because of their potential versatility, especially in the capture and/or adsorption, the enhanced

43   catalytic effects on air-borne pollutants (due to high selectivity, chemical and thermal stability in

44   the low and mid temperature range, moderate/low heat of adsorption, and enhanced mass uptake

45   (e.g., through modification of the pore size).[8-17] Thus, MOFs/PCPs are recognized as alternative

46   sorbent or catalytic media to replace or support conventional materials (such as charcoal,

47   activated carbon, alum inosilicates, and zeolites) for adsorbent and catalytic degradation

48   applications **(Figure 1).**[12]

49   Basically, a framework of coordinately bound metal ions with organic linkers can offer flexible

50   chemical properties, extremely low framework density (0.2–0.6 g.cm^{-3}), wide range of tunable

51   pore sizes, and specific high surface areas with quasi-infinite selection of crystal structure.[18-19]

52   More interestingly, various options for synthetic methods (solvothermal, hydrothermal,

53   microprecipitation, layer by layer, etc.) for PCPs or MOFs facilitate the expansion of their

54   applicabilities. For instance, MOF-5, MOF-177, and MOF-199 have demonstrated unique

55   optical, electrochemical, and electromechanical properties to trap guest species.[20-23] Additionally,

56   improvement in modification of rigid MOFs chemical structure (modified functionalized MOFs,

57   isoreticular metal organic frameworks (IRMOFs), multivariate metal organic framework

58   (MVTMOFs), etc.) allows to enhance chemical flexibility with reversible variable pore sizes

59   (and volumes) to simulate a 'breathing effect'.[18-23] Furthermore, excellent catalytic property at

60   the low and mid temperature ranges was regarded as the ideal goal of air purification treatment

61   to produce low-risk secondary emissions to some extent; it should thus allow to overcome many

62   limitations encountered in sorptive approaches, e.g., secondary emission of captured pollutants

63   after saturation.[24-25] If one enables fine tuning of the catalytic properties of MOFs, then it

64   possibly degrade toxic substances into nontoxic products. However, as there are only a limited

65   number of reports detailing such processes, it is desirable to establish future scientific

66   benchmarks that can be directly applicable to AQM.

67   Many advances in (human) lifestyle quality have been achieved through the improvements in

68   air quality and its protection. A number of review articles and monographs have been reported to

69   describe the fundamental science of MOFs on the applications of adsorptive and catalytic

70   treatment of pollutants.[18-28] In this review; we discuss the synthesis methods of MOF/PCP to

71   account for their application toward the adsorption and catalytic degradation of airborne

72   pollutants. To this end, the underlying capacity of MOFs has been evaluated in viewpoint of their

73   potent role in the technological advancement of AQM. The state of art performance of MOFs in

74 AQM is hence described by emphasizing a number of case studies made in field applications.

75 The scope of this review will be extended further to address the future opportunities to furnish a

76 desirable roadmap for their applications to AQM.

77

78 **Current strategy for MOFs in AQM**

79   The excellent identified features of MOFs for AQM applications can be achieved or

80 maximized with the aid of effective strategies in their synthesis. For their synthesis, the

81 combination of several variables like the choice of metal ions, organic linkers, solvents,

82 synthetic/post synthetic methods, and experimental conditions is important.[29-30] In addition,

83 improved performance of MOFs have also been reported by modifying their structures (e.g.,

84 functionalization, pre-functionalization of organic linkers, mixed organic linkers, mixing of

85 different metal nodes, thin film coating, hybrid textiles, and shell adsorbent).[29-36] For instance,

86 one target can be retained strongly in preference to others through particular surface chemistry

87 offer by MOFs. Likewise, adsorption selectivity can easily enhanced through change in the

88 structural properties towards coordination bonding, acid–base/electrostatic interactions, π-

89 complex/H-bonding formation, open metal sites on the pore surface in MOFs.[37-40]

90   In terms of cost-effectiveness, the synthesis cost of MOF/PCP is much high relative to

91 commercialized/conventional agents for AQM. As such, it becomes major question as to their

92 practical applications on a megascale. For instance, if CO_2 is adsorbed and desorbed by MOFs

93 using a temperature–swing adsorption (TSA) approach, then both energy and financial cost are

94 expected to be very uncompetitive compared to existing sorbents. According to a survey, the free

95 on board (FOB) commodity prices (in USD) for two of the mostly studied MOFs (MOF-5 and

96 MOF-177) are \$200/kg and \$130k/kg, respectively which are highly more expensive in

97 comparison to more conventional sorbent materials (such as monoethanolamine (\$2.66/kg) and

98   quicklime (\$0.18).[41-42] In the case of MOF-TSA, the energy cost is high due to high parasitic

99   energy consumption and in addition, the MOF material costs are extremely high. Thus, for an

100   example, if two columns of MOFs are working 14 hours per cycle for capturing CO_2 using a

101   parasitic 220 megawatt (MW) power load from 500 MW coal-fired power plant, the actual cost

102   for CO_2 capture and storage using MOF/PCP would be \$0.66 M per day.[41-42] In comparison, a

103   conventional and well established material like that MEA, would be \$0.26 per kg for CO_2

104   capture and storage. Hence, MOF/PCP has currently a low appeal for future industrial

105   applications for CO_2 capture based on material and infrastructure costs. Therefore, an effective

106   and low cost MOF synthesis strategy is a primary requirement for any industrial application.

107   However, some excellent performance features (e.g., chemical tunability, high adsorption

108   capacity, and adsorption selectivity) of MOF/PCP can partly offset the high material costs and

109   thus play an increasingly promising role for AQM in the near future.

110   In addition, separation and regeneration of MOFs for the purpose of heterogeneous catalyst

111   has been considered one of the most attractive research areas for AQM. The catalytic activity of

112   MOFs has yet fully been investigated for the removal of toxic airborne gaseous chemicals.[8-9, 43-44]

113   Basically, as the catalytic activity is highly contingent on MOF/PCP's crystal lattice structure,

114   specific synthetic strategies for the selection and arrangement of basic building blocks (metal or

115   organic linkers) with desired chemical structure and properties could be expected. Interestingly,

116   heterogeneous catalysts in MOFs were thought to occur by host-guest mechanism through

117   transition state recognition, regulation of luminescence, and allosteric nature enforced by their

118   physical, chemical, and environmental stimuli response.[45-46] Nonetheless, a number of issues

119   (waste disposal and high cost) still remain as the major drawbacks in the heterogeneous catalysts

120   of porous materials. Therefore, there is a crucial need for functional engineering of MOF/PCP to

121   attain excellent and specific catalysis properties with their advantageous physicochemical

122   properties for their future practical utilizations.

123

124   **MOFs as media for adsorptive removal of air pollutants**

125   Among various AQM control techniques, the use of sorbents have been most developed and

126   employed as an effective option to treat or remove toxic air pollutants. Various commercialized

127   sorbent materials (e.g., activated carbon, zeolites, polymers, activated alumina, silica gel, etc.)

128   have been evaluated and utilized for storage, separation, purification, and removal of pollutants

129   in industry (**Table 1**).[47-59] However, these existing conventional sorbents may not fully meet the

130   high quality standard required for the future technological demands in terms of environmental

131   regulations (e.g., disposal of spent sorbents) and more stringent "greener" energy requirements.

132   This section will therefore focus on these issues and present an up-to-date appraisal and

133   information on the various and numerous MOFs reported in the literature.

134

135   **Fundamental aspect and mechanism of adsorptive removal by MOF/PCP**

136   The unique permanent porous structure of MOFs (in air) has been recognized and led to

137   practical AQM applications.[60-61] The PCPs/MOF adsorption properties depend on well-known

138   factors: 1] solute hydrophobicity, 2] sorbent surface area and porosity, and 3] organic carbon

139   content and mineral composition.[61-63] In addition, fundamental mechanism for selective

140   adsorption is favored by various adsorption mechanisms (such as electrostatic interaction, acid-

141   base interaction, hydrogen bonding, π—π stacking/interaction, and hydrophobic interaction) for

142   AQM (**Figure 2**).[63] These different MOF mechanism classes have also been described for

143   hazardous organics from aqueous media.[63] This well organized review was helpful to explain

144   selective adsorption mechanism with respect to MOFs. In this review, we are mainly focusing to

145 describe the fundamental aspects of these diverse mechanisms for the selective adsorption

146 processes mainly to deal with various airborne species.

147 Adsorption isotherms have generally been interpreted by well-known theories developed by

148 Freudlich, Langmuir, and Brunauer–Emmett–Teller (BET).[8-9] Basically, an adsorption isotherm

149 is the plot of adsorbate mass on the surface of adsorbent as function of adsorbate partial pressure

150 at constant temperature. The recommended definitions and characteristics of adsorption isotherm

151 hysteresis have been discussed in an IUPAC report (1985) with an update is scheduled in 2015 to

152 classify the effect of important variables (e.g., pore size, isotherm type, and hysteresis loops). [63]

153 In this review, we have followed the definition of the adsorption isotherm and hysteresis given in

154 the older IUPAC report (1985). [64] **Figure 3** illustrates the classification of different fundamental

155 isotherms and hysteresis types.[60,64] For the sorptive removal by MOFs, adsorption isotherm can

156 provide the direct information regarding their hydrophilic and hydrophobic nature. In some

157 mesoporous materials, hysteresis loops are always close and adsorbate remains in the pores even

158 at near zero pressure. In such materials, high temperature should either lead to desorption or

159 irreversible adsorption in pores the same size of the adsorbate molecules. [8,66] The adsorption

160 processes in MOFs can proceed according to their chemical nature and structure stability in

161 aqueous or non-aqueous phase with isotherm type I (microporous MOFs with strong adsorbate-

162 adsorbent interactions), III (an unusual hybrid with a larger pore size), and IV (mesoporous

163 MOFs with $\geq$ 20 Å diameter pore size).[59] Note that type II isotherms have been investigated for

164 unrestricted monolayer-multilayer adsorption from non-porous or macroporous materials.[66]

165 However, there should be very different adsorption mechanisms between different MOFs, e.g.,

166 MOF-53 due to its flexible chemical nature and stability.[65-66]

167

168 **MOFs for the removal/storage of greenhouse gas (GHG): CO$_2$**

169 In last few years, a large number of MOFs were investigated to generate extensive

170 experimental data on the strategic adsorption of pollutants for industrial applications. The

171 adsorption, storage, and removal of CO_2 under standard temperature pressure (STP) conditions

172 have been reported for more than 130 MOFs (e.g., Cu-BTTri, CPO-27, HKUST-1, bio-MOF-11,

173 MIL-53, MOF-5, MIL-100, MIL-101, and YO-MOF).[67-71] The performance or capacity of CO_2

174 capturing by MOFs can be classified by the following criteria: open metal sites, flexible

175 chemical structure, and functionalization.[69] Likewise, the combination of open metal sites and H-

176 bonding donor-acceptor groups in MOFs should contribute to the efficient removal of other

177 gaseous pollutants as well. Functionalization or surface modification of MOFs (e.g., with

178 ethylene diamine and other alkyl amines) has been investigated to seek for the extension of their

179 applications in a more broad areas (as per discuss in Section 2).

180 In this section, the adsorption capacity of the modified/functionalized MOFs is explored for

181 low molecular weight gases at low pressure with a special emphasis on CO_2 **(Table 2)**.[72-82] For

182 examples, Britt et al. [72] investigated open magnesium sites based Mg-MOF-74 for the

183 CO_2 capture with 8.9 wt% dynamic capacity which underwent facile CO_2 release at significantly

184 lower temperature (80 °C). These results were obtained at ambient atmosphere and regeneration

185 of Mg-MOF-74 was also demonstrated on the breakthrough apparatus under N_2 atmosphere at

186 least 250 °C before use.[72] Recently, a highly robust unprecedented anionic MOF (JUC-132)

187 based on an aromatic 12-carboxyl ligand 1,3,5-tris(3,5-di(3,5-dicarboxy-phenyl-1-yl)-phenyl-1-

188 yl)benzene (H_{12}TDDPB) and two Cd clusters ($Cd_2(COO)_6$ and $Cd(COO)_4$) synthesis was

189 investigated for selective adsorption of CO_2 over CH_4.[73] JUC-132 exhibited high heat of

190 adsorption for CO_2 with high selectivity over CH_4 due to high interactions between CO_2 and

191 filling of dimethylammonium ions in the pores. He et al.[73] reported uptake values of activated

192 JUC-132 for CO_2 (2.72 mmol g^{-1} and 1.71 mmol g^{-1} at 1 atm) and CH_4 (0.28 mmol g^{-1} at 1 atm)

193 at different temperatures (273K and 278K, respectively).

194   To enhance the adsorption capacity of CO_2, the capacity of several virgin (and some

195   modified/functionalized) MOFs is compared in **Table 2.**[72-82] A simple modification or

196   functionalization of Mg(DOBDC) MOF was carried out with ethylene diamine (ED) to improve

197   the adsorption properties of CO_2 at low partial pressures.[76] Based on theoretical and

198   experimental analysis, these authors confirmed that one ED molecule was added to each unit cell

199   of Mg(DOBDC) MOF. This modification allowed improved CO_2 adsorption-desorption

200   temperature swings (give both low and hi temps) with increased CO_2 adsorption capacity at

201   ultra-low CO_2 partial pressures at 1 atm total pressure together with improved Mg(DOBDC)

202   MOF regenerability over 20 swings. According to this report, the first MOF was demonstrated to

203   yield significant adsorption capacities from simulated ambient air (e.g., 400 ppm CO_2 at 1 bar

204   pressure) compared to the common conventional adsorbents (e.g., amine-oxide composites).[76]

205   Similarly, diamine-functionalized en-Mg$_2$(dobpdc) was achieved through post modification to

206   yield the exceptionally high sorption capacities (e.g., 3.62 mmol g^{-1}, 13.7 wt% for both ambient

207   air (4.0x10^{-4} bar of CO_2) and typical post-combustion flue gas (0.15 bar of CO_2) at 1 bar.[76] The

208   adsorption of CO_2 onto the free amines of MOF/PCP led to the formation of carbamic acid

209   which significantly increased the CO_2 adsorption capacity. Finally, to facilitate the practical

210   utilization of MOF, the adsorption–desorption cycling of CO_2 was optimized at the real dilute

211   concentrations of air and flue gas.[76]

212   A pioneering work on the unprecedented mechanism of step-shaped isotherms was carried out

213   by McDonald et al. (2015).[80] Their study demonstrated that the replacement of Mg^{2+} with other

214   divalent metal ions (e.g., Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+}) can tailor the CO_2 adsorption isotherm

215   steps depending on the metal-amine bond strength. Here, the diamine-appended MOF/PCP

216   behaved as 'phase-change' adsorbents to facilitate the efficient capture of CO_2.[80] The CO_2

217   adsorption was thus improved via thermodynamically non-spontaneous reaction at low pressure

218   which had been demonstrated by spectroscopic, X-ray diffraction, and adsorption analysis.

219   Actually, the proton transfer and nucleophilic attack of N proceeded simultaneously on a CO_2

220   molecule to form ammonium carbamate. The amine coordination at the next metal site was then

221   destabilized by diamine-appended MOF/PCP to initiate the cooperative adsorption of CO_2 by a

222   chain reaction **(Figure 4).**[80]

223

224   **MOFs for the removal/storage of common gases and hazardous air pollutants (HAPs)**

225   The utilization of MOFs for low molecular weight gases other than CO_2 has also been studied

226   extensively for their storage potential (e.g., for H_2 and CH_4 as alternative vehicle fuels).[83-96]

227   Other adsorbent media for low molecular weight gasses (such as H_2, CH_4, N_2O, and N_2) using

228   various approaches have been tested. In this respect, Eddaoudi et al. (2001) reported a

229   remarkable improvement in CH_4 storage capacity by series of isoreticular MOFs (IRMOFs).[84]

230   Likewise, IRMOFs-6 with exceptionally high surface area and pore volumes was also tested for

231   sorption measurement (10 $mmol(CH_4).g^{-1}$ at 40 atm but at lower pressures, e.g., 1 atm, the

232   sorption is only ~0.4 $mmol (CH_4).g^{-1}$ implying good PSA performance at constant temperature

233   **(Figure 5 A & B)**.[84] In an analogous way, Duren et al. (2004) evaluated storage capacity of CH_4

234   based on molecular modeling of IRMOFs, two zeolites, MCM-41, and carbon nanotubes.[85]

235   Accordingly, the amount of adsorbed CH_4 per volume increased by 23% and 36%, when 1,4-

236   tetrabromobenzenedicarboxylate and 9,10-anthracenedicarboxylate were used as organic linkers,

237   respectively. Their experimental study underlined the usefulness of grand canonical Monte Carlo

238   (GCMC) simulations method as a screening tool to identify new materials for adsorption

239   applications and for the design of novel materials. For hydrogen adsorption studies, similar

240   approaches were also investigated.[86-87] Furthermore, GCMC simulation results demonstrated that

241   chemical structural properties in MOFs with unsaturated metal centers can be incorporated to

242   increase the magnitude of hydrogen interaction within their framework.[90] Such molecular

243   modelling method was also utilized to determine the adsorption of ammonia for a number of

244   MOFs (MIL-47, IRMOF-10, IRMOF-1, IRMOF-16).[87]

245   It is found that the selection of different functional groups (e.g., –OH, -NH$_2$, –COOH and

246   metal ions (Cu^{++}, Ag$^+$, Na$^+$ or K$^+$) can be made to enhance chemisorption hydrogen-bonding

247   between MOFs and ammonia for improved adsorbate removal.[88-96] For example, Britt et al.

248   (2008) investigated NH$_3$ adsorption and dynamic breakthrough using -NH$_2$ functionalized

249   MOFs (IRMOF-3).[91] The adsorption capacity of IRMOF-3 was found as 6.2 mmol g^{-1} which

250   was superior to the most commonly studied MOF-5 (0.35 mmol g^{-1}) as a reference. It may be

251   due to the presence of Zn$_4$O SBUs in MOF-5 which becomes unstable when exposed to

252   ammonia. However, in the case of IRMOF-3, the capacity of ammonia adsorption increased

253   due to hydrogen bonding between the −NH$_2$ pendant groups and ammonia.[90-92] In another

254   study, -OH functionalization of DUT-6 was found to improve the uptake of ammonia from

255   12.0 to 16.4 mmol g^{-1} at 1 bar and 298 K (**Figure 6 A & B**).[93] Such enhancement in sorption

256   capacity was accounted for by strong binding between ammonia and functional groups (−OH).

257   [93]

258   For the removal of ammonia from air, a number of Zr-based MOFs (UiO-66 (UiO-66-OH,

259   UiO-66-(OH)$_2$, UiO-66-NO$_2$, UiO-66-NH$_2$, UiO-66-SO$_3$H, and UiO-66-(COOH)$_2$) were also

260   investigated.[94] Comparison of performance was made between those Zr-based functionalized

261   MOFs synthesized by solvothermal method. Accordingly, different functional groups such as (-

262   OH, -NO$_2$, -NH$_2$, -SO$_3$H, and –COOH) played an important role in ammonia adsorption

263   processes under dry and humid (80% RH) conditions due to competitive interactions between

264   water and ammonia molecules for the active sites. Interestingly, –COOH and −SO$_3$H based

265   functionalization of Zr-MOFs showed lower ammonia capacity as compared to -OH and NH$_2$

266   (UiO-66-OH and UiO-66-NH$_2$) due to the presence of high and least bulky functional groups

267   which caused significant reduction in the framework porosity (surface area and pore volume),

268   respectively. Finally, the adsorption capacity of ammonia by UiO-66-OH was reported as

269   ~5.7 mmol/g under dry conditions.[94] The GCMC simulations were also carried out for the

270   practical applications of pressure swing adsorption (PSA) using a MIL-53 (Al). [94] These authors

271   investigated the feasibility of MOFs for methane purification at industrial-scale. The adsorption

272   capacity of MIL- 53 (Al) (4.3 mol.kg^{-1} at 3.5 bar) was assessed against CO_2 and CH_4 by dynamic

273   experiments in a fixed-bed reactor and 303 K). As MIL-53(Al)-based separation is found to be

274   highly energy-efficient, the proposed PSA was suggested as a promising option for the

275   separation of CO_2 and CH_4. [94]

276   MOFs have also been identified as attractive sorbent candidates for PSA separation of O_2.

277   Many research groups investigated the O_2 selectivity against H_2, CO_2, or N_2 based on the

278   tunability of MOFs with unsaturated metal centers (UMCs). [91-99] For example, the selectivity of

279   O_2 over N_2 was examined through utilization of two different MOFs ($Cr_2(BTC)_3$ vs.

280    $Fe_2(DOBDC)$) prototypical phases that have accessibility to UMCs for single gas sorption

281   studies at 298 K.[97] Likewise, the combination of experimental and molecular modeling was

282   tested more recently using metal-substituted Cu-BTC (HKUST-1) with enhanced O_2 selectivity

283   versus N_2.[97] Here, the structure-property relationship was examined between the metal centers

284   and the gas adsorption (O_2 or N_2) at variable temperatures (77 K vs. 273−298 K) **(Figure 7 A &**

285   **B)**.[97] A comparative analysis was also made for O_2 versus N_2 sorption capacities and binding

286   energy dependency on temperature based on density functional theory (DFT) calculations and

287   GCMC.[97] Moreover, MOFs have also been studied for purification and storage of C_1, C_2, and C_3

288   light hydrocarbons.[98-99] As part of such efforts, Fu et al. (2015) recently reported the FIR-51

289   (CPs/MOF) for selective sorption of light hydrocarbons (**Figure 8 A & B**).[99] The synthesized

290   MOF/PCP was highly stable (thermally and chemically) to exhibit high storage capacity (3.12 -

291   7.06 mmol g^{-1}) for light hydrocarbons with high selectivity for C_2 and C_3 over methane at 273

292   and 294 K (**Figure 8 B**). [99]

293   Presently, the efficient adsorption removal of hazardous air pollutants (HAPs) is one of the most

294   attractive research areas in AQM. This section summarizes the recent efforts made on the

295   adsorptive removal of those pollutants contained in fuel, water, and air by employing advanced

296   MOFs. For the adsorptive removal of H_2S, VOCs, and PAH, the feasibility of many MOFs (such

297   as Material de Institut Lavoisier (MIL), IRMOFs, and M-CPO) has been investigated intensively

298   (**Table 2)**. The interactions between HAPs and different MOFs should proceed via diverse

299   mechanisms; (a) adsorption through coordinately unsaturated site, (b) acid-base interaction, (c)

300   complex formation, (d) hydrogen bonds, (e) electrostatic interaction, and (f) lattice breathing.[99-

301   105]

302   Recently, amino functionalized UIO-66 was reported to absorb pyridines with the hydrogen

303   bonding and base-base repulsion in both liquid and vapour phases.[101] The possible interaction

304   between pyridine and amino functionalized UIO-66 is shown in **Figure 9 A**.[101] The temperature

305   effect on such absorption by functionalized UIO-66 is also illustrated in **Figure 9 (B, C, and**

306   **D).**[101] It was concluded that the uptake rate of pyridine increased for both vapor and liquid

307   phases in line with the amino group content in UiO-66s. The specific and favorable interactions

308   between pyridine and NH_2-UIO-66 should be carefully interpreted with the opening of pores of

309   UiO-66 with increasing temperature to accommodate pyridine.[95] Likewise, a number of other

310   similar studies are shown in **Table 2.** [100-105]

311   In a recent study, the absorption capacity of Cu-BTC was examined against three toxic

312   hydride gases (ammonia, arsine, and hydrogen sulfide) with the changes in its color **(Figure 10**

313   **A).**[105] The capacity of Cu-BTC for these hydride gases was determined from a micro-

314   breakthrough test using a real-world packed-bed with both dry and at high humidity conditions

315   **(Figure 10 B).**[105] These authors demonstrated the potential for Cu-BTC as an effective adsorbent

316   for ammonia. They also used it for sensing purposes through colorimetric and fluorescence

317   changes. Interestingly, a recent computational study on Cu-BTC has been made to validate its

318   potential for ammonia capture in the presence of water through quantum chemical methods.[104-105]

319   The free energies of binding were calculated for the first time for ammonia and water separately

320   with a series of metal catecholates (i.e. Be-, Cu-, Zn-, Pt-, and Pd-catecholates). As a result, Pt-

321   and Cu-catecholates were found as the excellent choice for ammonia capturing under humid and

322   dry conditions, respectively.[101-105]

323

324   **MOFs for catalytic degradation -Fundamental aspects and mechanism**

325   In **Table 3,** a list of MOFs employed for the catalytic degradation of airborne pollutants are

326   summarized based on the synthesis processes, active metal ions, and the basic mechanism.[107-114]

327   As long as the precise synthesis plan is established and used, different catalytic sites can be

328   tailored in MOFs such as (A) embedding of their active sites in the cavities, (B) the use of

329   postsynthetic methods, and (C) incorporation (or encapsulation) of guest species (such as

330   functional group, metal nanoparticles, and other guest molecules) (**Figure 11**).[45]

331   Recently, Al, Zn, Fe, Zr, and Cu-based MOFs have been utilized for photo-catalytic

332   applications to degrade chemicals (of varying toxicity) such as phenols, alcohols, and toxic

333   chemical warfare agents (CWA) (**Figure 12**).[8] For example, Wang et al. first reported UiO-67

334   (Zr-MOF) heterogeneous catalyst for the photocatalytic reduction of CO_2, water oxidation, and

335   visible light-driven organic photocatalysis (**Figure 13 (A & B))**.[106] This doped MOF/PCP

336   behaved like efficient aerobic oxidation catalyst for thioanisole, as shown in the **Figure 13 B.**[106]

337   Moreover, the doped MOF is convenient to reuse for heterogeneous catalysis, while effective

338   enough to provide mechanistic insights into CO_2 reduction.[106] Similarly, Shen et al. reported

339   efficient visible-light-driven photocatalysis for selective oxidation of alcohols with the reduction

340   of aqueous Cr(VI) using a multifunctional Zr-2-NH_2-benzenedicarboxylate (UiO-66(NH_2)).[107] In

341   another study, photocatalytic degradation of organic pollutants was also achieved by the

342   chemical oxidation with strong oxidative agents. Because of the transition metal species present

343   in MOFs, oxidants can be generated for the activation of free radicals. For example, MIL-53(Fe)

344   was tested for the decolorization of methylene blue (MB) dye.[108] MIL-53(Fe) exhibited the first-

345   order kinetics in the photocatalytic decolorization of MB.[108] The rate of photocatalysis decreased

346   in the order of (H_2O_2 > $(NH_4)_2S_2O_8$ > $KBrO_3$) under the normal UV–vis light irradiation.

347   However, under visible light irradiation, its ordering changed to $(NH_4)_2S_2O_8$ > H_2O_2 > $KBrO_3$.

348   Interestingly, MIL-53(Fe) showed the first-order kinetics with the rate constant (0.0133 min^{-1}

349   and 0.0036 min^{-1}) which is comparable with TiO_2 under UV–vis light and visible light

350   irradiation, respectively. [108]

351

352   **MOFs as media for catalytic degradation of air pollutants**

353   Although a number of MOFs have been employed for catalytic treatment, there are only a few

354   reports that actually covered or described their applications toward diverse air pollutants. Many

355   excellent features of MOFs (such as controlled fine structure, dispersion of active sites, high

356   crystallinity, and no theoretical pore size limitations) have been recognized for catalytic

357   applications.[109-119] However, to employ these advanced materials in such aspect, one has to

358   overcome the major conventional problems such as secondary emissions after adsorbent

359   saturation.[8-9, 109-115] Nonetheless, the versatile nature of MOFs is advantageous to use in a variety

360   of catalytic degradations. For example, Ferey et al. (2005) demonstrated the potent role of

361   nanoporous metal-organic framework (e.g., MIL-101) through immobilization of Keggin

362   heteropolytungstate within the cages of the framework.[116] Interestingly, a rigid crystal structure

363   of MOF with large pores and outstanding surface area exhibited a great structural resistance to

364   air, water, and common solvents with thermal treatment.[116]

365   The potential role of MOFs as photocatalytic agent has been proposed for artificial

366   photosynthesis wherein gaseous CO_2 can be converted into useful products.[98-103] However, as of

367   now, MOFs have not been studied intensively with that respect. For example,

368　$[Re^I(CO)_3(dcbpy)Cl]-Zr_6O_4(OH)_4(bpdc)$ MOF yielded carbon monoxide from CO_2 and H_2O at a

369　rate of 42 μmol $(CO).h^{-1}.g^{-1}$ under 450 W Xe lamp irradiance. [117] In a practical sense, one may

370　consider a hypothetical case in which a 500 MW power station burning coal (specific energy

371　content of 24 $MJ.kg^{-1}$ and 85% carbon content) is operating at 50% thermal efficiency.[106-119]

372　Then, the amount of CO_2 produced from such operation would correspond to 11,000 $tonne.day^{-1}$.

373　Hence, in order to convert $CO_2 + 2H_2O$ into CH_4 and $2O_2$ (ΔH = 890 $kJ.mol^{-1}$ (NIST)), the area

374　of a hypothetical MOF/PCP/solar farm, operating at 100% quantum efficiency and 12-hour

375　averaged solar irradiance of 100 $W.m^{-2}$, should be ~52 km^2 (maximum CO_2 uptake is 215 $g.day^{-}$

376　^{1}). If the following conditions are taken (MOF catalyst bed = 1 mm deep, MOF density = 0.5

377　$g.m^{-3}$, and MOF cost = 2000 $USD.ton^{-1}$), then the amount required and cost would be ~26,300

378　tonnes and 53 B USD, respectively. Based on this proposed hypothetical case for utilization of

379　MOF/solar farm area, conversion of CO_2 into useful products is impractical for industrial

380　applications. In other sense, this area still needs to put immense efforts to meet economic

381　feasibility.

382

383　**The use of MOF for catalytic degradation of chemical warfare**

384　 MOFs have also been investigated for the catalytic degradation of chemical warfare agents

385　(CWA) due to huge environmental contamination problem after their deployment.[107-121] Usually,

386　redox or acid-base active MOFs have been used as catalyst agents for degradation processes.

387　Interestingly, CWAs can be degraded either by oxidation and as well as by hydrolysis after

388　exposure. For the interested readers, catalytic degradation mechanisms for selected CWAs can

389　be found in a study by Mondloch et al. (2015) (**Figure 14**).[110] These authors reported both

390　experimental and computational analysis of catalytic hydrolysis of the nerve agent stimulants

391　like dimethyl 4-nitrophenyl phosphate (DMNP) and O-pinacolyl methylphosphonofluoridate

392　(Soman) using NU-1000 and NU-1000-dehyd (Zr-MOFs), respectively.[110] In their experimental

393   study, catalytic hydrolysis of DMNP by NU-1000 was carried out efficiently in aqueous N-

394   ethylmotpholine buffered solution (at pH 10) with the formation of p-nitrophenoxide monitored

395   by visible-region adsorption spectroscopy at E_{max} = 407 (**Figure 14 A & B**).[110] In this report,

396   computational simulations have also been investigated on soman and O-ethyl S-

397   diisopropylaminoethyl methylphosphonothiolate (VX) using Cr-MOFs. Cr-MOFs was the fastest

398   heterogeneous catalyst of all tested MOFs (e.g., HKUST-1) due to the π-stacking behaviour of

399   DMNP and more general attractive van der Waals interactions between organic linker and alkyl

400   group of GD or its analog.[110]

401   Catalytic degradation of diisopropylfluorophosphate (DIFP) sarin simulant was also

402   investigated similarly using both NH_2-MIL-53(Al) and NH_2-MIL-101(Al) (Al-NH_3-MOF)

403   through the incorporation of highly nucleophilic 4-methylaminopyridine residues.[119] This

404   progressive strategy was developed by depositing the MOF particles on a reactive adhesive

405   material composed of polyisobutylene/toluene diisocyanate (PIB/TDI) blends. These modified-

406   MOFs exhibited highly mechanical flexibility with the capability of degrading diisopropyl

407   fluorophosphates (DFP) due to their reactivity between the covalent attachment to protective

408   surfaces.[113]

409   The detoxification of some CWAs (e.g., VX and soman) by HKUST-1 (Cu-MOF) was

410   monitored by NMR.[113] However, Cu-MOFs underwent slow degradation of these CWAs (more

411   than one day (VX) and 13 hr. (soman)) due to the Lewis acidic nature and the presence of Cu

412   open metal sites. This type of the interaction was found to be crucial in determining the

413   hydrolysis processes between Cu-MOF and CWAs.[113] It was also found that the catalytic activity

414   of $H_3[(Cu_4Cl)_3(btc)_8]_2[PW_{12}O_{40}]_3(C_4H_{12}N)_6$ (NENU-11) should be stimulated by the

415   incorporation of acid polyoxometalates in the pore structure.[113] Consequently, NENU-11

416   exhibited the good sorption behavior (15.5 molecules per formula unit) for a model nerve agent

417   dimethylmethylphosphonate (DMMP) while facilitating its decomposition (**Figure 15**).[113]

418

419   **Summary**

420   It is found that most MOFs reported recently in the literature (2005 – 2015) have a number of

421   shortcomings for AQM applications. Most of these studies generally lacked a systematic

422   approach to evaluate practical performance metrics in some important respects, e.g., (a) low final

423   product cost and well established synthesis methods, (b) hydrothermal stability, (c) chemical

424   stability towards humidity and temperature, (d) simple regeneration at low energy penalty, and

425   (e) recycling and disposal of spent material. Because of such a research gap in this emerging

426   area, one needs a systematic evolution of MOFs for air purification to comply with international

427   guidelines (e.g., OSHA/NIOSH). Furthermore, it is very important that every investigation on

428   the MOFs for air purification be evaluated at partial pressures of environmental pollutants at

429   ambient air pressure (1 bar). However, such specific conditions for the adsorption are found to be

430   difficult to attain to cover all different permanent and/or toxic gases (such as CO_2, O_2, ammonia,

431   sulfur dioxide, chlorine, iodine and cyanogen chloride) due to the physical interaction of

432   functional groups of MOFs. Therefore, specific chemistry of MOFs needs to be specified for

433   any practical application in AQM.

434   The functional tailorability of MOFs is recognized as a great merit to offer improved

435   performance for capturing and storage of gaseous pollutants over conventional materials (such as

436   MEA, activated carbon, or other filtration media). In addition, direct and low cost functional and

437   hierarchical pore structures of MOFs are desirable for developing novel approaches for post

438   synthetic modification (such as controlled etching). Such applications may open a great

439   opportunity for their practical implementation at industrial scale. It is anticipated that in the near

440   future, research and development on MOFs will find its special need to fulfill various demands

441   for AQM.

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451   **BIOGRAPHIES**

Dr. Pawan Kumar obtained his Ph.D. (Engineering) from the Academy of Scientific and Innovative Research - Central Scientific Instruments Organization (AcSIR-CSIO), Chandigarh (India). He has more than one year of post-Ph.D. experience in the fields of nanotechnology, analytical and environmental engineering and is currently involved in the different projects such as development of, novel electrode materials for high energy density storage devices, sensors, porous materials based environmental, and clinical applications. His research interests also

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465

Prof. Ki-Hyun was at Florida University for an M.S. in 1986 and received a PhD from Marine & Atmospheric Science at University of South Florida in 1992. He was a Research Associate at Oak Ridge National Lab., USA from 1992 to 1994 and then an Assistant Professor at the Sang Ji University, S. Korea from 1995 to 1998. In 1999, he joined the Dept of

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482

483 **Prof. Kwon** completed his Ph.D. in the Department of Earth

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495

496

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505 He has modified and built a number of mass spectrometers. In January 2001, he first joined the

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507   interfacing of a gas chromatograph (GC) to an FT-ICR MS (GC/FT-ICR MS) for environmental

508   and breath analysis. He is the lead co-author of a 2010 review on the efficacy of breath analysis

509   for cancer diagnosis (IEEE Sensors J., vol. 10, pp 185-210). In 2012, he joined as a research

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511   he moved to Hanyang University with Prof. K.-H. Kim's laboratory and is currently a professor.

512   Since 2012, his research interests include air quality management, air pollution, climate change,

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514   performance. He has published over 60 scholarly articles in SCI journals.

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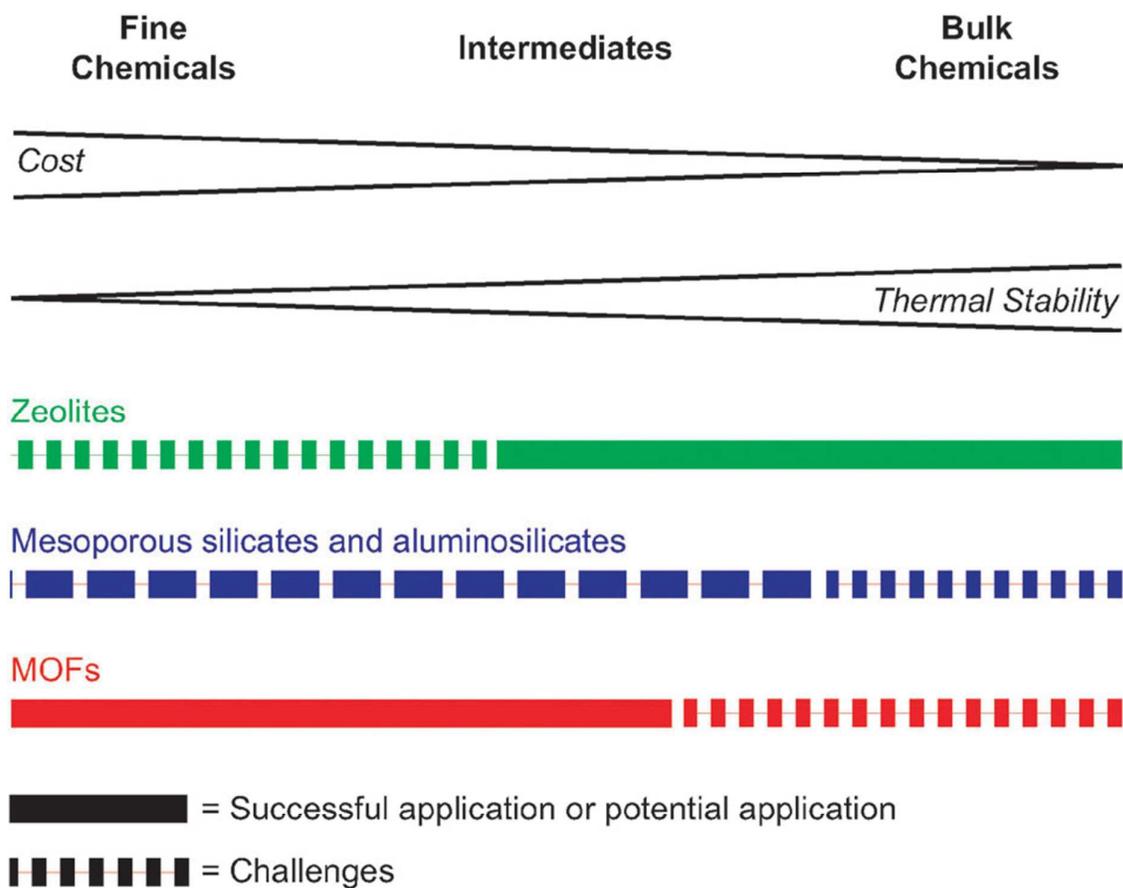
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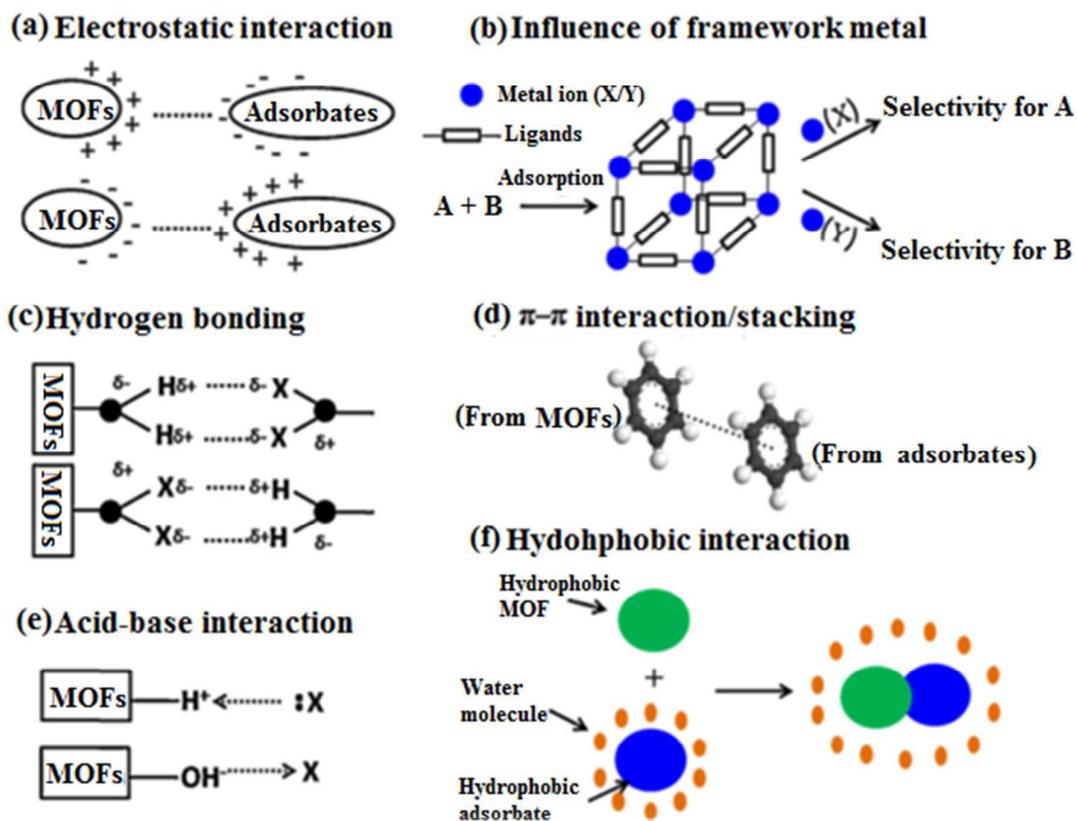
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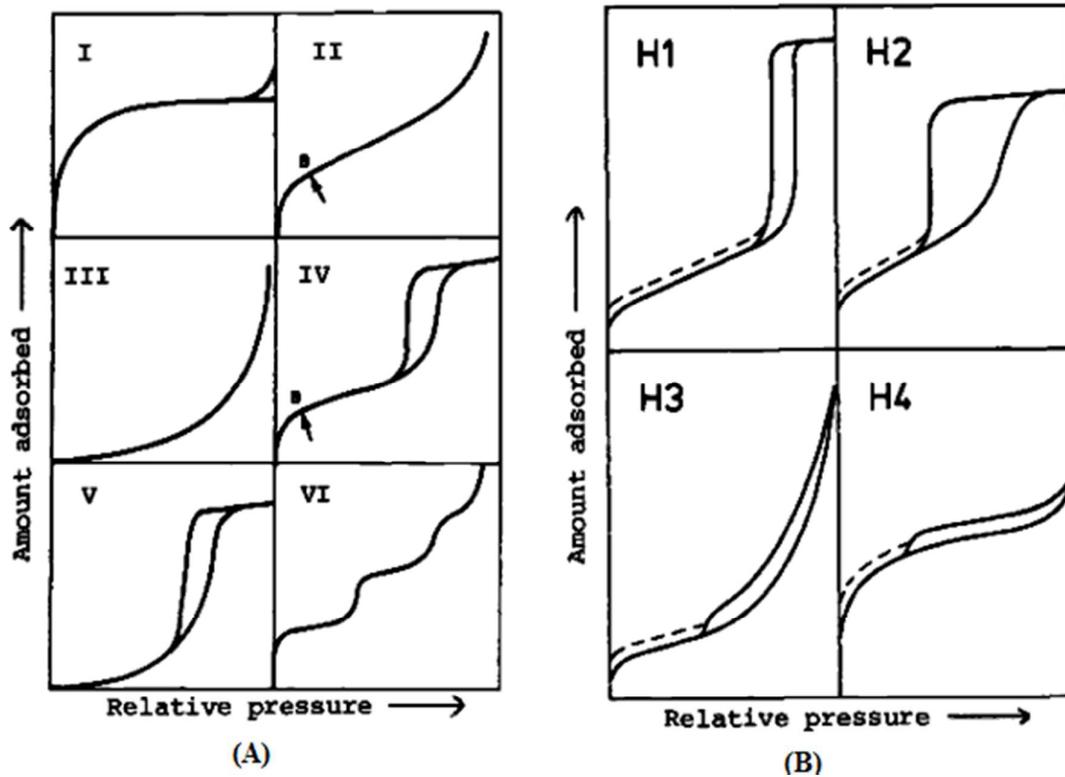
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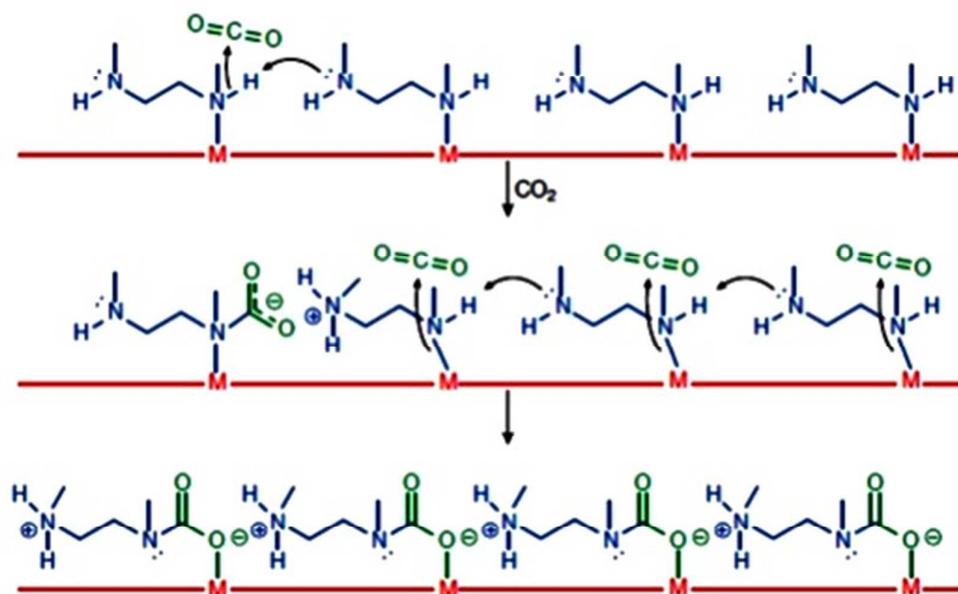
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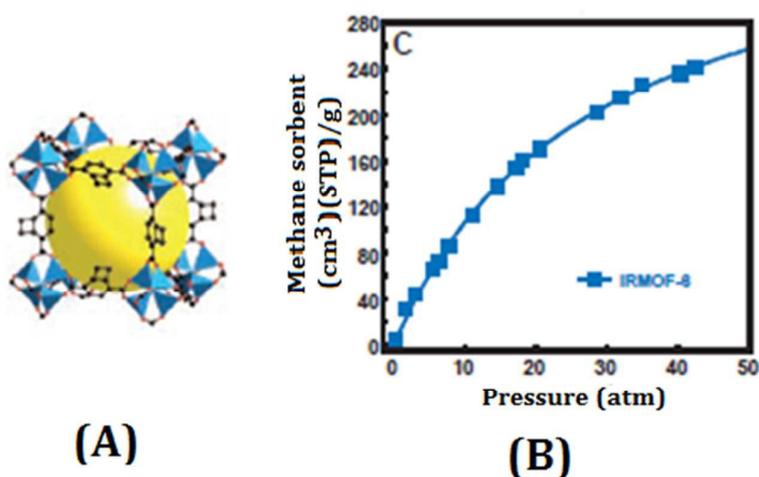
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(B)
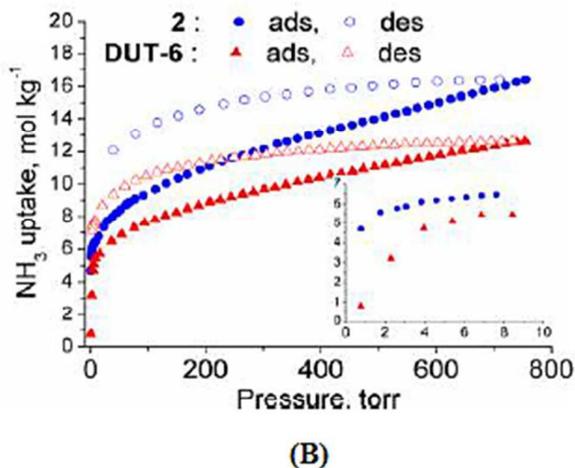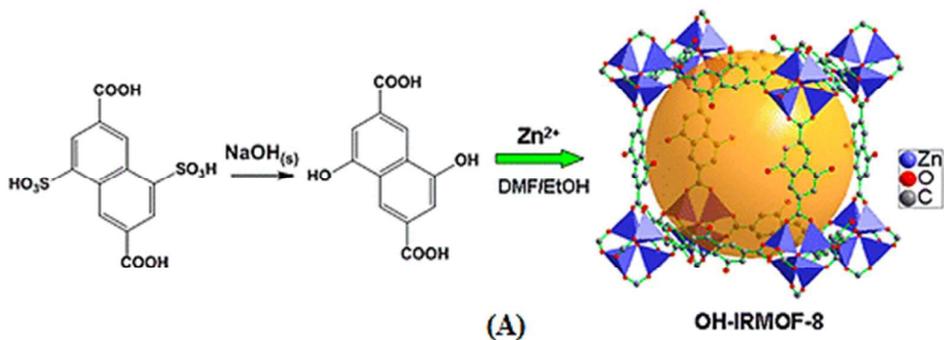
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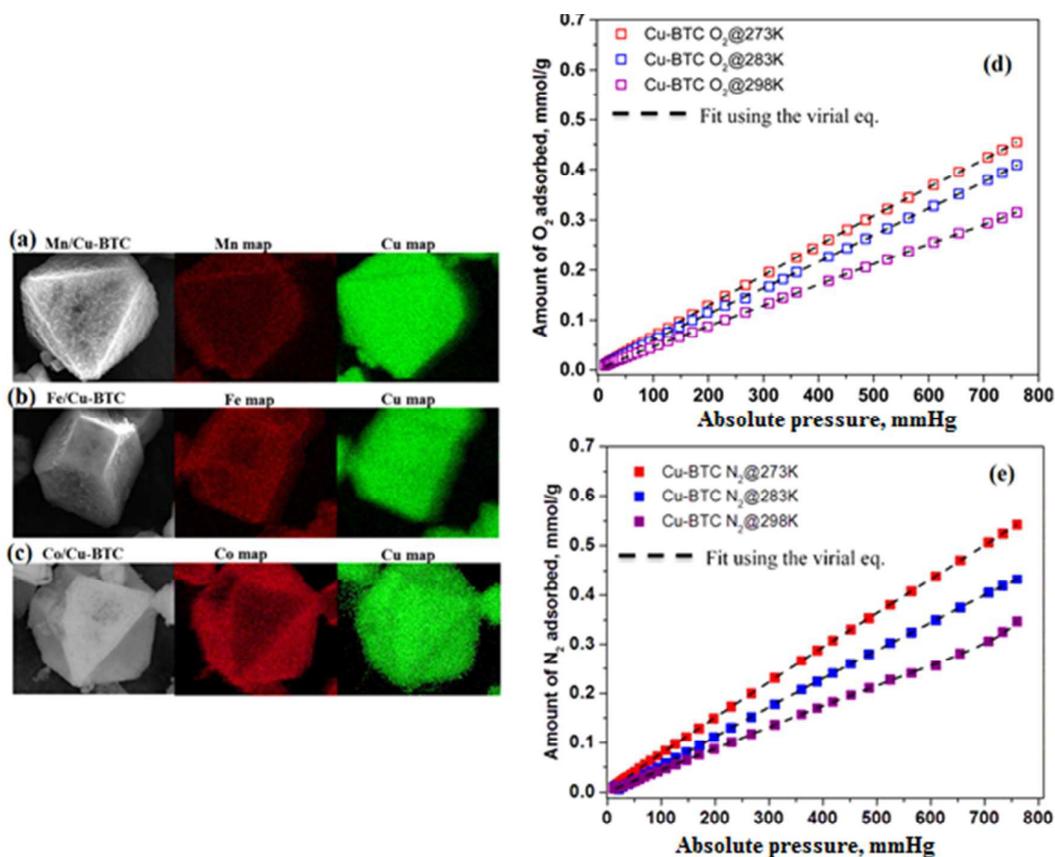
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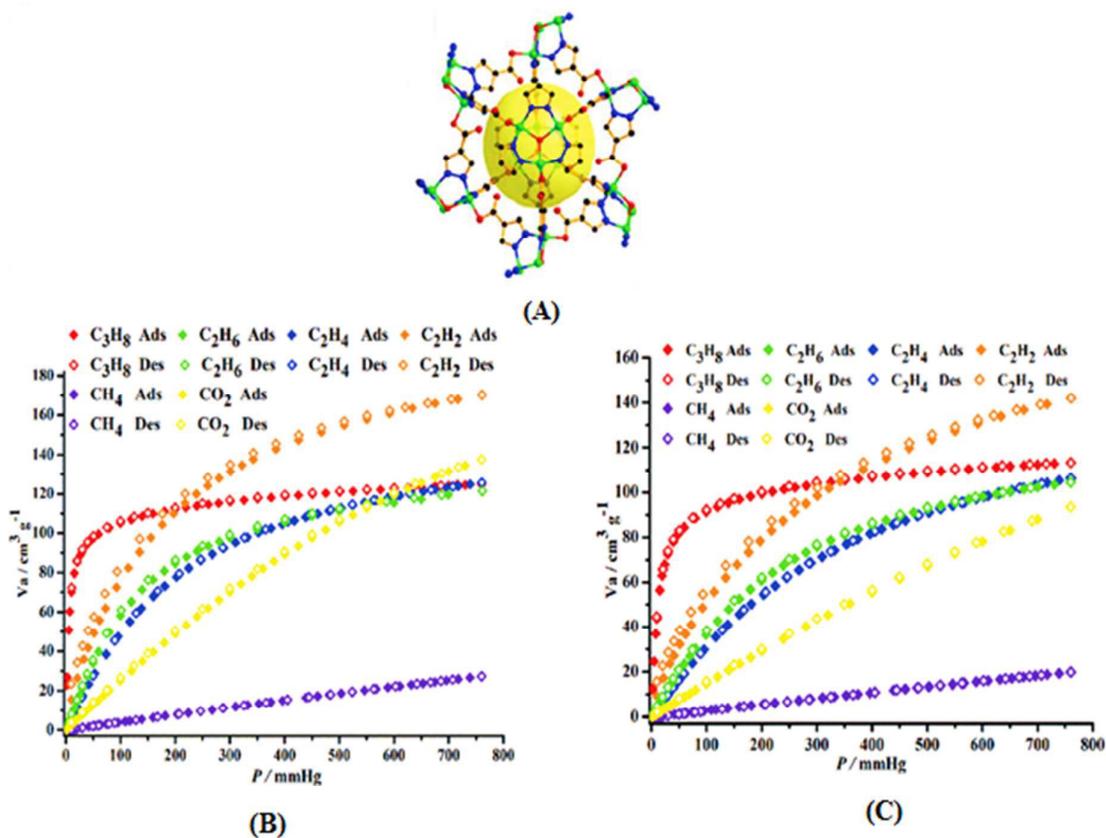
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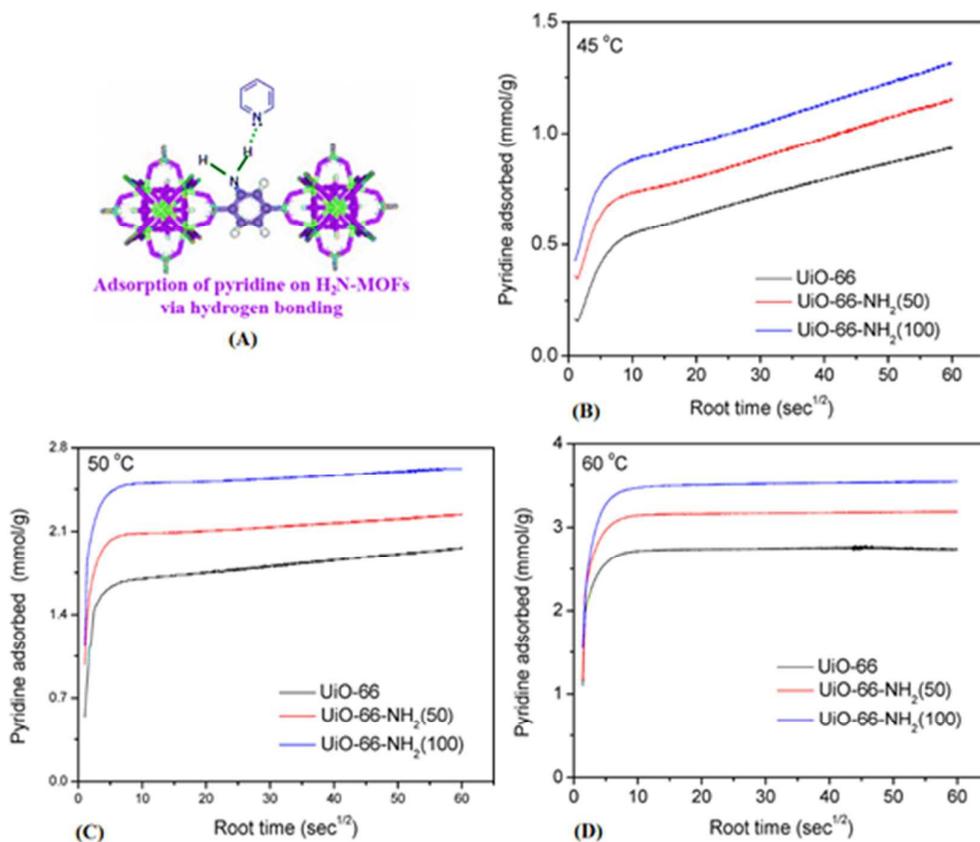
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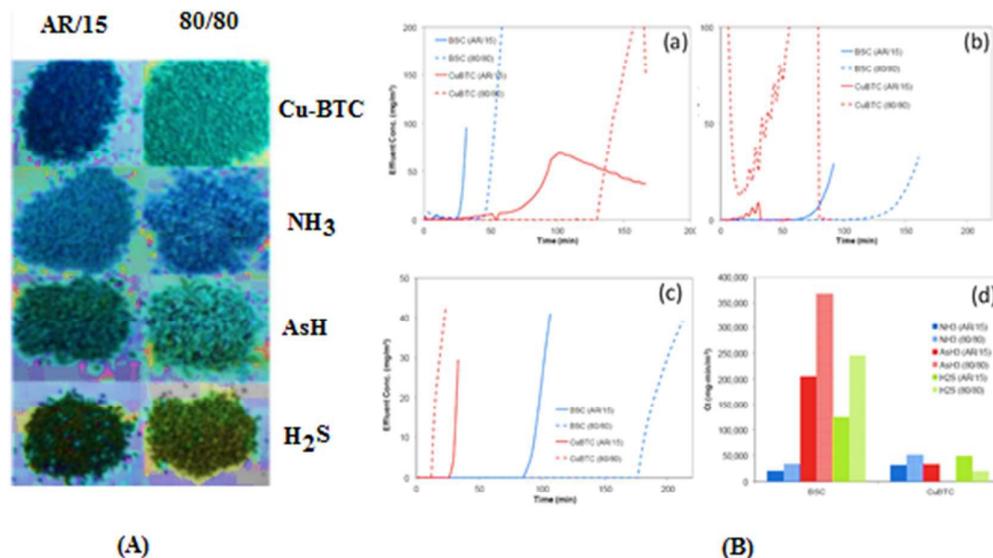
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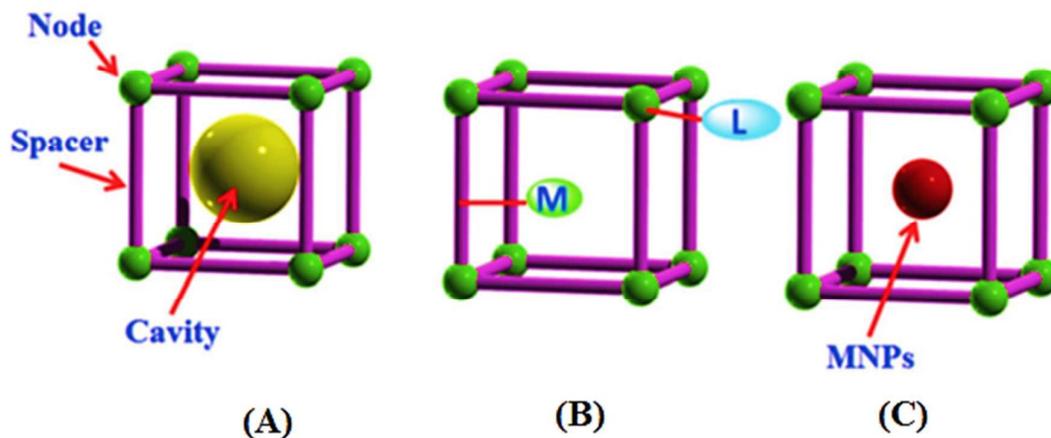
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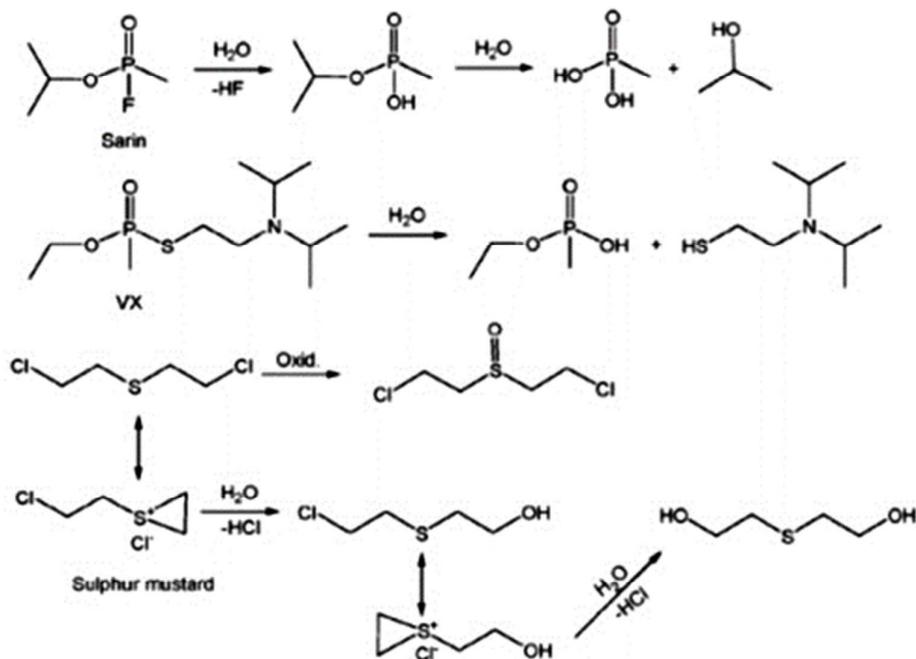
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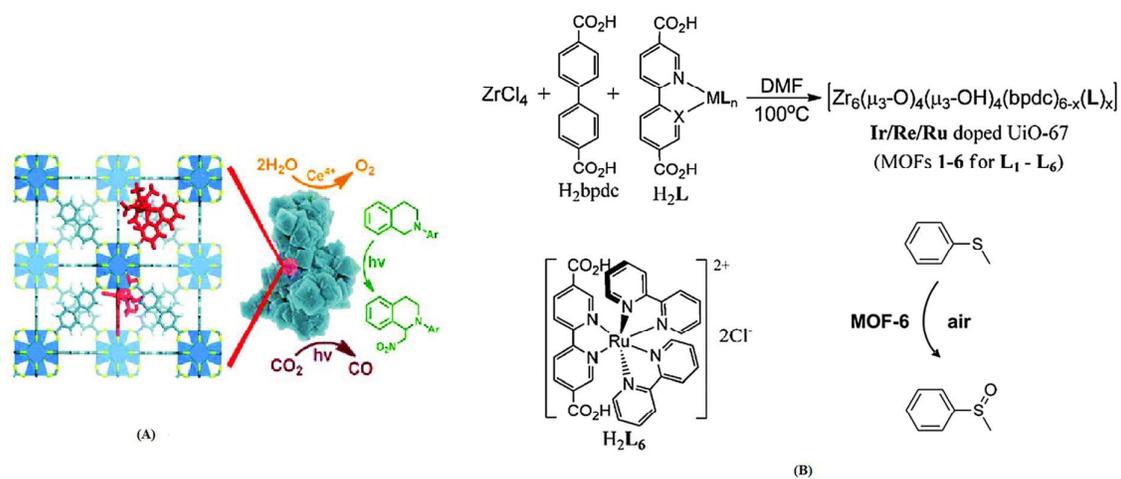
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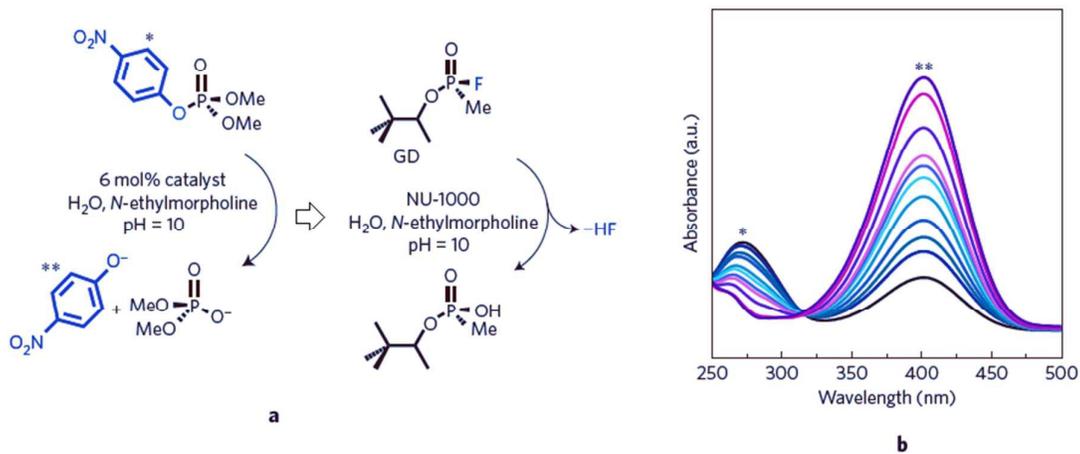
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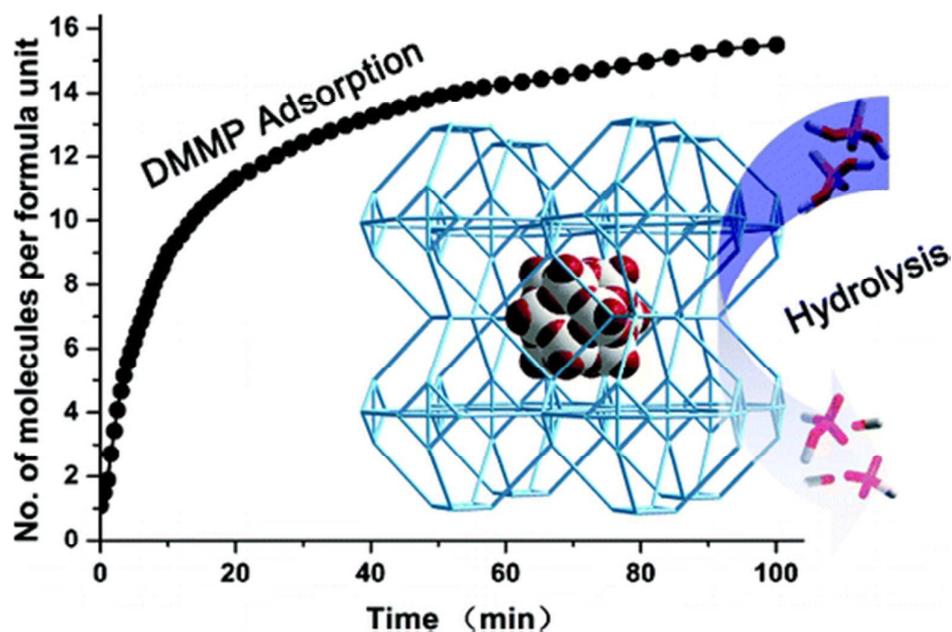
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Tables

Table 1. A list of conventional materials with respect to their CO_2 adsorption capacities.

Order	Conventional materials	Name	Experimental conditions Temp. (K) / CO_2 partial pressure (bar)	CO_2 adsorption capacity (mmol g^{-1})	Analytical Method	Reference
1	Activated Carbon	GAC[a]	298/0.1	0.057	Gas chromatography	53
2	Calcium oxides	CaO and Rb/CaO	723/0.4	4.5	Thermogravimetric analysis	54-55
3	Zeolites	APG-11[b]	393/0.15 (Humid)	0.38	Mass spectrometer	56
4	Silica	SBA-15[c]	333/0.15	0.03	Gas chromatography	57
5	Lithium Zirconates	Li_2ZrO_3	773/0.02	4.5	Thermogravimetric analysis	58
6	Organic Hybrid Adsorbents	DETA[d]	298/1	0.91	Thermogravimetric analysis	59

[a]GAC = Granular Activated Carbon,
[b]SBA-15 = Aminosilane-modified Zeolite
[c]APG -11 = Na [(AlO) (SiO$_2$)]-xH.O,
[d]DETA = Diethylentriamine

Table 2. MOFs used as sorptive media for the treatment of airborne pollutants.

A. Major targets: CO_2, O_2, CH_3, and NH_3

Sr. No.	MOF	Mechanism	Synthesis	Performance/ Capacity (mmol g^{-1})	Experimental conditions (Temperature /Pressure)	Reference
1	Mg-MOF-74	Metal Substitution	Solvothermal	8	296K at 1 bar	72
2	JUC-124	π–π stacking	Hydrothermal	2.72 &1.71	273+293K at 1 bar	72
3	Co-MOF-74	Weak physisorption interactions	Solvothermal	5.66	298K at 1 bar	74
4	MOF-5	Postsynthesis thermal annealing	Solvothermal	2	293 K at 1 bar	75
5	MIL- 53 (Al)	CO_2	Pressure swing adsorbation (PSA) process	4.3	303 K at 3.5 bar	76
6	EN-Mg$_2$(dobpdc)	Weak physisorption interactions	Hydrothermal	4.57 (16.7 wt%), 3.00 (11.7 wt%)	298+423 K at 1 bar	77
7	Amine- Mg(DOBDC) MOF	Weak physisorption interactions	Hydrothermal	9.09	-	78
8	QI-Cu-MOF	Hydrophobic Interaction	Solvothermal	4.56	293 K at 1 bar	79
9	NOTT-101	Hydrophobic	Solvothermal	3.93	293 K at 1 bar	80

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		Interaction				
10	M(dobpdc) (M = Mg, Mn, Fe, Co, Zn) Diamine-appended MOF/PCP	Thermodynamically non-spontaneous reaction (low P)	Solvothermal	2.2–2.3 MJ per kg (regeneration energies of $Mg_{2(}$dobpdc) and mmen-Mn_2(dobpdc) for CO_2 captured)	-	81
11	{Zn(bpydb)(bpy)}n (amino- and pyridine-functionalized pores)	Mixed-ligand strategy	Hydrothermal	3.6	273K at 1 bar	82

B. MOF for CH_4 treatment

12	IRMOFs series (1-16)	Weak physisorption interactions	Solvothermal	240 cm^3/g at standard temperature and pressure	298 K and 3.6 atm	83
13	IRMOF-1 and IRMOF-6	π–π stacking/interaction	Solvothermal	217.45 and 208.39 cm^3(STP)/g	273K at 3.5 bar	84

C. MOF for NH_3 treatment

14	Cu-MOF/GO		Solvothermal	8 m	-	88
15	HKUST-1		Solvothermal	6.8	348K at 1 bar	89
16	IRMOF-3	Electrostatic interaction	Solvothermal	6.2	293K at 1 bar	90
17	MOF-5		Solvothermal	0.35		91
18	MOF-5 and MOF-177	Electrostatic interaction	Hydrothermal	12.2	-	92
19	DUT-6	Hydrogen	Hydrothermal	13.6	273 K	93

No.	MOF			Value	Conditions	Ref
			bonding interaction		at 1 bar	
20	Zr-based MOFs		Hydrothermal	5.7		94
21	IRMOF-8		Hydrothermal	16.4	298K at 1 bar	97
D. MOF for O$_2$ treatment						
22	Cu-BTC		Hydrothermal		77 K, 273−298 K	97
23	(Cr$_2$(BTC)$_3$	Unsaturated metal centers based mechanism	Hydrothermal		273K at 1 bar	98
24	Fe$_2$(DOBDC))		Hydrothermal		273K at 1 bar	98
25	FIR-51	Light hydrocarbons	Acid-base interactions	3.12 - 7.06	273 K at 1 bar	99
E. MOF for other targets by Hydrothermal synthesis						
26	MIL-101-Cr	Anionic dye or Methyl orange	Electrostatic interaction	2.59	273K at 1bar	100
27	ED-MIL-101-Cr and PED-MIL-101-Cr	Anionic dye or Methyl orange		3.86 and 4.40	273K at 1bar	101

28	NH$_2$-MIL-101-Al	Methyl blue and orange	Electrostatic interaction	17.31 and 4.27	-	102
29	MOF-235	Anionic dye or Methyl orange		10.84 and 4.25	-	103
30	Cu-BTC	Quantum chemical methods	Solvothermal	−82.32 kJ/mol	-	104
31	Cu-BTC		Solvothermal	−81.48 kJ/mol		105
32	Metal catecholate (Be-, Cu-, Zn-, Pt-, and Pd-catecholates) Based MOFs		Solvothermal	2.10 and 1.36 mmol/g	-	109

F. MOF for other targets by solvothermal method

33	MIL-101-Cr and ZIF-8	Uranine	Electrostatic interaction	2.86 and 2.27	-	116
34	MIL-101-Cr	Xylenol orange	Electrostatic interaction	7.06	-	117
35	NH2-UIO-66	NH$_3$, H$_2$S, and arsine	Hydrogen bonding	1.13-2.27	353 K at 1 bar	118
36	Cu-BTC	Pyridine	π–π stacking/ interaction	7.8 (Dry) and 7.7 (Humid)	373K at 1 bar	119

Table 3. Functionalized MOFs utilized for catalytic treatment media of airborne pollutants

Sr. No.	Target Pollutants	CP/MOFs	Active metal ions	Catalytic mechanism/ strategies	Reference
A. Solvothermal synthesis					
1	CO_2 and Thioanisole	UiO-67	Ir, Re, and Ru	Photocatalytic reduction	106
2	Alcohols	UiO-66(NH_2)	Zr	Visible-light-driven photocatalysis	107
3	Methylene blue	MIL-53(Fe)	Fe	UV–vis light irradiation	108
4	DMNP and Soman	NU-1000		Hyderogeneous catalyst	109
		NU-1000-dehyd (Zr-MOFs)	Zr		
5	VX and soman	HKUST-1	Zr, Cu	Hydrolysis process	110
B. Hydrothermal synthesis					
6	DIFP and DFP	NH_2- MIL-101(Al)	Fe, Al	Hyderogeneous degradation	111
7.	DMMP	NH2-MIL-53(Al)) and NENU-11	Cu	Hydrolytic degradation	112
8	DMMP	NH_2-MIL-53(Al)	Fe	Hyderogeneous catalyst	113
9	Aldehyde acetalization with ethanol	CHS@MOF	Cu	Self-template strategy	114

Metal organic frameworks for the control and management of air quality: Advances and future direction

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