Turnitin Originality Report

Metal–Organic Frameworks and Their Hybrid Composites for Adsorption of Volatile Organic Compounds by Shella Santoso

From Similarity Check (check paper Jakad SPS)

Processed on 28-Feb-2022 15:40 WIB
ID: 1772794070
Word Count: 14210

Similarity Index	Similarity by Source	
7%	Internet Sources:	N/A
	Publications:	7%
	Student Papers:	N/A

sources:

1 1% match (publications)
"Front Matter", Wiley, 2020

2 1% match (publications)
Nicholas C. Burtch, Himanshu Jasuja, Krista S. Walton. "Water Stability and Adsorption in Metal–Organic Frameworks", Chemical Reviews, 2014

3 < 1% match (publications)
Konstantin I. Hadjiivanov, Dimitar A. Panayotov, Mihail Y. Mihaylov, Elena Z. Ivanova et al. "Power of Infrared and Raman Spectroscopies to Characterize Metal-Organic Frameworks and Investigate Their Interaction with Guest Molecules", Chemical Reviews, 2020

4 < 1% match (publications)
Lida Hashemi, Ali Morsali. "Pillared Metal-Organic Frameworks", Wiley, 2019

5 < 1% match (publications)
Ahmed, Imteaz, and Sung Hwa Jhung. "Applications of metal-organic frameworks in adsorption/separation processes via hydrogen bonding interactions", Chemical Engineering Journal, 2016.

6 < 1% match (publications)
"Materials and Processes for CO2 Capture, Conversion, and Sequestration", Wiley, 2018

7 < 1% match (publications)
He, Wen-Wen, Guang-Sheng Yang, Yu-Jia Tang, Shun-Li Li, Shu-Ran Zhang, Zhong-Min Su, and Ya-Qian Lan. "Phenyl Groups Result in the Highest Benzene Storage and Most Efficient Desulfurization in a Series of Isostructural Metal-Organic Frameworks", Chemistry - A European Journal, 2015.

8 < 1% match (publications)
Myunghyun Paik Suh, Hye Jeong Park, Thazhe Kootteri Prasad, Dae-Woon Lim. "Hydrogen Storage in Metal–Organic Frameworks", Chemical Reviews, 2011

9 < 1% match (publications)
Vanish Kumar, Suresh Kumar, Ki-Hyun Kim, Daniel C.W. Tsang, Sang-Soo Lee. "Metal organic frameworks as potent treatment media for odorants and volatiles in air", Environmental Research, 2019

10 < 1% match (publications)

"Handbook of Porous Solids", Wiley, 2002

---

11 < 1% match (publications)

Kowsalya Vellingiri, Akash Deep, Ki-Hyun Kim. "Metal–Organic Frameworks as a Potential Platform for Selective Treatment of Gaseous Sulfur Compounds", ACS Applied Materials & Interfaces, 2016

---

12 < 1% match (publications)

"Physiology and Genetics", Springer Science and Business Media LLC, 2018

---

13 < 1% match (publications)

Xiaoling Ma, Wenlong Wang, Chenggong Sun, Hui Li, Jing Sun, Xin Liu. "Adsorption performance and kinetic study of hierarchical porous Fe-based MOFs for toluene removal", Science of The Total Environment, 2021

---

14 < 1% match (publications)

"Biotechnology Set", Wiley, 2001

---

15 < 1% match (publications)

Xuejiao Sun, Qibin Xia, Zhenxia Zhao, Yingwei Li, Zhong Li. "Synthesis and adsorption performance of MIL-101(Cr)/graphite oxide composites with high capacities of n-hexane", Chemical Engineering Journal, 2014

---

16 < 1% match (publications)

Felipe Gándara, Alberto García-Cortés, Concepción Cascales, Berta Gómez-Lor et al. "Rare Earth Arenedisulfonate Metal−Organic Frameworks: An Approach toward Polyhedral Diversity and Variety of Functional Compounds", Inorganic Chemistry, 2007

---

17 < 1% match (publications)

"Handbook of Marine Macroalgae", Wiley, 2011

---

18 < 1% match (publications)

Felipe Gándara, Enrique Gutiérrez Puebla, Marta Iglesias, Davide M. Proserpio, Natalia Snejko, M. Ángeles Monge. "Controlling the Structure of Arenedisulfonates toward Catalytically Active Materials", Chemistry of Materials, 2009

---

19 < 1% match (publications)

Xin Zhou, Wenyu Huang, Jinpeng Miao, Qibin Xia, Zhijuan Zhang, Haihui Wang, Zhong Li. "Enhanced separation performance of a novel composite material GrO@MIL-101 for CO2/CH4 binary mixture", Chemical Engineering Journal, 2015

---

20 < 1% match (publications)

Lucia Oro, Erica Feliziani, Maurizio Ciani, Gianfranco Romanazzi, Francesca Comitini. "Volatile organic compounds from Wickerhamomyces anomalus , Metschnikowia pulcherrima and Saccharomyces cerevisiae inhibit growth of decay causing fungi and control postharvest diseases of strawberries", International Journal of Food Microbiology, 2018

---

21 < 1% match (publications)

Barea, Elisa, Carmen Montoro, and Jorge A. R. Navarro. "Toxic gas removal – metal–organic frameworks for the capture and degradation of toxic gases and vapours", Chemical Society Reviews, 2014.

22 < 1% match (publications)

Eva Martínez-Ahumada, Alfredo López-Olvera, Vojtech Jancik, Jonathan E. Sánchez-Bautista et al. " MOF Materials for the Capture of Highly Toxic H S and SO ", Organometallics, 2020

23 < 1% match (publications)

Jiang, Zhongwei, and Yuanfang Li. "Facile synthesis of magnetic hybrid Fe3O4/MIL-101 via heterogeneous coprecipitation assembly for efficient adsorption of anionic dyes", Journal of the Taiwan Institute of Chemical Engineers, 2016.

24 < 1% match (publications)

Patricia Horcajada, Ruxandra Gref, Tarek Baati, Phoebe K. Allan et al. "Metal–Organic Frameworks in Biomedicine", Chemical Reviews, 2011

25 < 1% match (publications)

Gopalram Keerthiga, Peramaiah Karthik, Bernaurdshaw Neppolian. "Application of Metal–Organic Framework and Their Derived Materials in Electrocatalysis", Wiley, 2020

26 < 1% match (publications)

Imteaz Ahmed, Sung Hwa Jhung. "Adsorptive desulfurization and denitrogenation using metal-organic frameworks", Journal of Hazardous Materials, 2016

27 < 1% match (publications)

Jeong-Geun Jee, Min-Bae Kim, Chang-Ha Lee. "Adsorption Characteristics of Hydrogen Mixtures in a Layered Bed: Binary, Ternary, and Five-Component Mixtures", Industrial & Engineering Chemistry Research, 2001

28 < 1% match (publications)

Kowsalya Vellingiri, Jan E. Szulejko, Pawan Kumar, Eilhann E. Kwon et al. "Metal organic frameworks as sorption media for volatile and semi-volatile organic compounds at ambient conditions", Scientific Reports, 2016

paper text:

112 **Metal–Organic Frameworks and Their Hybrid Composites for Adsorption of Volatile Organic Compounds Shella Permatasari** Santoso1,2*, **Artik Elisa** Angkawijaya3, **Vania** Bundjaja1, **Felycia Edi** Soetaredjo1,2 **and Suryadi**

Ismadji1,2 1Chemical Engineering Department, Widya Mandala Surabaya Catholic University, Surabaya, East Java, Indonesia 2Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan, Taipei 3Graduate Institute of Science and Technology, National Taiwan University of Science and Technology, Taiwan, Taipei Abstract Environmental pollution caused by anthropogenic emissions is a growing concern throughout the world; volatile organic compounds (VOCs) are the main constitu- ents that make up the emissions. In handling VOCs, adsorption is considered the most efficient method to date. Engineers have been intensively studied the syn- thesis and usage of metal–organic frameworks (MOF) as versatile adsorbents for many types of VOC. Improving adsorption efficiency and performance is a rou- tine agenda in the development of the MOF; prior to achieving an efficient MOFs as VOCs adsorbents, insight to MOF-key features such as structure, pore, and the functional group is very crucial. To this end, several topics related to adsorption of VOCs by MOF is discussed; specifically, the

1**adsorption performance of some MOFs against VOCs, the effect of some key-features of MOF to the adsorption performance, the development of MOF composite for improvement of adsorption performance, analytical method for** modeling **the adsorption, and factors** influ- encing **the adsorption performance**

. Keywords: Metal–organic framework, MOF, volatile organic compound, adsorption, porous adsorbent, dynamic sorption, breakthrough curve *Corresponding author: shella_p5@yahoo.com Inamuddin, Rajender Boddula, Mohd Imran Ahamed and Abdullah M. Asiri (eds.) Applications of Metal–Organic Frameworks and Their Derived Materials, (313–356) © 2020 Scrivener Publishing LLC 313 314

4**Applications of Metal–Organic Frameworks 12.1**

Introduction The deployment of air pollution caused by toxic and hazardous sub- stances worsens as a result of the rapid increase in anthropogenic emis- sions. Chemicals combustion, evaporation, reaction, and purification are the predominant sources of anthropogenic emissions and are growing concerns of worldwide. A substantial amount of hazardous gases such as hydrocarbons, volatile organic compounds, sulfuric compounds, nitrogen compounds, and greenhouse compounds are produced from those emissions. The

21**volatile organic compounds (VOCs) are considered** as **major air pollutants**

since they always produced in every activity involving chemicals [1, 2]. As reported by the United States Environmental Protection Agency (US EPA), 50% of VOCs is contained in the emission of fossil fuel combustion [3]. Moreover, given the continuous development of industry throughout the world, it is prominent that VOCs emissions will continue to increase in the future. VOCs are those organic compounds that quickly evaporate at standard ambient conditions. Acetone, benzene, chloroform, ethanol, formalde- hyde, isopropanol, naphthalene, propane, and toluene are several types of VOCs. VOCs are dangerous health threats that are often underestimated since they are commonly not physically visible. The entry of VOCs into the respiratory tract leads to various health problems ranging from mild to acute, such as irritation, headache, nausea, tissue or organ damage, and cancer. Unwittingly, VOCs pollutions may come from daily items and/or various surrounding materials; i.e., natural gas, paint, adhesive, candle, room freshener, ink, household cleaner, cigarette, varnish, disinfectant, rubbing alcohol, pesticide, cosmetic, etc. VOCs have a peculiar strong odor that signifies high concentration, at low concentration the odor may remain unnoticeable; nevertheless, the damaging effects may potentially fatal. The presence of VOCs as an airborne contaminant can aggravate global warming since they cause stratospheric depletion, greenhouse effect, and smog accumulation. Thus VOCs considered as one of the root of climate problems [1–4]. Numerous VOCs removal techniques have been introduced, including photo-catalysis, filtration, oxidation, biological degradation, condensation, and adsorption [5, 6]. Adsorption by using natural or synthetic adsorbent is the most frequently performed since it offers various advantages such as flexible (can be used in removal of specific or non-specific VOCs), low cost, simple, and controllable. The development of engineered-adsorbents has been substantially examined with priority to acquire adsorbent that effectively eliminates VOCs. Out of various engineered-adsorbents, Adsorption of VOC by Using MOF and Hybrids 315 metal–organic frameworks (MOFs) are being intensively developed as adsorbent of VOCs; MOFs offer a large specific surface area that relates to the adsorption ability. MOFs can be easily constructed, designed, and fabricated by coordinating organic compound (ligand) and metal at the particular condition. Some MOFs possess semiconducting nature that makes them capable of self-regeneration by photo-degrading the

VOCs. Furthermore, recyclability is also one of the superiority of MOFs. Provided with those superior properties, the emergence of utilization and develop- ment of MOFs to eliminate VOCs is obviously visible. 12.2 VOCs and Their Potential Hazards VOC is an epithet for carbon-containing compounds, which possess dis- tinct characteristics such as high vapor pressure, low boiling point, evap- orate freely, and reactive at a standard temperature and pressure. There are certain usual extents, related to the characteristics of VOCs, between each country that causes a slight difference in the definition of VOCs. Several agencies issuing the standard of VOCs are

21**National Institute for Occupational Safety and Health (NIOSH**

), Environmental Protection Agency (EPA), Air Quality Management (AQM), Environmental Protection Department (EPD), Department of Occupational Safety and Health (DOSH), etc. In general, the standards over the countries gives the following specific characteristics of VOCs; viz. boiling point of 50°C to 250°C and vapor pressure equal to 0.01 kPa (9.87 × 10−5 atm) or higher (measured at 293.15 K and 101.325 kPa). VOCs sources increase every decade due to increasingly diverse type of emissions that may come both from natural sources and anthropogenic sources. Undoubtedly anthropo- genic sources, which mainly due to the rapid development of industrial sections in various parts of the world, contribute the highest VOCs emis- sions. Daily activities such as cooking, smoking, driving, printing, and burning, are also pay a role for this VOCs emissions [3, 7]. VOCs come in a variety of structures ranging from aromatic, alcohol, aldehyde, alkene, ketone, polycyclic, and halogenated forms, as listed in Table 12.1. The concentration index of VOCs that is likely to cause dan- gerous threat is proposed by NIOSH as immediately dangerous to life and health (IDLH). The index can be expressed as recommended exposure limit (REL) from adverse health effects over a working lifetime, and 10% of the lower explosive limit (LEL) for safety considerations related to the potential for explosion hazards. Health and/or life threats caused by VOCs vary depending on the length of exposure time, number of toxicants, and T able 12.1 Properties of some VOCs and their IDLH levels as proposed by NIOSH [8]. IDLH Compound Alcohols Formula b.p. (K) p (kPa) LEL (ppm) REL (mg/m3) Ethyl alcohol C2H5OH 351.39 7.91 1,900b 3,300 Methyl alcohol CH3OH 337.85 16.93 260b 6,000 Isopropyl alcohol CH3CHOHCH3 355.45 6.05 980b 2,000 Phenol C6H5OH 454.90 0.05 19a 1,800 Aldehydes Acetaldehyde CH3CHO 293.95 120.26 n.e. 4,000 Formaldehyde H2CO 253,65 518.62 n.e. 7,000 Benzaldehyde C6H5CHO 451.85 0.17 NA 1,400 Alkanes n-Hexane C6H14 341.88 20.40 180a 1,100 n-Heptane C7H16 371.53 6.13 350a 1,050 Octane C8H18 398.77 1.88 350a 1,000 (Continued) 316 Applications of Metal–Organic Frameworks T able 12.1 Properties of some VOCs and their IDLH levels as proposed by NIOSH [8]. (Continued) IDLH Compound Formula b.p. (K) p (kPa) REL (mg/m3) LEL (ppm) Aromatics Aniline C6H5NH2 457.25 0.09 n.e. 1,300 Benzene C6H6 353.23 12.64 3.2a 1,200 T oluene C7H8 383.75 3.79 375a 1,100 Naphthalene C10H8 491.05 0.01 50a 900 Chlorobenzene C6H5Cl 404.75 1.60 NA 1,300 Carboxylics Acetic acid CH3COOH 391.05 2.09 25a 4,000 Formic acid HCOOH 374.15 5.68 9a 18,000 Esters Ethyl acetate CH3COOC2H5 350.25 12.43 1,400a 2,000 Diethyl phthalate C6H4(COOC2H5)2 568.15 0.0003 5a 700* Halogenated Benzyl chloride C6H5CH2Cl 447.15 0.16 5c 1,100 (Continued) Adsorption of VOC by Using MOF and Hybrids 317 T able 12.1 Properties of some VOCs and their IDLH levels as proposed by NIOSH [8]. (Continued) IDLH Compound Chlorine Formula Cl2 b.p. (K) 239.11 p (kPa) 777.27 1.45c n.f. LEL (ppm) REL (mg/m3) Chloroform CHCl3 334.27 26.26 9.78b n.f. Ketones Acetone (CH3)2CO 329.23 30.80 590a 2,500 2-Butanone CH3C(O)CH2CH3 352.74 12.08 590a 1,400 Cyclohexanone (CH2)5CO 428.75 0.67 100a 1,100 Peroxides Hydrogen peroxide H2O2 423.35 0.26 1.4a n.f. Pnictogens Ammonia NH3 239.80 999.92 18a 15,000 Dimethylamine (CH3)2NH 280.45 202.65 18a 2,800 Miscellaneous Hydrogen sulfide H2S 212.82 2026.50 15a 4,000 n.e. none established (potential occupational carcinogenic); n.f. nonflammable; n.a. not available. a8-h time-weighted average (TW A); b60-min short-term exp osure limit (STEL); cCeiling value *measured at 368°F = 459.8 K 318 Applications of Metal–Organic Frameworks Adsorption of VOC by Using MOF and Hybrids 319 route of exposure. Age and pre-existing health conditions are also deter- mining factor in level of hazard. Acute health effect usually can be seen soon after exposure includes irritation to the eyes, skin, upper respiratory—the nose, nasal cavity, and throat, and lower respiratory—the larynx, trachea, bronchi, and lungs, and other short-term effects such as headache, grogginess, drowsiness, fatigue, nausea, and vomiting. Long-term exposure of some VOCs is associated with persistent diseases and even life-threatening diseases, such as damage of liver, kidneys, lungs, nerves, and other organs [8]. Known and probable human carcinogenic properties were also observed for several VOCs as reported by the International Agency for Research on Cancer (IARC) and the US National Toxicology Program (NTP). Health and/or life threats caused by VOCs vary depending on their reactivity. 12.2.1 Other Sources of VOCs Air emissions by VOCs are traditionally only associated with various anthropogenic activities. However recent observations revealed that bio- mass also contributed to the VOCs emission. The VOCs emitted by bio- mass is known as biogenic volatile organic compounds (bVOCs); with isoprene, methanol, acetone, acetaldehyde, limonene, and myrcene are several types of bVOCs. Soil is commonly linked to the emission of bVOCs due to biotic or abiotic activities of living organisms in soil. bVOCs pro- duced by the living organisms mostly end up buried and accumulated in the soil; then, after certain (high) concentration, the bVOCs are released from soil. In this context, soil may acts as a complex-adsorbent material that restrains the immediate release of bVOCs [9]. The litter of diverse pine trees can produce bVOCs including acetone, methanol, acetaldehyde, ethane, hexane, also some groups of alkanes, and terpenes. The emission rates of those bVOCs are relatively low, between 936 to 0.35 μg/m2 in an hour. This emission rate normally increased at hot season due to increased temperature and solar irradiance. Some stud- ies revealed that plant-roots commonly emit bVOCs in the form of alde- hydes, alcohols, and ketones [9, 10]. Microorganisms, such as bacteria and fungi, dwell in the soil also contributed to the formation of bVOCs as a result of their metabolism. Bacillus subtilis metabolism is known to pro- duce 2,3-butanediol. Saccharomyces cerevisiae and Lactobacillus produce ethanol in their fermentation. Clostridium species fermentation produces acetone and butanol. Biodegradation of organic matter done by micro- organisms is known to produce methane, one of the greenhouse gases. 320 Applications of Metal–Organic Frameworks Some flavoring compounds, such as pyrazines, are produced from the bio- synthesis of some bacteria. A similar type of bVOCs can also be produced by fungi [9, 10]. Although bVOCs are usually not being considered as hazardous sub- stances due to their relatively low emission rate and their natural charac- teristics, it is worth to mention to broaden insight about VOCs sources. Moreover, some bVOCs are known to have antifungi activity and plant- growth promoting effect. For instance, bacteria-VOCs can inhibit the growth of phytopathogenic fungi Rhixoctonia solani. Trimethylamine, dimethyloctylamine, and benzaldehyde produced by bacteria are known to have strong antifungi activity. Ryu et al. stated that 2,3-butanediol pro- duced by bacteria could promote the growth of plant [11]. Several other bVOCs and their producing organism are listed in Table 12.2. 12.3 VOCs Removal Techniques A considerable number of VOCs handling techniques are mandatory due to the noticeable harmful impact of VOCs on environmental sustainabil- ity and human health. There are two fashions in the handling of VOCs that is recovery-based and destruction-based techniques [6]. Recovery technique is based on the idea of capturing VOCs using a transfer media to be reused later; the method is including adsorption, evaporation– condensation, absorption, and membrane separation. Whilst, destruction technique is a process of degrading VOCs into air constituents such as water vapor and carbon dioxide by combustion, oxidation, biodegrada- tion, or plasma treatment [6]. Some studied removal techniques of VOCs are listed in Table 12.3. So far, recovery-based methods are more appealing than destruction-based methods from many viewpoints such as: • VOCs recovery allow for reuse which is considered benefi- cial economically • Absence of environmentally toxic by products such as reac- tive oxygen species and greenhouse gases • Low energy necessity • Comparable removal efficiency with the destruction techniques • A relatively shorter process T able 12.2 Some biogenic volatile organic compounds and their producing organisms. Biomass Produced VOCs Ref. Plant species Arabidopsis thaliana (mouse-ear cress) Limonene, ethyl acetate, rhizathalene, ethanol, aldehydes, ketones [12] Artemisia tridentate (sage brush) Limonene, nerol, camphor, caryophyllene, neryl isovalerate [13] Citrus aurantium (bitter orange) Monoterpenes (e.g., limonene, terpinolene, sabinene, camphene, camphor, carvone, geranyl acetate), monoterpenoid (e.g., linalool, citronellol, geraniol, [14] Pinus sylvestris (Scots pine) nerol, citronellal, perillaldehyde), 1-octanol, octanal, dodecanal, decanal Acetone, isoprene, tricyclene, α- and β-pinene, camphene, limonene, careen, γ-lerpinene [15] Zea mays (corn) Hexadecanal, tetradecanal, β-macrocarpene, β-bisabolene, (E)-β-caryophyllene [16] Bacteria species Saccharomyces cervisiae

Ethanol, ethyl acetate, 3-methyl-1-butanol, 2-methyl-1-butanol, ethyl octanoate, phenylethyl acohol [17] (Continued) Adsorption of VOC by Using MOF and Hybrids 321 T able 12.2 Some biogenic volatile organic compounds and their producing organisms. (Continued) Biomass Produced VOCs Ref. Wickerhamomyces anomalus

> 20**Acetaldehyde, ethyl acetate, ethyl butyrate, isoamyl acetate, ethyl hexanoate**, [18] **phenylethyl acetate 2-phenyl-ethanol, isobutanol, amylic alcohol, isoamyl**

Lactobacillus helveticus Ketones (e.g., 2-propanone, 2-butanone, diacetyl), esters (e.g., ethyl acetate, ethyl butanoate, isoamyl acetate), benzaldehyde, phenylacetaldehyde, alcohol [19] Staphylococcus aureus phenylethanol, ethanol, 2- and 3-menthylbutanal 3-Methyl-butanal, 3-methyl-butanoic acid [20] Clostridium beijerinckii acetone, butanol, ethanol [21] Fungi species Muscodor vitigenus Naphtalene [22] Phomopsis sp. Sabinene, 1-butanol, 3-methyl, benzeneethanol, 1-propanol, 2-propanone [23] Phoma sp. Trans-caryophyllene, naphthalenes, alcohols [24] Trametes versicolor δ-cadinene, β-guaiene, γ-patchoulene, isoledene [25] Metarhizium anisopliae n-tetradecane, alkenes [26] 322 Applications of Metal–Organic Frameworks T able 12.3 Several studied VOCs removal techniques and their performance. Operating Removal T echnique Material VOC condition efficiency Ref Destruction-based techniques Catalytic oxidation Au/MnOx/3DOM SiO2 T oluene 225°C 90% [31] Thermal oxidation Porous cordierite packed bed Mix: methanol, xylene, ethyl acetate 400–975°C 90% [32] Biofiltration Candida utilis biofilm on sugar cane bagasse Ethanol 30°C, pH 6, moisture 63% 70% [33] Recovery-based techniques Absorption Polypropylene bioscrubber Mix: oxygenated, aromatic, Room temp. 12–36% [34] Adsorption Diatomite stellerite halogenated butyl propionate 25°C 59.3% 9.2% [30] Membrane separation vitric tuff Poly-dimethyl- siloxane/ α-alumina Mix: toluene, propylene, butadiene 20.5% 21°C, 3–5 mbar 95% [35] membrane Adsorption of VOC by Using MOF and Hybrids 323 Adsorption is acknowledged as the most favorable recovery-based VOCs elimination techniques because of its notable effectiveness (selective for each type of adsorbent and adsorbate), practical operation, and economic feasibility [27–30]. The characteristic of the solid adsorbent (porosity, selectivity, and activity) play the most vital role in the performance of adsorption. Metal organic framework (MOF) is a rising adsorbent material that is recognized for its large surface area, high porosity, ease fabrication, modifiable selectivity, high efficiency, etc. Many engineering processes are being developed to synthesize MOF with high efficiency in adsorption. The specificity of MOFs for adsorption of certain VOC is very dependent on their active adsorption sites. Many studies stated that high porosity and surface area of MOFs is not adequate for achieving efficient adsorption towards specific VOC gases/vapors. In fact, the strong interaction between host adsorbent and guest adsorbate is depended on each other compatibil- ity. For instance, some interactions (i.e., van der Waals interactions, π–π interaction, and coordination bond) can increase the adsorption efficiency and/or selectivity when unsaturated (open sites) metal centers and organic ligand with certain functional groups interact. 12.4 Fabricated MOF for VOC Removal Beside the potential of VOCs adsorption, the development of novel MOFs has been extensively carried out in the basis of their extent of freedom and easiness in fabrication, pore tunability, and strong durability. MOFs are constructed from the coordination of organic compounds as the primary building blocks to metal cluster (or ion) as the secondary building blocks. Substantial choices of building blocks are available to synthesize MOFs which offers distinct structural diversity of MOFs. However, a proper understanding of the occurring coordination/interaction between MOF and VOC is crucial prior to gain insight in their adsorption mechanism. Physically, the adsorption potential of MOFs arises from the porous nature that grants them with large surface area and deep pore volume. The large surface area of MOFs provides large active adsorption sites, while the deep pore volume allows the adsorbate to be entrapped in the pore of MOFs. The choice of building blocks is important in designing the molec- ular structure of MOFs; it is usually based on the size and chemical fea- tures of the building blocks. However, along with progress, more and more cases disclose that the merit of MOFs is not enough for efficient adsorptive removal of VOCs. Instead, effective adsorption requires specific interac- tions and coordination between the VOCs adsorbate and MOFs adsorbent. Adsorption of VOC by Using MOF and Hybrids 325 In this section, the adsorption performance of several analogs of MOF, such as MIL series MOFs, the isoreticular MOFs, and some MOF derivatives, is gathered. Only dynamic adsorption of some common VOCs such as acetaldehyde, acetone, benzene, ethyl acetate, formaldehyde, etc, is discussed. 12.4.1 MIL Series MOFs MIL, which represents

4**Materials of the Institute Lavoisier, series**

of MOFs consist of

11**MIL-53, MIL-47, MIL-100, and MIL-101**

. MIL-53 and MIL- 47 share the same geometrical structure, while MIL-100 shares the same structure with MIL-101. The difference in MIL-53 and MIL-47 is mostly based on their properties which caused by the different metal used for the synthesis.

24**In the** synthesis **of MIL-100 and MIL-101 different**

type of organic linker (ligand) is used, that is trimesic acid for MIL-100 and tere- phthalic acid for MIL-101. The building blocks and the shape of MIL series MOFs are presented in Figure 12.1. Here we can see only several metals that often used for the MIL synthesis is given. MIL-53 consists of three structural analogues that were synthesized with different metal ions, namely Cr, Sc, Fe, or Al, through a hydrothermal reaction between metal nitrate salt and terephthalic acid (H2BDC) in water (1:0.5:80 in molar ratio) at a temperature of 180°C. MIL-53 arranged of one

11**MIL-53 MIL-47 MIL-100 MIL-101**

Organic

12**HO O OH O HO** OH **O OH O HO OH** linker **O** BDC **O** BDC **HO O O** BDC O BTC **OH**

Metal Cr, Sc, Fe, or Al V Cr or Fe Cr or Fe Geometry (structu re) simple view framework simple view framework 12.1 Organic and metal building blocks of

11**MIL-53, MIL-47, MIL-100, and MIL-101**

, and their structures. MIL-53 and MIL-47 built f rom octahedral metal cluster Figure coordinated to organic linkers

24**to form a 3D network with 1D** diamond-shaped **pores**

. MIL-100 and MIL-101 built from trimer of metal octahedral coordinated with organic linkers to form a 3D dodecahedron with the large pore. Adapted from Ref. [36–42]. dimensional parallel chains of the octahedral metal cluster (that is M(O4) (OH)2, where M = Cr3+, Fe3+, Sc3+, or Al3+) coordinated to terephthalic organic linkers into a three dimensional network with diamond-shaped pores (up to 8.5 Amstrong in size) [43–45]. MIL-53 is known to have unique behavior, namely breathing behavior which portrays MIL-53 reversible structural change from an open pore to a closed pore structure. The structural transformation of MIL-53 is induced by heating. An expo- sure of MIL-53 to high temperature caused pore opening and change in crystalline structure into the orthorhombic crystal system, while low tem- perature condition caused pore closing and monoclinic crystal arrange- ment [38, 43–45]. Breathing behavior is explained further in subsection 12.8.1. Constructed from the same organic linker as the MIL-53, MIL-47 pos- sesses a similar geometry with MIL-53. MIL-47 is constructed with VO6 octahedral metal cluster, it has a one dimensional pores which shaped like diamond and diameter of 7.5 Å. MIL-47 is as stable as MIL-53, where no structural collapse observed after the adsorption process. MIL-47 has a rigid structure which not allowing the occurrence of breathing behavior. The rigidity of MIL-47 can be preserved up to mechanical pressure of 178.1 MPa; which also confirmed by the X-ray diffraction (XRD). The XRD anal- ysis shows no (or slight) orthorhombic pattern change upon exposure to a pressure up to 178.1 MPa; where the unit cell volume maintained approxi- mately 1500 Amstrong3. At 178.1 MPa, the coexistence of open and closed pores is observed and the crystallinity pattern altered to monoclinic; where the observed unit cell volume (belong to the dominantly closed pore) is 950 Å3 approximately. Further increase in pressure (up to 340.1 MPa) caused the absence of opening pore; the observed unit cell volume is 870 Å3. The pore closing phenomena encountered by MIL-47 does not cause destruction to the framework. The pore can be expanded back upon pres- sure release (decompression) [38, 42]. MIL-100 build from trimesic acid (H3BTC) as the organic linker and tri- valent metal such as Fe, Cu, Al, or Cr, in common. MIL-100 can be synthe- sized by hydrothermally reacting the organic compound and metal salt of choice in a water solvent, at the temperature of 200–220°C for 4–8 h. MIL- 100 is categorized as a large member of MOFs that have pore size up to 34Å [37]. MIL-101 can be hydrothermally synthesized from terephthalic acid with metal such as Fe, Cu, Al, or Cr, in common. The reacting condition is similar to that of the synthesis of MIL-100. Earlier synthesis of MIL-101 (also MIL-100) was done by using hydrofluoric acid as solvent, but recent studies showed that either MOF-100 or MOF-101 can be obtained by using water as solvent without addition of hydrofluoric acid [36, 40]. Adsorption of VOC by Using MOF and Hybrids 327 The summarized adsorption capacity of MIL series MOF is available in Table 12.4. Among the MIL series of MOFs, MIL-53(Al or Cr) and MIL- 47(V) are the one known to possess reversible adsorption behavior owing to their breathing capability. The reversible properties of MIL-53 and MIL- 47 have been extensively studied against hydrogen sulfide (H2S) gas under different pressure. While the pore structure of MIL-47 remains the same after H2S adsorption at

4**a pressure** below **1.8 MPa; MIL-53** encounter **a**

sequence of pore opening and closing. At high pressure of H2S, MIL-53 encounters pore opening while at low pressure of H2S MIL-53 encoun- ters pore closing. Both MIL-53 and MIL-47, are able to maintain their structural stability after the adsorption process.

26**The adsorption** in **MIL-53 and MIL-47** happened trough **the** H-bonding between **the**

adsorbate and carboxylic groups of the MOFs.

5**In the case of MIL-53**, especially with **Cr** building block, **H2S** acts as **the**

H-acceptor. On the contrary, H2S acts as H-donor against

26**MIL-47(V**) [38]. **In the** similar **adsorption**

process against H2S as adsorbate,

5**MIL- 100**(Cr) **and MIL-101**(Cr) exhibit **irreversible** desorption **due to the**

par- tial structural collapse of the building blocks which initiated by the strong adsorptive interactions between H2S and the MOFs. This phenomenon also indicated the lack regenerative ability of MIL-100 and MIL-101, thus limit its reusability and practical application [38]. The adsorption performance of breathable MOFs (MIL-100 and MIL-101) against other VOCs also has been investigated in other studies. They show different adsorption capacity for each studied VOC. It is emphasized that different type of VOC has a different affinity towards the adsorbent, depending on their dominant bonding characteristics (such as π or σ bond, proton, or H bond, etc.). 12.4.2 Isoreticular MOFs Isoreticular is a term given for MOFs with similar topological structure. In this section, the dynamic adsorption capacities of six isoreticular MOFs (Figure 12.2), namely, MOF-177, MOF-5, MOF-74, IRMOF-3, MOF-199, IRMOF-62, are discussed. MOF-177 has been widely syn- thesized and used for the adsorption of gas and VOCs [29, 46–49]. A MOF-177 was synthesized from zinc nitrate hexahydrate as the metal source and synthesized-organic-ligand namely

3**4,4 ,4 ,-benzene-1,3,5- triyl**-trisbenzoic **acid (H3BTB**

) and are

14**used for the preparation of**. H3BTB is **a** well-known **building block for**

producing MOFs with a high surface area up to 5000 m2/g; this property also serves it as a good gas storage material. As previously introduced by many researchers, the T able 12.4 Studied adsorption performance of MIL series MOFs against some VOCs. Pore volume Adsorption Adsorption MOF BET (m2/g) (cm3/g) type model Adsorption capacity MIL-47 (V) ~1000 MIL-53(Cr) ~1000 Static Static 14.6 mmol/g (H2S). 13.12 mmol/g (H2S). MIL-53(Fe) ~1000 Static 11.77 mmol/g (H2S). MIL-53(Al) ~1000 Static 8.53 mmol/g (H2S). MIL-100(Cr) 1695 Static SL 0.38 (phenol), 0.20 (p-nitrophenol). V alue in mmol/g. MIL-100(Cr) 1900 MIL-100(Fe) 1675 Static Static SL 0.38 (phenol), 0.23 (p-nitrophenol). V alue in 16.7 mmol/g (H2S). mmol/g. MIL-101(Cr) 4293 2.43 Dynamic FL-PFO 83.44 (benzene), 97.74 (toluene), 7.34 (xylene), 98.47 (n-hexane), 81.97 MIL-101(Cr) 2736 1.50 Static DA (n-heptane). V alue in wt%. 0.16 (n-hexane), 0.53 (toluene), 0.83 (butanone), 0.99 (dichloromethane), 1.47 FL-PFO: fractal-like pseudo-first-order, DA: Dubinin-Astakhov, SL MIL-101(Cr) 2600 Static : Sips and Langmuir. 38.4 mmol/g (H2S). (methanol), 12.8 (n-butylamine). V alue of limiting adsorption capacity in mmol/g. Ref [38] [38] [38] [38] [27] [38] [27] [41] [39] [38] 328 Applications of Metal–Organic Frameworks O OH OH H3BTB H2BDC H4DOBDC NH2-H2BDC H2BTC O H2BDB O

17**O O O OH** L **OH HO HO HO** NH2 **OH OH OH HO OH** HO HO OH **O O O O O O** O **OH**

4**O O O O O O M**

—OO N+ ZNn+2OO+— —OO NZNn++2OO+— —OO N+ N+ N+ ZNn+2OO+— —OO ZNn+2OO+— —OO CNu+2OO+— –OO Zn2OO+– O O O O O P MOF-177

5**MOF-5 MOF-74 IRMOF-3 MOF**-199 IR **MOF**

-62 Figure 12.2 Organic and metal building blocks of the isoreticulars MOF-177,

5**MOF-5, MOF-74, IRMOF-3, MOF**-199, **and IRMOF-62**

. L = o rganic ligand, M = metal ion source, and P = MOF product. Adapted from Ref. [46]. preparation of the H3BTB ligand involve two step reactions; first step by electrophilic reaction involving AlCl3, and second step by Hofmann rearrangement involving NaOBr. The preparation of MOF-177 itself is conducted solvothermally, in N, N-diethylformamide solvent (common solvent for synthesizing cubic-shaped zinc oxide). Characteristics of the reported MOF-177 have slight differences from each other, which might be caused by aberrations in the concentration and purity of the starting materials, also differences in heating and cooling rate. The relative char- acteristics of MOF-177 are Langmuir surface area of 4,170–5,640

9**m2/g, BET surface area** of **2**

,970–4,630 m2/g, pore volume of 1.11–1.69 cm3/g, and pore diameter 0.94–1.06 nm. The synthesized MOF-177 has a crystal clear appearance with a slightly yellow color and thermally stable in the air up to a temperature of 350°C [46]. Combination of terephthalic acid (1,4-benzenedicarboxylate, abbrevi- ated as H2BDC) and zinc nitrate as building blocks are used to synthe- size MOF-5. The as-synthesized MOF-5 (also called as IRMOF-1) have a chemical composition of Zn4O(BDC)3 which have a three-dimensional cubic shape. MOF-5 is reportedly having a high surface area of 2,500 to 3,000 m2/g owing to its scaffolding-like nature [46]. Both MOF-74 and IRMOF-3 have similar building blocks to that of MOF-5 but with the addition of functional groups in the organic linker structure. MOF-74 is synthesized from 2,5-dihydroxyterephthalic acid (H4DOBDC) that has a similar structure to that of H2BDC but with additional of two hydroxyl groups while in IRMOF-3, the functional group comes from its NH2- site. Compared to that MOF-5, the addition of a functional group in the organic building block of IRMOF-3 and MOF-74 induce their reactivity towards VOCs. MOF-199 is another name given for MIL-100 (as discussed in sec- tion 12.4.1.3.), also refer to HKUST-1, is a copper-based MOF produced through a solvothermal reaction. While IRMOF-62 is synthesized from diacetylene-1,4-bis-(4-benzoic acid) and zinc acetate [46]. 12.

14.2.1 Adsorption Comparison of the Isoreticular MOFs

The adsorption capacity of the isoreticular MOFs is summarized in Table 12.5. Apparently, the adsorption capacity of the investigated MOFs not only depends on the surface area of MOFs, but also VOC type and reactivity, and

2**the presence of** MOF **functional groups. The** dependence of **adsorption** performance **of**

MOFs toward the type of VOCs is apparent, in which a MOF might be effective in adsorbing one type of adsorbent but ineffective for other types of VOC. For instance, MOF-177 can adsorb ammonia 42-times higher than the other tested VOCs. Most of the inves- tigated MOFs failed to adsorb chlorine; this is because chlorine cannot act as a ligand that binds to the metal cluster; unlike other VOCs. IRMOF-3 shows successful adsorption towards chlorine; this is ascribed to the reac- tive nature of the gas and also the effect of

22**open metal sites as Lewis acids** that **interact with**

the adsorbate gases as Lewis base [46]. In the case of aromatic VOC (i.e., benzene), the adsorption may improve due to π–π interaction [29]. Based on Table 12.5, it is noted that a larger surface area not always in accordance with a higher adsorption capacity. MOF-177 and MOF-5 have larger BET surface area than other investigated MOFs, but they have the worst dynamic adsorption performance. MOFs with a large surface area may have a high capacity for thermodynamic adsorption; however, they are less effective in kinetic adsorption due to the absence of functional group that essential for the adsorbate-adsorbent interactions. The high surface area of IRMOF-62 seems to assist in enhancing the adsorption capacities; however, the lack of functional group caused IRMOF-62 to be less effective against certain VOC (i.e., sulfur dioxide) [46]. The role of MOF-functional groups in improving the adsorption per- formance can be noticed by comparing MOF-5, MOF-74, and IRMOF-3. Addition of NH2– functional group to the organic building block of MOF-5 produces IRMOF-3 which have better dynamic adsorption capacity; i.e., IRMOF-3 possesses adsorption capacity towards ammonia 18-times higher than MOF-5. Addition of OH– functional group (i.e., in producing MOF-74) also accentuate the adsorption performance. Such improvement T able 12.5 Dynamic adsorption performance of some isoreticular MOFs against VOCs at gas flow 25 ml/min [46] and 600 ml/min [29]. Properties MOF-177 MOF-5 MOF-74 IRMOF-3 MOF-199 IRMOF-62 BET surface area (m2/g) 3,875 2,205 632 1,568 1,264 1,814

13**Adsorption capacity (mg/g)** at gas **flow rate** of 25 **ml/min**

Ammonia 42 6 93 105 87 23 Chlorine <1 a a 335 36 92 T etrahydrothiophene <1 1 90 7 351 84 Sulfur dioxide <1 1 194 6 32 <1 Benzene 1 2 96 56 176 109 Dichloromethane <1 <1 32 1 55 19 Ethylene oxide <1 1 110 2 95 11 BET surface area (m2/g) 2,970

13**Adsorption capacity (mg/g)** at gas **flow rate** of 600 **ml/min**

Benzene 800 aExperiments not conducted due to apparatus corrosion by chlorine. Adsorption of VOC by Using MOF and Hybrids 331 in adsorption capacity is due to the additional functional groups, such as amine, which function as electron rich groups that readily form hydrogen bonding with the adsorbate-molecules [46]. The vacant coordinated metal sites of MOF act as Lewis acids that is deficient of electron hence generate a stronger interaction with adsorbate molecules that can act as Lewis base, such as ammonia. The role of metal as Lewis acids can be observed in MOF-199 and MOF-74. Both MOF- 199 and MOF-74 have open copper sites which can readily adsorb VOCs [46]. As presented in Table 12.5, apparently a larger gas purge flow may stimulate adsorption driving force thus promote penetration of VOC gas molecules into the porous matrix of the MOF. This insight can be drawn from adsorption capacity of MOF-177 at 600 ml/min gas flow which gave 800-times-higher benzene adsorption capacity compared to the studies done at 25 ml/min gas flow [29, 46]. 12.4.3 NENU Series MOFs A group in NENU (Northeast Normal University) synthesized another series of isoreticular MOF namely NENU-X. Prior to the synthesis of NENU-X MOFs, the organic linker used in a series of NENU MOFs was synthesized by integrating thiophene-containing bidentate ligand into benzene-1,3,5-tribenzoate (BTB). The MOFs were then synthesized through a solvothermal method with N,N-diethyl-formamide as a sol- vent (85°C, 2 days), and zinc nitrate was used as the metal source. The, as synthesized NENU-511 was built from coordination of

7**six BTB to a six-connected node and**

possess meso- and micro-sized pore. Meanwhile,

7**NENU-512, NENU-513, and NENU-514**

have more disorderly structure due to their large-size pores [50]. The NENU-X MOFs have an enormous BET surface area up to 4240 m2/g, which play an important role in the adsorption of VOC, namely benzene. The adsorption capacity of the NENU-X MOFs against benzene is shown in Table 12.6. Adsorption of benzene onto NENU-511 and NENU- 512, which do not possess a specific functional group on their inner matrix, is ascribed from their spacious matrix that can accommodate significant amount of benzene. Their spacious matrix also postponed their saturation to P/P0 = 0.20. Meanwhile, NENU-513 and NENU-514 showed earlier sat- uration at P/P0 = 0.10. This is due

7**to the** presence **of phenyl-rings on the inner surfaces**

. While these phenyl-rings helps to enhance the adsorption towards benzene by raising the π–π interaction, excessive occurrence of phenyl-rings on the inner surface may reduce MOFs porosity and cause Table 12.6 Surface area and adsorption capacity of NENU series toward benzene [50].

7**NENU-511 NENU-512 NENU-513 NENU-514**

Surface area (m2/g) BET 4240 3648 3554 3457 Langmuir 6491 5640 5438 5320 Adsorption capacity (mg/g) 1556 1519 1687 1311 repulsion effect between each adsorbate molecules thus adversely affect adsorption capacity [50]. Another NENU-X MOF, namely NENU-520, has been synthesized by using a tetrazolate-containing ligand. However, no work has been done to study its adsorption ability against VOCs. Adsorption data of NENU-520 for CO2 uptake has been reported by Lan et al., where the uptake capacity is 79.9 cm3/cm3 at standard temperature and pressure [51].

1**12.4.4 MOF-5, Eu-MOF, and MOF-199**

A research study by Vellingiri et al. demonstrated the superiority of MOF as adsorbent of VOC and semi-VOC, which is comparable to some com- mercial adsorbents (

3**Tenax TA, Carbopack-X, and Carboxen-1000**) [28]. **The**

adsorption ability of

3**MOF-5, Eu-MOF, and MOF-199**

against hydro- carbons, carboxylics, phenolics, and indoles VOC are investigated in their study. Some of the dynamic adsorption data from their research are shown in Table 12.7. MOF-199 show better adsorption performance compared to the other investigated MOFs; which was attributed from the effect of vacant copper–metal sites of MOF-199 that also act as Lewis sites. The lower adsorption capacities of Eu-MOF may be in consequence to the absence of vacant coordination sites and low adsorption energy of Eu metal. Meanwhile, the poor adsorption performance of MOF-5 is sug- gested to be the effect of its cubic-pore that eliminates the functionality of the frameworks. Density functional theory (DFT) estimation revealed some specific interaction between the six-member ring compounds and MOFs that occurs during the adsorption of VOCs. The AA-stacking phenomena can be observed in the case of adsorption by using MOF-5, while higher Table 12.7 The equilibrium adsorption capacity of

28**MOF-5, Eu-MOF, and MOF- 199** against several types **of VOCs**

(selected from the Ref. [28]). MOF Properties

28**MOF-5 Eu-MOF MOF-199**

Surface area (m2/g)a 535 281 1591 Pore volume (cm3/g) 0.22 0.95 0.46 SEM morphology Cubic crystal Grass-like crystal Octahedral crystal Adsorption capacity (mg/g) Aromatic VOCs mixture (pi b) Benzene (8.6 mPa) n. m.c 1.00 >1.1d Tolu ene (6.8 mPa) n. m. 0.95 >2.6d p-Xylene (6.0 mPa) n. m. 0.76 >5.2d Styrene (5.5 mPa) n. m. 0.85 >4.9d Phenol VOCs mixture Phenol (12 mPa) n. m. 1.50 13.0 p-Cresol (9.8 mPa) 1.50 3.00 15.0 aLangmuir surface area; bpartial pressure of each species in VOCs mixture in parenthesis; cn.m. refers to not measurable; dsaturation of those adsorbates were not achieved within 15 L sample loading. energy AB-stacking phenomena are observed for MOF-199. Moreover, the Cu-metal sites of MOF-199 can attract the compound containing polar –OH group thus increasing the adsorption capacity; this phenomenon does not occur in MOF-5 with Zn-ion as the central [28]. 12.4.5 Amine-Impregnated MIL-100 MIL-100(Al) with amine functional group, coded as NH2-MIL-101(Al) can be synthesized by reacting aluminum chloride salt with 2-amino terephthalic acid in DMF solvent (403K, 3days).

23**The as synthesized** NH2- **MIL-101** has **BET** surface **area**

of 1943 m2/g. In static (liquid-phase) adsorption experiment, by using phenol and p-nitrophenol as adsorbate, NH2-MIL-101(Al) can adsorb up to 1.2 mmol/g which is higher than some NH2 functional group main framework O H OH OH p-nitrophenol

12**N O H N N O** H **N O H**

NH2-MIL-101 Figure 12.3 Adsorption of p-nitrophenol solution onto functionalized MOF. Amine group of NH2–MIL-101(Al) provides proton donor to the oxygen atoms of nitro group of p-nitrophenol. Redrawn form Ref. [27]. highly crosslinked-polymer such as HJ-1 (1.0 mmol/g) and Amberlite XAD (0.4 mmol/g). Hydrogen bonding

22**plays an important role in** promot- ing **the adsorption of** p-nitrophenol onto **the**

amine-containing adsorbent as illustrated in Figure 12.3 [27].

1**12.4.6 Biodegradable MOFs MIL-88 Series**

The sorption of nitric oxide (NO) onto a series of biocompatible and biodegradable Fe-based MOFs, namely MIL-88, has been studied. Various organic ligands, for instance fumarate-acetic acid, 1,4-benzenedicarboxylate (1,4-bdc), 2-nitroterephthalate (2-NO2-bdc), and 2,5-dihydroxyterephthalate (2,5-dhbdc), have been used in the synthesized of MIL-88A, MIL-88B, MIL- 88B-NO2, and MIL-88B-2OH, respectively. It is observed that the MIL- 88 MOFs can adsorb a relatively low amount of NO approximately 1–2.5 mmol/g. The adsorption performance of MIL-88 series is affected by the accessibility of the gas penetration to the pore matrix which is quite low due to the absence of breathing ability; as a result, the gas cannot easily diffuse to interact with the central Fe metal cluster [52]. 12.4.7 Catalytic MOFs A certain metal cluster can produce MOFs with catalytic activity. A series of rare earth arenedisulfonate MOFs have been produced and tested for their catalytic activity. The tested MOFs are coded as

16**LnPF-1 (Ln = La, Nd**, Pr), **LnPF-2 (Ln = Nd), and LnPF-3 (Ln = Nd**

) from the Ln(OH)(1,5- NDS)H2O (1,5-NDS = 1,5-naphthalenedisulfonate), [Ln(OH)(1,5-NDS) (H2O)]4, and Ln(OH)4.5(2,6-NDS)1.5(H2O)2](H2O) (2,6-NDS = 2,6-naph- thalenedisulfonate), respectively.

16**LnPF-1, LnPF-2, and LnPF-3**

showed catalytic activity in the conversion of linalool to produce cyclic hydroxyl ethers (furanoid and pyranoid) by H2O2 and MeCN at 70°C. The Ln-PF1 MOFs show the best catalytic activity with conversion yields (%) of 76, 94, and 100 (for Ln = Nd, Pr, and La, respectively) in relatively shorter reac- tion time (22-24 hours) compared to Ln-PF2 and LnPF-3 which barely can achieve 51% and 17% conversion after 48 h. The catalytic activity of the Ln-PF1, Ln-PF2, and Ln-PF3 induces by their metal clusters. There are eight neodymium (Nd) coordinations in Ln-PF1, and 9 Nd coordina- tion in LnPF-2 and Ln-PF3; the high NdO9 coordination in LnPF-2 and LnPF-3 makes it difficult for guest molecules to reach the active centers and thereby reducing the actuality of the catalyst. Better catalytic activity is shown by using praseodymium (Pr) and lanthanum (La) as the metal clusters in Ln-PF1, which is related to the decreasing of their radii [53]. Some other studied catalytic MOFs is the ytterbium (Yb) based MOFs, namely Yb-LRH with the cationic

18**formula [Yb4(OH)10(H2O)4]n2+ and**

Yb-RPF-5

18**with formula [Yb(OH)(2,6-AQDS)(H2O)] (AQDS** = anthraqui- none-**2,6-disulfonate**

). The Yb-LRH is shown a selective-catalytic activity for the sulfide oxidation, while Yb-RPF-5 can catalyze hydrodesulfur- ization of thiophene (7 bar, 70°C) [54]. The use of Au as a metal cluster produced a MOF (Au@ZIF-8) that can catalyze the oxidation of carbon monoxide into CO2 [55]. The NH4[Cu3(OH)(capz)]-MOF, together with t-butyl hydroperoxide, show catalytic activity in the oxidation of cyclo- hexane and cyclohexene [56]. Also, it is worth to mention, a lot of molyb- denum (Mo)-based MOFs show a catalytic behavior in the epoxidation of alkenes [57]. 12.4.8 Photo-Degradating MOFs Some MOFs possess adsorption and photo-degradation ability toward VOCs. The hybrid of TiO2 nanoparticles within a typical

NH2-UiO-66 MOF, namely TiO2@NH2-UiO-66, have an excellent interface contact that allow the penetration of visible light and consequently accelerate the pho- togenerated electron–hole separation. The hybrid MOFs, which contain 5% TiO2, show a remarkable photo-degradation activity against styrene gas into CO2; with removal efficiency >99% within 10 hours [58]. The Ti-Zr based MOFs, NH2-MIL-125 (TiZr15), shows a high photo-degradation activity of acetaminophen (with a pseudo-first order rate of 0.0121/min); the activity was found to be better compare to the bare Ti MOF. A bet- ter photo-degradation activity was achieved at lower Zr proportions. The efficiency of photocatalytic activity of TiZr15 remains above 90% upon three successive acetaminophen conversion; which indicate its stability and reusability [59]. 12.4.9 Some Other Studied MOFs Various divalent metal ions have been used

2**in the** preparation **of M-MOF- 74** (where M = Zn, **Co**, Ni, **Mg**

) and each metal produced MOF with differ- ent surface area, specifically 1206, 835, 599, 496 m2/g for

3**M-MOF-74** with **M = Mg, Co, Ni**, Zn, respectively. **The** adsorptive ability **of**

M-MOF-74 is tested against ammonia, cyanogen chloride, and sulfur dioxide. It is noted that the dynamic adsorption performance was different when conducted in dry and humid condition. As shown in Table 12.8, all MOF-74 ana- logs show better adsorption performance at dry condition. The adsorption capacity for all type of adsorbate was reduced when exposed to the humid gas stream; which suggests that there is a competition between the water molecules and adsorbate molecules to attach on the MOF surface [60]. Pyrazolate ligands and nickel hydroxo metal cluster have been used to synthesized some hydrophobic isoreticulars MOFs, namely, [Ni8(OH)4(H2O)2(L)6] or [Ni8(L)6]; where L symbolized various ligands such as

6**H2L1 (1H-pyrazole-4-carboxylic acid; H2L2 (4-(1H-pyrazole- 4-yl)benzoic acid), H2L3 (4,4 -benzene-1,4-diylbis(1H-pyrazole)), H2L4**

Table 12.8 Dynamic adsorption data of MOF-74 analogues [60]. Adsorption capacity (mmol/g) Co-MOF-74 Mg-MOF-74 Ni-MOF-74 Zn-MOF-74 Dry Wet Dry Wet Dry Wet Dry Wet Ammonia 6.70 4.30 7.60 1.70 2.30 1.90 3.70 2.80 Cyanogen chloride 5.60 0.05 1.20 0.08 2.40 0.17 3.60 0.10 Sulfur dioxide 0.63 0.03 1.60 0.72 0.04 0.02 0.26 0.04 Amount of adsorbed water on adsorbent at different relative humidity (RH) 15% RH 0.46 0.25 0.08 0.19 50% RH 0.49 0.31 0.11 0.24 80% RH 0.50 0.39 0.13 0.32 (4,4 -

4**buta-1,3-diyne-1,4-diylbis(1H-pyrazole**)), H2L5 (**4,4 -(benzene-1,4-diyldiethyne-2,1-diyl)bis(1H-pyrazole**)), or H2L5-**R (R = methyl**, triflu- oromethyl). **The** geometry **of**

the resulting MOFs is the combination of an octahedral and two tetrahedral cavities which analogues to that of UiO series MOFs. The BET surface area of the MOFs increases with the longer ligand chain; where the BET ranges between 205–2215 m2/g with [Ni8(L1)6] have the lowest BET (205 m2/g), while [Ni8(L5)6] have the larg- est BET (2215 m2/g). The [Ni8(L)6] series have been proven to be stable against hydrolysis with their bipyrazolate linkers are unaltered even after 24 h soaking in water. The hydrophobic nature of the [Ni8(L)6] series allows performing adsorption under humid condition. Increase in hydro- phobicity was observed by the presence of a fluorine functional group in [Ni8(L5-CF3)6]. As reported, at 80% relative humidity, [Ni8(L5-CF3)6] is not suitable for water molecule adsorbent, in contrast to non-fluorine MOFs, e.g., [Ni8(L4)6] and [Ni8(L5)6] which possess high water adsorption capac- ity. The [Ni8(L5-CF3)6] show efficient adsorption against diethylsulfide under a very humid condition [61]. 12.5 MOF Composites

1**12.5.1 MIL-101 Composite With Graphene Oxide**

Combination of graphene oxide (GrO) with MIL-101 produced a compos- ite (GrO@MIL-101) which suggest its potential in CO2 and CH4 removal. GrO@

9**MIL-101** has **the higher surface area and** larger **pore volume** than that **of MIL-101** prepared in **the**

study; where the BET surface are (

9**m2/g), and pore volume (cm3/g**) for **MIL-101**

are 2670 and 1.28, while for GrO@ MIL-101 are 2950 and 1.42. As revealed by SEM, the addition of GrO induced irregular particle shape of originally octahedral shaped MIL-101 [62]. The static adsorption study of the composite revealed that

19**GrO@MIL- 101 composite** could remove **CO2** and **CH4**

more effectively than MIL-101, as shown in Table 12.9. Also,

19**at 1.5 bar, the** adsorption **selectivity of GrO@ MIL-101** against **CO2/CH4** was **up to**

32.

1**12.5.2 MIL-101 Composite With Graphite Oxide**

Composites of

15**MIL-101(Cr**) and **graphite oxide (GO**), coded as **MIL-101@ GO**-n, have been **synthesized**

via the hydrothermal method by Sun et al. In their study, the composites were prepared by introducing n-amount of GO (n = 2, 5, 10, and 15 wt%). As characterized by XRD, the addition of GO gives a reduction to the crystallinity of MIL-101(Cr). The SEM images Table 12.9 Static adsorption performance of MIL-101 and its composite against CO2 [62]. Adsorption capacity MOF Adsorption Pressure (mmol/g) Desorption model MIL-101(Cr) DSLFa composite 25 (b ar) CO2 50.39 CH4 26.17 efficiency GrO@MIL- 101(Cr) DSLFa 25 66.12 37.21 >95% aDual Site Langmuir Fre undlich (DSLF) model equati on. revealed that the addition of GO causes the alteration of octahedral MIL- 101(Cr) into irregular-shape particles. All of the composites possess a Type I isotherm-sorption as analyzed by N2-sorption. The addition of GO also affecting the surface area of the prepared MOF-composites; where the

8**BET surface area (m2/g) and pore volume (cm3/g**

, value in parenthesis) value are 2881.1 (1.36), 2988.6 (1.54), 3502.2 (1.75), 3318.6 (1.72), 1742.7 (1.00) for MIL-101, MIL-101@GO-2,

15**MIL-101@GO-5, MIL-101@GO-10, and MIL-101@GO-15**

, respectively [63]. There is no certain decrementing or incrementing trend, caused by the addition of GO, observed for the surface area and pore volume. Reportedly, the addition of GO has been proven to increase the adsorption capacity toward n-hexane, as shown in Table 12.10. As shown in Table 12.10, MIL-101@GO-5 exhibit the highest adsorption of n-hexane compared to the other investigated MOF. The excellent adsorption

23**performance of MIL-101**@GO-5 **is not only** related **to the** high **surface**

Table 12.10 Static (vacuumed) adsorption performance of MIL-101 and its composite against n-hexane [63]. MOF Adsorption Pressure Adsorption Desorption composite model (mbar) capacity (mg/g) efficiency MIL-101 L-Fa 175 540.3 MIL-101@ GO-5 L-Fa 175 1042.1 MIL-101@ GO-10 L-Fa 175 952.8 96.78 a Langmuir–Freundlich (L–F) model equation. are but also due to the addition of GO in the proper ratio which in turns affect their surface dispersive force [63].

112.6 Generalization Adsorptive Removal of VOCs by MOFs

MOFs with the adsorptive surface that contain certain functional groups or vacant metal sites are more likely to have an enhanced adsorption effi- ciency toward adsorbate compounds. The organic building block of MOF which contain certain functional site can generate an electrostatic interac- tion or hydrogen bonding that can enhance their adsorption activity; mean- while, vacant metal sites can promote coordination bond or π-interaction against the VOCs adsorbate. Adsorption transpires through continuous pore filling by VOCs to the inner and outer pore surfaces of the MOF. Pore filling by VOCs is possible since VOCs are vapors which have verge properties to non-ideal gases, with some deviations due to their gas-liquid phase equilibrium. The VOCs detention by MOF is consolidated through the non-covalent coupling involving the π-system of the metal cluster of MOF and VOCs. The π-interaction is triggered due to the different charge loading between the metal and VOCs. The metal cluster of MOF is an electron-poor system; meanwhile, the VOCs are the electron-rich system. The π-interaction is common, especially for the aromatic VOCs. The adsorption of VOCs containing saturated chain, nonpolar property, and unbranched sites (e.g., hexane, heptane, and octane) are more likely occur due to physical interactions of the adsorbate molecules with the adsorbent lattice [64]. For aromatic molecules, a combination of physical and chemical adsorption may occur from the adsorbate and adsorbent interactions. Liu et al. demonstrated that the binding of benzene to the Lewis site of metal emerges due to the van der Waals and covalent bonding [65]. In adsorption of VOCs which behave as Lewis base (e.g., ammonia), the adsorption usually occurs as the effect of Lewis acid and Lewis base interaction. Ammonia mol- ecules act as the Lewis base, while the metal sites serve as Lewis acid. 12.7 Simple Modeling the Adsorption 12.7.1 Thermodynamic Parameters The Clausius–Clapeyron equation can be applied to estimate the heat of adsorption. The variation of retention volume (Vg) with the change of temperature (T) can be translated into a mathematical equation to estimate the heat of adsorption ΔHads, Eq. (12.1) [61]. δ(lnVg) ∆Hads = −R δ(1/T) (12.1)

10**where R is the** ideal **gas constant. The**

Vg is directly related to

14**Henry's law constant** (Hlc), **the** constant that stated **the**

proportionality between the

14**partial pressure** of **the gas phase** to **the** quantity **of** gas dissolved [61]. **In** adsorption, **the**

value of Hlc is directly related to that of the amount of gas adsorbed. The calculation of Hlc can be translated into a mathematical for- mula, as shown in Eq. (12.2). Hlc = nads m × P (12.2) where, nads is the amount of gas adsorbed,

10**m is the mass of adsorbent** used, **and** p is **the** outlet pressure **of**

gas. A virial-type expansion, with virial coefficient Ai and Bi, also can be applied to estimate the heat of adsorption. ln P = ln nads + 1 m n T ∑Ainaids + ∑Biniads i=0 i=0 ∆Hads = −R mi=0 Ainaids ∑ (12.3) (12.4) where

8**m and n** are **the number of coefficients** used **to** determine **the**

iso- therms [48]. 12.7.2 Dynamic Sorption Methods The determination of adsorption capacity of porous materials to adsorb gas adsorbate mostly done by using dynamic sorption methods since, in real practice, the gas adsorption is always done dynamically. Static volu- metric measurements are one of (semi)-dynamic sorption methods in which the process conducts in a closed chamber, then the amount of gas adsorbed upon saturation at a given pressure (p / p0) is recorded. The sche- matic diagram of the static volumetric and its resulting plot are shown in Figure 12.4. The measurement only can be done for a single component, which is become the shortage of this method [66–69]. The amount of adsorbed gas can be calculated by treated the gas component as an ideal gas, as shown by the Eq. (12.5) below. nadsorbed = ndosed − nfree = ⎛⎜⎝ RpVT ⎞⎟⎠ dose − (Vdose + Vchamber) ⎛⎜⎝ RpT ⎞⎟⎠ chamber (12.5) where n is the mol of gas, p is pressure, V is volume, T is temperature, and R is the ideal gas constant. The adsorption isotherm curve can be obtained by plotting amount of gas adsorbed vs. the given pressure. A dynamic method proceeds under forced-flow conditions. The result- ing data (that is adsorption time (duration of the test) vs. concentration of adsorbate in the effluent stream) is depicted as a breakthrough curve. The breakthrough curve (dynamic method) process is similar to that sep- aration process in the industry, where the adsorbent is a gas mixture. The measurement itself is done in an open system while maintaining the pres- sure of the feed. The schematic diagram of the experimental setup and its corresponding breakthrough curve are depicted in Figure 12.5. Control of the gas flow rate is an important parameter that affected the amount of VOC introduced to the adsorption system, the acceleration of gas flow rate also directly

27**related to the contact time between** the VOC **and** MOF- **adsorbent. The**

dynamic adsorption capacity can be calculated through breakthrough data by using the following series of equations [60, 66–69]. (a) pressure gauge n mPa chamber Feed in adsorbent 3.5 3.0 (b) 2.5 loading, mol/g 2.0 1.5 1.0 0.5 0.0 0.0 0.2 0.4 0.6 0.8 1.0 1.2 p/p0 Figure 12.4 (a) Schematic diagram of static volumetric measurement; a single component of VOC gas is pressurized to the desired pressure and then introduced into a closed chamber filled with a certain amount of adsorbent. (b) Adsorption curve; obtained by plotting amount of gas adsorbed at saturation per given pressure. (a) (b) Zone 1 Zone 2 Zone 3 Effluent Feed in pressure gauge n mPa adsorption column detector concentration t0 t1 time tE Figure 12.5 (a) Schematic diagram of dynamic method; the pressurized mixture of VOC gases continuously flowed into the adsorption column (filled with adsorbent) and the gas effluent is measured by using analytical device/detector. (b) Ideal S-shape breakthrough curve; zone 1—unsaturated zone, zone 2—mass transfer zone, zone 3—saturated zone. The concentration of VOC over time (Ct, mg·min/m3) is calculated by multiply concentration of the feed (Cfeed, mg/m3) with the length of time that the feed passed (tf, min), as shown in Eq. (12.6). Ctfeed = tfCfeed (12.6) m3) done by the adsorbent until the flow stopped can be calculated by inte- The subsequent eluted concentration of VOC per time (Ctelution, mg·min/ grating under the elution curve, as shown by Eq. (12.7); which also can be applied for desorption. Ctelution = tts=0 Cn + Cn−1 × (tn−1 − tn) ∑ 2 (12.7) in this case, ts is saturation time (min), tn is the time n (min), and Cn is the concentration at time n (mg/m3) [60]. Note that there are many options of a modified form of the equations that can be used to modeling the adsorp- tion experiment. Zone 1, unsaturated zone, cannot be obtained by using the static vol- umetric measurements. Zone 2 is a mass transfer zone (also abbreviated as MTZ), the approximation of the effective-amount of adsorbent can be determined by analyzing the steepness of this zone. A very narrow zone 2 indicates that the adsorbent has a low adsorption capacity. The saturated zone, zone 3, is similar to that of the equilibrium value of adsorption iso- therm in which the adsorption capacity can be determined. An ideal break- through curve would have an S-shaped curve, as shown in Figure 12.5. An alteration (a skewed curve), however, may occur due to heterogeneity of the adsorbent [66–71]. 12.8 Factor Affecting VOCs Adsorption 12.8.1 Breathing Phenomena Breathing phenomena of MOF refers to the turnover structure from closed pores (non-porous) to open pores (porous). The phenomenon is pio- neered by Ferey and Kitagawa et al. This dynamic phenomenon in adsorp- tion is stimulated by atomic displacement (dipole moment interaction, in specific) which is caused by the presence of adsorbate. The phenomena are introduced by Kitagawa et al., in their study on pillared layer MOFs. Kitagawa et al. declared that MOF is undergoing a locking and unlocking phenomena before and after adsorption, respectively [72, 73]. The distor- tion of the molecular structure of MOFs and cell-dimensions expansion occurred along with the breathing phenomena. A similar breathing behavior observed for MIL-53. A reversible change in the pore volume happened when the MIL-53 (Al or Cr) is being air-cooled after heating at high temperature. As illustrated in Figure 12.6, a decrease in pore volume occurred when MIL-53 is at low temperature due to absorption of water molecules and reversed back to original volume when water mole- cules are removed by treating in high temperature. Upon high temperature treatment, the H-bond between the water molecules is getting weaker an (a) (b) H2 O 2O H open pore closed pore Figure 12.6 Illustrated breathing phenomena of MIL-53. (a) Open pore after high temperature treatment (unit cell volume 1522 Amstrong3); (b) closed pore (unit cell volume 1013 Amstrong3) after air cooling due to H-bond interactions between water molecules. Adapted from Ref. [74]. eventually disappeared along with the dehydration process; subsequently, the pores of MIL-53 convert back to large open pores [74]. A similar breathing phenomena also observed upon pressurized-CO2 exposure to the hydrated MIL-53 at low temperature. CO2 exposure at low pressure (<5 bar) is not sufficient to cause pore opening to MIL- 53. The co-existence of open and closed pores is observed when the more CO2 molecules are introduced, and consequently, the pressure is increased. Further increase of CO2 pressure, > 15 bar (approximately 7.2 mmol/g), allow the presence of MIL-53 with the whole open pores. In this case, there is a slight different dehydrated phenomenon; that is, a two steps pore transition (open–closed–specific) is observed. Upon dehydration, a plateau (steady pore size) happens when 3.0 mmol/g CO2 introduced. Hereafter, the pores start to expand as the CO2 added (up to 7.7 mmol/g) before another plateau occurs.

The plateau is suggested to be the effect of steric hindrance between the water molecules. The structural change due to the breathing effect also caused alteration to the sorption– isotherm behavior of MOFs. At dehydrated state, the N2-sorption of MIL- 53 (both with Al or Cr building blocks) shows a Type-I-sorption-isotherm which indicate the dominance in microporous structure. A behavioral discrepancy is observed for MIL-53 with ferric (Fe) and scandium (Sc) metal center. Both dehydrated MIL-53(Fe) and (Sc) show nonporous structure; this difference is due to the two MOFs is initially have a closed or very-narrow pores unlike MIL-53(Al) or (Cr). When CO2 introduced, instead of N2, a Type-VI-sorption-isotherm is observed. MOF attributed with breathing ability reportedly is chemically more stable than other MOFs without this ability. MIL-53, for instance, remains indestruc- tible either in the presence of water molecules or heat up to 500°C [44, 75, 76]. 12.8.2 Activation of MOFs Many studies reported that the enormous

10**surface area and porosity** of MOFs **can be** achieved **by** removing **the** guest molecules **from the**

frame- work matrix without destroying the integrity of the structure and pores [77]. This process is called activation or sometimes referred to as purifica- tion. The presence of guest molecules is originated by the excess reactant, solvent, and reaction intermediate ion or molecules. Often, those guest molecules cause pore blocking, thus reducing the surface area as well as pore volume of MOFs; subsequently, they may also demote the adsorp- tion performance of MOFs. For instance, the presence of dimethylfor- mamide (DMF) residual-guest molecules in the structural of BioMIL-3 ([Ca2(azbz-TC)-(H2O)(DMF)], azbz-TC = 3,3 ,5,5 -azobenzenetetracar- boxylate) cause steric hindrance and diffusion blocking thus constraint the interaction of the gas adsorbate (nitric oxide) with the metal sites [78]. In some cases, activation of MOFs may also grant breathing ability to MOFs [79]. Several activation processes have been developed by engineers, such as heat treatment, vacuum treatment, chemical treatment, solvent exchange, supercritical treatment, and freeze drying. Ideally activation process by using heat treatment can only be success- fully applied to MOFs with high thermal stability. However, in most cases, the implementation of heat activation fails to purify the pore and may destruct the crystallinity of the MOFs in response to the demolition of the coordination bond of MOFs by a large amount of heat energy. A subclass of MOFs namely ZIF-8 (ZIF = zeolitic imidazolate framework) with sur- face area 874 m2/g show an improvement in adsorption activity upon heat treatment. The adsorption capacity of ZIF-8 towards toluene increased from 5.4 to 41.1 mg/g after heating treatment at 300°C [80]. Similarly, vac- uum treatment is also known to cause loss of crystallinity due to the large capillary forces and surface tension (as the liquid phase transforms into gas phase) that result in the destruction of MOF coordination bonds. In chemical treatment, a strong acid solution is commonly used to rigorously wash the guest molecules out of the pore of MOF. Activation by the solvent is done by exchanging the high boiling point solvent with a lower boiling point solvent, this is to minimize the molecular forces caused by the sol- vent during activation. Supercritical treatment is basically similar to that solvent exchange, but the treatment is done at supercritical condition by using liquid CO2 as the common solvent. The implementation of freeze drying activation is preceded by the introduction of benzene into MOFs followed by several freezing-thawing cycles [77, 81–84]. 12.8.3 Applied Pressure Application of pressure

3**play an important role in** promoting **the**

adsor- bate-adsorbent interaction. Hamon et al. show that

3**adsorption of H2S** onto **MIL-53(Cr) at** low **pressure**

(4.5 kPa) resulting in low

3**adsorption capacity of** 3.02 **mmol/g. At**

higher applied pressure of 1.6 MPa, 13.12 mmol H2S can be adsorbed per gram of MIL-53(Cr). This behavior attributed to the breathing of MIL-53(Cr). At low pressure, closing pore phenomena occurs due to the strong interaction of OH-group of MOF with H2S. At higher pressure, there is a complete pore vacancy as the interaction of OH-group of MOF with H2S getting weaker. The pore opening is allowing the total filling of the pores, which leads to higher adsorption capacity [38]. 12.8.4 Relative Humidity Adsorption which performed in humid gas flow or in the presence of water molecules, may have a decreased adsorption capacity. As shown in Table 12.5, the adsorption performs in a dry gas flow have better adsorp- tion capacities than that of wet flow. A similar phenomenon also occurs in the adsorption study of MOF-177 by Yang et al. The adsorption of tolu- ene and trichloroethylene on MOF-177 is decreased steeply as the relative humidity altered from 0% to 50%. The water molecules initiate competi- tion against adsorbate to bind to the open metal sites of MOF, thus cause suppressions to the adsorption performance. The other possibility is that the exposure of water to MOF may disrupt its structure [29, 60]. In partic- ular, [Ni(bpb)] MOF may effectively adsorb VOCs in a humid condition. In a dynamic adsorption experiment with 60% humidity, 1 g of [Ni(bpb)] (which synthesized from organic linker namely 1,4-(4-bispyrazolyl)ben- zene (bpb)) can adsorb 340 mg of thiopene [85]. 12.8.5 Breakthrough Conditions As so called breakthrough curve give a full depiction of adsorption dynamic. The curve shows the change of VOC concentration in the efflu- ent throughout adsorption time. The sorption capacity, thermodynamic (heat transfer or release), kinetics (adsorption rate), selectivity, and gas flow rate are the crucial parameters that influence the curve. An adsorbent with large sorption capacity will have longer breakthrough times since it can retain more adsorbate molecules. However, if the sorption kinetics proceed very slowly, there is a possibility of the spontaneous breakthrough, this will cause alteration in the shape of the curve. A rapid mass transfer (high flow rate) produces a steep breakthrough curve and narrow mass transfer zone. Broadening

27**of the mass transfer zone** may occur **in**

the case of exothermic adsorption. The temperature increase due to heat release by adsorption leads to flatter and more asymmetric curve. An evenly mass dispersion may also lead to broadening of the mass transfer zone [69]. 12.8.6 Functional Group of MOFs The presence of functional groups of MOF in enhancing the adsorption has been demonstrated. A particular functional group may also help to prevent competition between adsorbate molecules and water molecules; conse- quently, the adsorption still performs excellently in the humid condition. Addition of fluorine in the building block of FMOF-1 (prepared by reacting monovalent silver and

8**3,5-bis(trifluoromethyl)-1,2,4-triazolate**) cause it **to**

be hydrophobic, therefore the water molecules cannot enter the pore of FMOF-1. The hydrophobicity of FMOF-1 also makes it be selective against certain VOCs (benzene, p-xylene, cyclohexane, toluene, and n-hexane) [86]. A similar phenomenon is observed for [

6**Ni8(OH)4(H2O)2(L5-CF3)6**

], which build from

2**4,4’-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1H**

-pyra- zole) abbreviated as L5. The presence of coordination of the metal with the pyrazole group induces the stability

2**of the MOF** against **water molecules**, and **the**

MOF still able to adsorb diethylsulfide at 80% relative humidity [61]. The presence of the ionic group in the MOF structure may induce selec- tivity against certain VOC. The NH4+ in the framework of MOF namely NH4[Cu3(OH)(capz)], where capz = 4-carboxypyrazolato, causes alteration in the pore structure of the MOF and also lead to adsorption selectivity toward cyclohexane–benzene mixtures, which related to the size-exclusion of the adsorbate molecules.

1**12.8.7 Concentration, Molecular Size, and Type of VOCs**

Adsorption can occur effectively when there is compatibility between VOCs and MOFs as the guest and host molecules. The key features of the compatibility, in this case, are the molecular size, molecular orientation, and the number of molecules of the VOC adsorbate. Adsorption can occur efficiently when all key features of VOCs are consistent with the pore struc- ture and crystal symmetry of MOF as adsorbent. For instance, MIL-53(Al) can adsorb doubled amount of p-xylene when the pore is in the vacant form. The availability of space in the vacant pore is adequate to accom- modate two molecules of p-xylene as illustrated in Figure 12.7. Also, the length of p-xylene

13**is compatible with the size of MIL**-53 **open pore**

[75]. If the amount of adsorbate molecules is too many, the active adsorption sites of the adsorbent may not enough to accommodate all of the desired adsor- bate molecules (saturation of the adsorbent). Also, there might be repul- sive force between the adsorbate molecules thus decrease the efficiency of the adsorption. The type of VOC adsorbents determines the adsorption performance. The strength of inter- or intra-molecular interaction of each type of VOC is determined by their affinity; the interaction can be polarization and/or electrostatic, acid-base, or physisorption. A density functional theory has been applied to investigate the adsorption energies between several small organic molecules with a copper metal cluster of HKUST- 1. It is revealed that only the adsorption energy of NH_3 can surpass the (a) e e p-xylene p - x yeln -xylen p p-xylene (b) p - x ylene p-xyle n e Figure 12.7 Adsorption of p-xylene by MIL-53 at open pore condition. (a) There is double amount of p-xylene adsorbed when the molecular orientation is compatible with pore structure and symmetry, (b) a lesser amount of p-xylene can be adsorbed since the orientation is not compatible. Adapted from Ref. [75]. water molecules; with the value of adsorption energies is decreased in the following order: $NH_3 > H_2O > PH_3 > H_2S > SO_2 > CO$ OCS CO_2 $NyOx > N_2 > O_2$ [87]. 12.9 Future Perspective The superiority and efficacy of MOF in overcoming VOCs has been proven by many engineers. MOF can be used as an efficient adsorbent for remov- ing and/or storing VOCs, some MOFs also have catalytic activity against VOCs. In many lab scale experiments, it has been shown that the MOF adsorption capacity is very high; i.e., can reach >1 g VOC per g MOF. But there are still very few experiments that show the feasibility of VOC adsorption by MOF on an industrial scale. The feasibility of MOF applica- tion in the industry can be said to be far from ideal, both in terms of eco- nomics and synthesis. This is because in industry, VOC is always produced in large quantities so it requires large amounts of MOF as an adsorbent; this will cause an increase in total production costs due to the high cost of MOF synthesis. References 1. Barea, E., Montoro, C. et al., Toxic gas removal – metal–organic frameworks for the capture and degradation of toxic gases and vapours. Chem. Soc. Rev., 43, 5419, 2014. 2. Wen, M., Li, G. et al., Metal–

organic framework-based nanomaterials for adsorption and photocatalytic degradation of gaseous pollutants: Recent progress and challenges. Environ. Sci. Nano, 6, 1006, 2019. 3. United States Environmental Protection Agency, 2017. Technical Overview of Volatile Organic Compounds, https://www.epa.gov/indoor-air-quality-iaq/ technical-overview-volatile-organic-compounds. 4. Shuai, J., Kim, S. et al., Health risk assessment of volatile organic compounds exposure near Daegu dyeing industrial complex in South Korea. BMC Public Health, 18, 528, 2018. 5. Lin, L., Chai, Y. et al., Photocatalytic oxidation for degradation of VOCs. Open J. Inorg. Chem., 3, 14–25, 2013. 6. Khan, F.I. and Ghosal, A.K., Removal of Volatile Organic Compounds from polluted air. J. Loss Prevent. Proc., 13, 527–545, 2000. 7. U.S. National Library of Medicine, 2017. Volatile Organic Compounds (VOCs), https://toxtown.nlm.nih.gov/chemicals-and-contaminants/volatile- organic-compounds-vocs. 8. The National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention, The NIOSH Pocket Guide to Chemical Hazards, https://www.cdc.gov/niosh/npg/pgintrod.html. 9. Loreto, F. and Fares, S., Biogenic Volatile Organic Compounds and Their Impacts on Biosphere–Atmosphere Interactions, in: Developments in Environmental Science, Matyssek, R., et al. (Eds.), pp. 57–75. 10. Peñuelas, J., Asensio, D. et al., Biogenic volatile emissions from the soil. Plant Cell Environ., 37, 1866–1891, 2014. 11. Ryu, C.-M., Farag, M.A. et al., Bacterial volatiles promote growth in Arabidopsis. PNAS, 100, 4927–4932, 2003. 12. Naznin, H.A., Kiyohara, D. et al., Systemic Resistance Induced by Volatile Organic Compounds Emitted by Plant Growth-Promoting Fungi in Arabidopsis thaliana. PLoS One, 9, e86882, 2014. 13. Jaeger, D.M., Runyon, J.B. et al., Signals of speciation: Volatile organic com- pounds resolve closely related sagebrush taxa, suggesting their importance in evolution. New Phytol., 211, 1393–1401, 2016. 14. González-Mas, M.C., Rambla, J.L. et al., Volatile Compounds in Citrus Essential Oils: A Comprehensive Review. Front. Plant Sci., 10, 12, 2019. 15. Shao, M., Czapiewski, K.V. et al., Volatile organic compound emissions from Scot pine: Mechanisms and description by alogarithms. J. Geophys. Res., 106, 20483–20491, 2001. 16. Rasmann, S., Köllner, T.G. et al., Recruitment of entomopathogenic nema- todes by insect-damaged maize roots. Nature, 434, 732–737, 2005. 17. Fialho, M.B., Toffano, L. et al., Volatile organic compounds produced by Saccharomyces cerevisiae inhibit the in vitro development of Guignardia cit- ricarpa, the causal agent of citrus black spot. World J. Microbiol. Biotechnol., 26, 925–932, 2010. 18. Oro, L., Feliziani, E. et al., Volatile organic compounds from Wickerhamomyces anomalus, Metschnikowia pulcherrima and Saccharomyces cerevisiae inhibit growth of decay causing fungi and control postharvest diseases of strawber- ries. Int. J. Food Microbiol., 265, 18–22, 2018. 19. Cuffia, F., Bergamini, C.V. et al., Characterization of volatile compounds pro- duced by Lactobacillus helveticus strains in a hard cheese model. Food Sci. Technol. Int., 24, 67–77, 2017. 20. Chen, J., Tang, J.N. et al., The production characteristics of volatile organic compounds and their relation to growth status of Staphylococcus aureus in milk environment. J. Dairy Sci., 101, 4983–4991, 2018. 21. Ezeji, T.C., Qureshi, N. et al., Production of acetone, butanol and ethanol by Clostridium beijerinckii BA101 and in situ recovery by gas stripping. World J. Microbiol. Biotechnol., 19, 595–603, 2003. 22. Daisy, B.H., Strobel, G.A. et al., Naphthalene, an insect repellent, is produced by Muscodor vitigenus, a novel endophytic fungus. Microbiology, 148, 3737– 3741, 2002. 23. Singh, S.K., Strobel, G.A. et al., An endophytic Phomopsis sp. possessing bio- activity and fuel potential with its volatile organic compounds. Microb. Ecol., 61, 729–739, 2011. 24. G. Strobel, D. Manker et al., Endophytic fungi and methods of use. U.S. Patent 7754203, assigned to Agra Quest, Inc. 2010. 25. Drilling, K. and Dettner, K., Electrophysiological responses of four fungi- vorous coleoptera to volatiles of Trametes versicolor: Implications for host selection. Chemoecology, 19, 109–115, 2009. 26. Hussain, A., Tian, M.Y. et al., Differential fluctuation in virulence and VOC profiles among different cultures of entomopathogenic fungi. J. Invertebr. Pathol., 104, 166–171, 2010. 27. Liu, B., Yang, F. et al., Adsorption of Phenol and pNitrophenol from Aqueous Solutions on Metal–Organic Frameworks: Effect of Hydrogen Bonding. J. Chem. Eng. Data, 59, 1476–1482, 2014. 28. Vellingiri, K., Szulejko, J.E. et al., Metal organic frameworks as sorption media for volatile and semi-volatile organic compounds at ambient condi- tions. Sci. Rep., 6, 27813, 2016. 29. Yang, K., Xue, F. et al., Adsorption of volatile organic compounds by metal–organic frameworks MOF-177. J. Environ. Chem. Eng., 1, 713–718, 2013. 30. Zhang, G., Liu, Y. et al., Adsorption of volatile organic compounds onto nat- ural porous minerals. J. Hazard. Mater., 364, 317–324, 2019. 31. Yang, H., Deng, J. et al., Au/MnOx/3DOM SiO2: Highly active catalysts for toluene oxidation. Appl.

Catal., A, 507, 139–148, 2015. 352 Applications of Metal–Organic Frameworks 32. Hao, X., Li, R. et al., Numerical simulation of a regenerative thermal oxidizer for volatile organic compounds treatment Environ. Eng. Res., 2018. 33. Christen, P., Domenech, F. et al., Biofiltration of volatile ethanol using sugar cane bagasse inoculated with Candida utilis. J. Hazard. Mater., 89, 253–265, 2002. 34. Lalanne, F., Malhautier, L. et al., Absorption of a mixture of volatile organic compounds (VOCs) in aqueous solutions of soluble cutting oil. Bioresour. Technol., 99, 1699–1707, 2008. 35. Rebollar-Perez, G., Carretier, E. et al., Volatile Organic Compound (VOC) Removal by Vapor Permeation at Low VOC Concentrations: Laboratory Scale Results and Modeling for Scale Up. Membranes, 1, 80–90, 2011. 36. Alivand, M.S., Shafiei-Alavijeh, M. et al., Facile and high-yield synthesis of improved MIL-101(Cr) metal–organic framework with exceptional CO2 and H2S uptake; the impact of excess ligand-cluster. Microporous Mesoporous Mater., 279, 153–164, 2019. 37. Du, P.D., Thanh, H.T.M. et al., Metal–Organic Framework MIL-101: Synthesis and Photocatalytic Degradation of Remazol Black B Dye. J. Nanomat., 2019, Article ID 6061275, 15 pages, 2019. 38. Hamon, L., Serre, C. et al., Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL- 101(Cr) Metal–Organic Frameworks at Room Temperature. J. Am. Chem. Soc., 131, 8775–8777, 2009. 39. Huang, C.-Y., Song, M. et al., Probing the Adsorption Characteristic of Metal–Organic Framework MIL-101 for Volatile Organic Compounds by Quartz Crystal Microbalance. Environ. Sci. Technol., 45, 4490–4496, 2011. 40. Leng, K., Sun, Y. et al., Rapid Synthesis of Metal–Organic Frameworks MIL- 101(Cr) Without the Addition of Solvent and Hydrofluoric Acid. Cryst. Growth Des., 16, 1168–1171, 2016. 41. Shafiei, M., Alivand, M.S. et al., Synthesis and adsorption performance of a modified micro-mesoporous MIL-101(Cr) for VOCs removal at ambient conditions. Chem. Eng. J., 341, 164–174, 2018. 42. Yot, P.G., Ma, Q. et al., Large breathing of the MOF MIL-47(VIV) under mechanical pressure: A joint experimental–modelling exploration. Chem. Sci., 3, 1100–1104, 2012. 43. Boutin, A., Coudert, F.-X. et al., The Behavior of Flexible MIL-53(Al) upon CH4 and CO2 Adsorption. J. Phys. Chem. C, 114, 22237–22244, 2010. 44. Alhamami, M., Doan, H. et al., A Review on Breathing Behaviors of Metal– Organic-Frameworks (MOFs) for Gas Adsorption. Materials, 7, 3198–3250, 2014. 45. Finsy, V., Kirschhock, C.E. et al., Framework breathing in the vapour-phase adsorption and separation of xylene isomers with the metal–organic frame- work MIL-53. Chemistry, 15, 7724–7731, 2009. 46. Britt, D., Tranchemontagne, D. et al., Metal–organic frameworks with high capacity and selectivity for harmful gases. Proc. Natl. Acad. Sci., 105, 11623– 11627, 2008. 47. Chae, H.K., Siberio-Pérez, D.Y. et al., A route to high surface area, porosity and inclusion of large molecules in crystals. Let. Nature, 427, 523–527, 2004. 48. Furukawa, H., Miller, M.A. et al., Independent verification of the saturation hydrogen uptake in MOF-177 and establishment of a benchmark for hydro- gen adsorption in metal–organic frameworks. J. Mater. Chem., 17, 3197– 3204, 2007. 49. Tranchemontagne, D.J., Hunt, J.R. et al., Room temperature synthesis of metal–organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0. Tetrahedron, 64, 8553–8567, 2008. 50. He, W.-W., Yang, G.-S. et al., Phenyl Groups Result in the Highest Benzene Storage and Most Efficient Desulfurization in aSeries of Isostructural Metal– Organic Frameworks. Chem. Eur. J., 21, 9784–9789, 2015. 51. Bao, S.-J., Krishna, R. et al., A stable metal–organic framework with suitable pore sizes and rich uncoordinated nitrogen atoms on the internal surface of microspores for highly efficient CO2 capture. J. Mater. Chem. A, 3, 7361– 7367, 2015. 52. McKinlay, A.C., Eubank, J.F. et al., Nitric Oxide Adsorption and Delivery in Flexible MIL-88(Fe) Metal–Organic Frameworks. Chem. Mater., 25, 1592– 1599, 2013. 53. Gándara, F., García-Cortés, A. et al., Rare Earth Arenedisulfonate Metal– Organic Frameworks: An Approach toward Polyhedral Diversity and Variety of Functional Compounds. Inorg. Chem., 46, 3475–3484, 2007. 54. Gándara, F., Puebla, E.G. et al., Controlling the Structure of Arenedisulfonates toward Catalytically Active Materials. Chem. Mater., 21, 655–661, 2009. 55. Jiang, H.L., Liu, B. et al., Au@ZIF-8: CO oxidation over gold nanoparticles deposited to metal–organic framework. J. Am. Chem. Soc., 131, 11302– 11303, 2009. 56. Procopio, E.Q., Linares, F. et al., Cation-Exchange Porosity Tuning in Anionic Metal–Organic Frameworks for the Selective Separation of Gases and Vapors and for Catalysis. Angew. Chem. Int. Ed., 49, 7308, 2010. 57. Shen, Y., Jiang, P. et al., Recent Progress in Application of Molybdenum- Based Catalysts for Epoxidation of Alkenes. Catalysts, 9, 31, 2019. 58. Yao, P., Liu, H. et al., Enhanced visible-light photocatalytic activity to volatile organic compounds degradation and deactivation resistance mechanism of titania confined inside a metal–organic framework. J. Colloid Interface Sci., 522, 174–182, 2018. 59. Gómez-Avilés, A., Peñas-Garzón, M. et al., Mixed Ti-Zr metal–organic- frameworks for the photodegradation of acetaminophen under solar irradi- ation. Appl. Catal., B, 253, 253–262, 2019. 60. Glover, T.G., Peterson, G.W. et al., MOF-74 building unit has a direct impact on toxic gas adsorption. Chem. Eng. Sci., 66, 163–170, 2011. 61. Padial, N.M., Procopio, E.Q. et al., Highly Hydrophobic Isoreticular Porous Metal–Organic Frameworks for the Capture of Harmful Volatile Organic Compounds. Angew. Chem. Int. Ed., 52, 1–6, 2013. 62. Zhou, X., Huang, W. et al., Enhanced separation performance of a novel composite material GrO@MIL-101 for CO2/CH4 binary mixture. Chem. Eng. J., 266, 339–344, 2015. 63. Sun, X., Xia, Q. et al., Synthesis and adsorption performance of MIL-101(Cr)/ graphite oxide composites with high capacities of n-hexane. Chem. Eng. J., 239, 226–232, 2014. 64. Hercigonja, R. and Rakić, V., Enthalpy–entropy Compensation for n-hexane Adsorption on Y Zeolite Containing Transition Metal Cations. Sci. Sinter., 47, 83–88, 2015. 65. Liu, W., Carrasco, J. et al., Benzene Adsorbed on Metals: Concerted Effect of Covalency and van der Waals Bonding. Phys. Rev. B, 86, 245405, 2012. 66. Möller, A., Eschrich, R. et al., Dynamic and equilibrium-based investigations of CO2-removal from CH4-rich gas mixtures on microporous adsorbents. Adsorption, 23, 197–209, 2017. 67. Grande, C.A., Blom, R. et al., High-Pressure Separation of CH4/CO2 Using Activated Carbon. Chem. Eng. Sci., 89, 10–20, 2013. 68. Bastos-Neto, M., Moeller, A. et al., Adsorption Measurements of Nitrogen and Methane in Hydrogen-Rich Mixtures at High Pressures. Ind. Eng. Chem. Res., 50, 10211–10221, 2011. 69. INSTRUMENTS GmbH & Co. KG, 2019. Dynamic Sorption, https:// www.dynamicsorption.com/dynamic-sorption-method/breakthrough- measurement/. 70. Hori, H., Tanaka, I. et al., Breaktrough Time on Activated Carbon Fluidized Bed Adsorbers. J. Air Pollut. Control Assoc., 38, 269–271, 1988. 71. Wang, W.-Z., Brusseau, M.L. et al., Nonequilibrium and Nonlinear Sorption during Transport of Cadmium, Nickel, and Strontium through Subsurface Soils. Adsorpt. Met. Geomedia, 427–443, 1998. 72. Kitagawa, S., Kitaura, R. et al., Functional Porous Coordination Polymers. Angew. Chem. Int. Ed., 43, 2334, 2004. 73. Foo, M.L., Matsuda, R. et al., An Adsorbate Discriminatory Gate Effect in a Flexible Porous Coordination Polymer for Selective Adsorption of CO2 over C2H2. J. Am. Chem. Soc., 138, 3022–3030, 2016. 74. Serre, C., Millange, F. et al., Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or CrIII(OH)·{O2C– C6H4–CO2}·{HO2C–C6H4–CO2H}x·H2Oy,. J. Am. Chem. Soc., 124, 13519– 13526, 2002. 75. Wu, H., Gong, Q. et al., Commensurate adsorption of hydrocarbons and alcohols in microporous metal organic frameworks. Chem. Rev., 112, 836– 868, 2012. 76. Llewellyn, P.L., Bourrelly, S. et al., How hydration drastically improves adsorption selectivity for CO2 over CH4 in the flexible chromium terephthal- ate MIL-53. Angew. Chem. Int. Ed., 45, 7751–7754, 2006. 77. Mondloch, J.E., Karagiaridi, O. et al., Activation of metal–organic framework materials. Cryst. Eng. Comm., 15, 9258–9264, 2013. 78. Miller, S.R., Alvarez, E. et al., A rare example of a porous Ca-MOF for the controlled release of biologically active NO. Chem. Commun., 49, 7773, 2013. 79. Engel, E.R., Jouaiti, A. et al., Activation-Dependent Breathing in a Flexible Metal–Organic Framework and the Effects of Repeated Sorption/Desorption Cycling. Angew. Chem. Int. Ed., 56, 8874–8878, 2017. 80. Jafaria, S., Ghorbani, F. et al., Removal of Toluene from Air by Zeolitic Imidazolate Framework-8: Synthesis, Characterization, and Experimental Breakthrough Curve. Int. J. Sci. Stud., 5, 1073–1082, 2017. 81. Abraham, B.F., Hoskins, B.F. et al., Assembly of porphyrin building blocks into network structures with large channels. Nature, 369, 727–729, 1994. 82. Bedia, J., Muelas-Ramos, V. et al., A Review on the Synthesis and Characterization of Metal Organic Frameworks for Photocatalytic Water Purification. Catalysts, 9, 52, 2019. 83. Férey, G., Mellot-Draznieks, C. et al., A chromium terephthalate-based solid with unusually large pore volumes and surface area. Science, 23, 2040–2042, 2005. 84. Cavka, J.H., Jakobsen, S. et al., A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. J. Am. Chem. Soc., 130, 13850–13851, 2008. 85. Galli, S., Masciocchi, N. et al., Adsorption of Harmful Organic Vapors by Flexible Hydrophobic Bis-pyrazolate Based MOFs. Chem. Mater., 22, 1664– 1672, 2010. 86. Yang, C., Kaipa, U. et al., Fluorous metal–organic frameworks with superior adsorption and hydrophobic properties toward oil spill cleanup and hydro- carbon storage. J. Am. Chem. Soc., 133, 18094–18097, 2011. 87. Supronowicz, B., Mavrandonakis, A. et al., Interaction of Small Gases with the Unsaturated Metal Centers of the HKUST-1 Metal Organic Framework. J. Phys. Chem. C, 117, 14570–14578, 2013.

Frameworks Adsorption of VOC by Using MOF and Hybrids 329 330

Frameworks Adsorption of VOC by Using MOF and Hybrids 333 334

Using MOF and Hybrids 335 336

Using MOF and Hybrids 337 338

Using MOF and Hybrids 339 340

Using MOF and Hybrids 341 342

Using MOF and Hybrids 343 344

Using MOF and Hybrids 345 346

Using MOF and Hybrids 347 348