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Metal – Organic Frameworks: State-of-the-art Material for Gas Capture and Storage

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Abstract: The capture and storage of gases for the applications of energy, environment, and biomedicine are closely related to the major concerns of the modern world about energy crisis, air pollution and global warming, and human's health. Many materials and techniques have been developed to tackle these widespread issues, in which metal-organic frameworks (MOFs) – a new class of porous materials with exceptionally high surface areas – have emerged as the most promising candidate for the capture and storage of gases based on the adsorption of gases on the surface of MOFs. This article provides a short overview of the current status in the capture and storage of gases within the structure of MOFs.

Keywords: Metal – organic frameworks, gas storage, hydrogen, carbon dioxide, methane, nitric oxide.

1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline, porous materials with the structures constructed from metal ions or metal clusters and organic ligands. Common metal ions are Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Fe^{2+}, Mg^{2+}, Al^{3+}, and Mn^{2+}. Common ligands are benzene-dicarboxylate (BDC), benzene-tricarbonxylate (BTC), polycarboxylate (BTB), imidazole, pyrazole, triazole, tetrazole, and mixed ligands. Because of the flexible combination of organic and inorganic components, MOFs offer many interesting features such as exceptionally large surface areas, ultrahigh porosity with an absence of blocked volume, complete exposure of metal sites, high mobility of guest species in regular nanopores of frameworks, and a fast growing number of organic–inorganic chemical compositions [1]. Therefore, MOFs can be widely used for gas capture and storage, gas separation, catalysis, drug delivery, and semiconductors, *etc*. [2].

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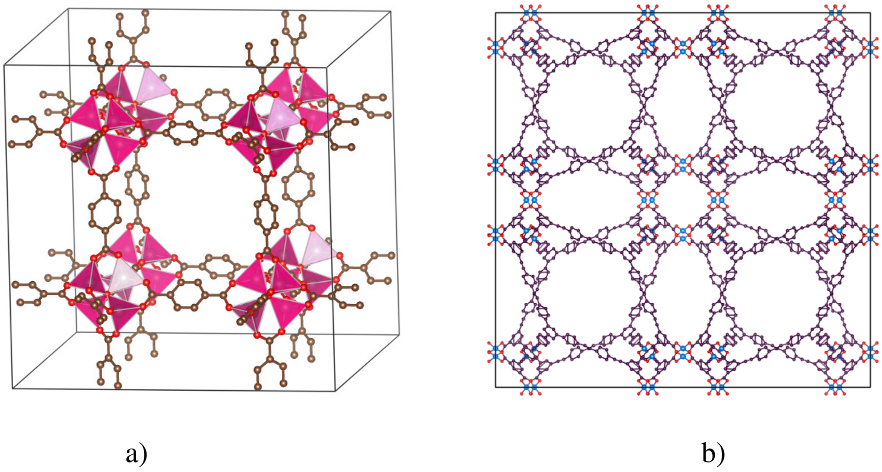
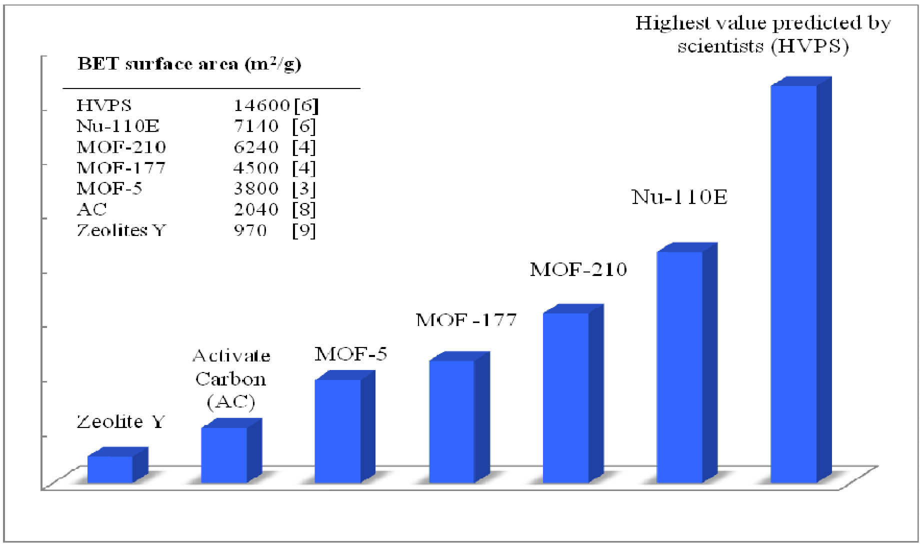

a) b)

Figure 1. (a) MOF-5 with the BET surface area of 3800 m^2/g, and (b) NU-110 with the highest BET surface area of porous materials reported so far.

MOFs were initially introduced as porous coordination networks (PCNs), microporous coordination polymer (MCPs), zeolite-like metal organic framework (ZMOFs) or porous coordination polymers. They have been developing on the academic level since 1990s. In the early of the 1990s, the research group of Professor Omar Yaghi at University of California Berkeley successfully synthesized a series of MOFs named from MOF-2 to MOF-11 [3], including MOF-5 (Figure 1a) – one of the most common MOFs nowadays [3]. Subsequently, many new MOFs have been designed and synthesized with much progress in both quantity and quality. During the last two decades, MOFs continuously set new records in terms of specific surface areas and pore volumes, and gas storage capacities. MOF-177 and MOF-210 are the two of MOFs which have been technically tested for hydrogen storage and carbon dioxide capture with an exceptionally high storage capacity at 77 K and relatively low pressure (under 100 bar) [4, 5]. Most recently, NU-109 and NU-110 exhibited the highest experimental Brunauer-Emmett-Teller (BET) surface area of any porous materials reported to date that is 7000 m^2/g and 7140 m^2/g, respectively (Figure 1b) [6]. The internal surface area of just one gram of NU-110 could cover one-and-a-half football field. The researchers also estimated the theoretical upper limit of the MOF surface areas, and they showed that the hypothetical maximum BET surface area of MOF materials is about 14600 m^2/g or even higher [6]. Figure 2 compares the surface areas of zeolites, activated carbon and several MOFs. Nowadays, thousands of different MOFs are known and still in continuously further development [7].

MOFs are typically synthesized by the combinations of organic ligands and metal salts in solvothermal reactions at relatively low temperatures (below 300°C). The reactants are mixed in the boiling and polar solvents such as water, dialkyl formamide, dimethyl sulfoxide, and acetonitrile. The most important parameters of the solvothermal synthesis of MOFs are temperature, the concentrations of the metal salts and the ligands, the extent of the solubility of the reactants in the solvents, and the pH value of the solutions. The characteristics of the ligands such as bond angles, ligand lengths, bulkiness, and chirality also play a crucial role in dictating what the resultant frameworks will be. Additionally, the tendency of metal ions to adopt certain geometries also influences on the structures of MOFs.



BET surface area (m^2/g)	
HVPS	14600 [6]
Nu-110E	7140 [6]
MOF-210	6240 [4]
MOF-177	4500 [4]
MOF-5	3800 [3]
AC	2040 [8]
Zeolites Y	970 [9]

Figure 2. BET surface areas of representative MOFs, activated carbon, and zeolites. Data were collected from Refs. [3, 4, 6, 8, 9].

Because of the novel properties and the widespread applications, MOFs have attracted much attention in both computational and experimental studies. In Vietnam, MOFs have been studied by several research groups. Some noticeable results have been achieved [10-13]; however, researches on MOFs in Vietnam should be extended to a larger scope. Therefore, the aim of this paper is to provide a short overview of this material for gas capture and storage to scientists and researchers in Vietnam.

2. Metal-organic frameworks for gas capture and storage

Current storage techniques such as high pressure tanks, cryogenic tanks, chemisorption, physisorption, and pre/post-combustion treatments have achieved the storage target at nearly practical levels; however, vital improvements and cost reduction are required to most of them. For example, the pressurized tank-based hydrogen storage suffers from the safety and economic issues. The chemisorption approach allows the formation of chemical bonds between the adsorbed gases and the storage materials, leading to a greater gas storage density, but the kinetics, reversibility and heat management are still challenging [7].

MOFs can be used to capture and store a wide range of gases thanks to their high surface area and porosity. Gas capture and storage in MOFs are primarily based on physisorption which is established by the weak interactions (mainly dominated by van der Waals force) between the adsorbed gases and the atoms of the MOFs. The advanced characteristics of MOF-based storage technologies compared to other techniques that are fast kinetics and absolute reversibility. Thus, using MOFs for gas adsorption could reduce the cost because of an easy desorption of the adsorbed gases and the reusability of the MOF material. In the following section, three main categories related to MOFs for gas capture and storage involving in energy usages, environmental issues, and biomedical applications will be discussed.

2.1. Gas storage for energy issues

2.1.1. Hydrogen storage

Hydrogen gas is a clean energy source and it can be used to replace the fossil fuels which are responsible for global warming and various nagging forms of pollution. The use of energy from hydrogen gas is environmental friendly and non-toxic under normal conditions. Because hydrogen source is most abundant in the nature as part of water, hydrocarbons and biomass and so on, it can meet the global consumption requirement in the near future crisis of energy. However, because of the volatile property of hydrogen under ambient conditions, hydrogen storage for on-board usage must be in extremely high pressure conditions that are cost and extremely dangerous. Materials with ultra-large surface areas as MOFs with the advantages of physisorption-based materials are of particular interest for hydrogen storage.

Various MOFs have proved a high capability of hydrogen adsorption and storage. The first research on hydrogen storage was carried out in 2003 for MOF-5 (or $Zn_4O(BDC)_3$) with the high BET surface area of 3800 m^2/g and the gravimetric hydrogen uptake of 4.5 wt% at 78 K, 0.8 bar and 1 wt% at 298 K, 20 bar [14]. This report has attracted much attention and opened a new direction of research to computational simulations. In 2004, Hüber *et al.* was the first group who used computer simulations based on MP2 (second order Møller-Plesset perturbation theory) method to clarify the interaction of hydrogen with benzene and naptalin by calculating the adsorption energy of molecular hydrogen, with the obtained values of the adsorption energy were 3.91 and 4.28 kJ/mol, respectively [15]. After that, many researches based on MP2 and DFT calculations have been performed in order to get the binding energies of gaseous hydrogen with MOFs [16]. In 2004, the capacity of hydrogen uptake in MOFs was first calculated using grant canonical Monte Carlo simulations (GCMC) and universal force field (UFF) by Ganz group [17], and then the adsorption isotherm with the aim of capturing the dependence of the gas storage capacity on pressures by force fields such as OPLS (OPLS-AA) force field used by the group of Yang and Zhong [18], UFF and DREIDING force fields used by Johnson group [19]. Despite of significant improvements, none of MOFs have reached the US Department of Energy (DOE) 2017 targets for hydrogen storage that are 5.5 wt% (*i.e.* 55 mg H_2/g system) in overall gravimetric and 40 g/L in overall volumetric capacity at a temperature of -40 to 60 °C (*i.e.* about 233 to 333 K) and a pressure below 100 bar [20]. Owing to the weak interaction of H_2 with MOFs and low isosteric heats of H_2 adsorption typically 4 – 13 kJ/mol, MOFs exhibited significant hydrogen uptake only at cryogenic temperature (see Figure 3) [21-22], and low hydrogen uptake at room temperature (see Table 1) [23-34].

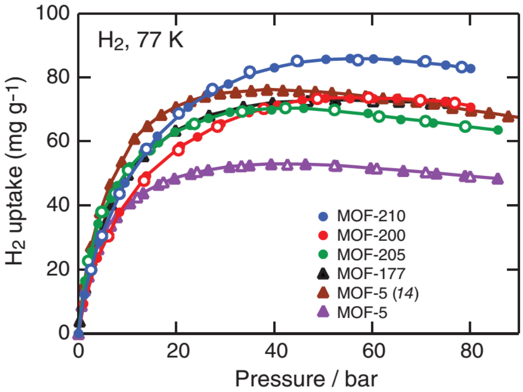


Figure 3. Hydrogen uptake capacities of several MOFs at high pressures and 77 K. Reprinted with permission from Ref. 4. Copyright 2010 American Association for the Advancement of Science.

Table 1. Hydrogen uptake capacities of selected MOFs at temperature 298 K and pressure below 100 bar.

MOF	BET surface area (m^2/g)	P (bar)	Excess/(Total) Gravimetric Uptake (wt%)	Ref.
$Zn_4O(BDC)_3$/MOF-5/IRMOF-1	2296	48	1.65	[23]
Ni(HBTC)(4,4'-bipy).3DMF	1590	72	1.20	[24]
$Zn_4O(dcdEt)_3$	502	48	1.12	[25]
$Zn_7O_2(pda)_5(H_2O)_2$		71	1.01	[26]
$Cu_3(ptei)$/PCN-68	5109	90	1.01	[27]
$Be_{12}(OH)_{12}(BTB)_4$	4030	95	1.01 (2.30)	[28]
$Cu(hfipbb)(h_2hfipbb)_{0.5}$		48	1.00	[23]
$Zn_4O(dcbBn)_3$	396	48	0.98	[25]
Co(HBTC)(4,4'-bipy).3DMF	887	72	0.96	[24]
$Mn_3[(Mn_4Cl)_3(BTT)_8MeOH]_2$/Mn-BTT	2100	90	0.94	[29]
$Co_3(NDC)_3(dabco)$	1502	17.2	0.89	[30]
$Cu_3(ntei)$/PCN-66	4000	90	0.785	[27]
$Cu_3(btei)$/PCN-61	3000	90	0.667	[27]
$Zn_4O(BTB)_2$/MOF-177	3275	99	0.62	[31]
$Sm_2Zn_3(oxdc)_6$	718.8	35	0.54	[32]
$Zn_4O(TCBPA)_2$/SNU-77H	3670	90	0.5 (1.19)	[33]
$Mg_2(dobdc)$/MOF-74(Mg)	1525	100	(0.8)	[34]

Up to date, the record in hydrogen uptake capacity was experimentally found in MOF-210 ($Zn_4O(BTE)_{4/3}(BPDC)$, the BET surface area of 6240 m^2/g) with the storage capacity of 8.6 excess wt% (86 mg/g) and 17.6 total wt% (176 mg/g) at 77 K and 80 bar [4]. Additionally, there are a huge number of potential MOFs that demonstrated a considerable capability for hydrogen storage such as MOF-200 with 7.4 excess wt% and 16.3 total wt% at 77K and 100 bar [3], MOF-205 with 7.0 excess wt% and 12.0 total wt% at 77 K and 80 bar [4], $Cu_2(SBTC)$ with 7.89 wt% at 30 K and 3.5 bar [35]. Although none of MOFs have reached the DOE 2017 targets, they contain several key characteristics that are expected to improve and ultimately produce new MOFs with exceptional properties for hydrogen storage. Several strategies for improving the storage capacity at ambient temperature have been endeavored. One of the most effective solutions is using MOFs with exposed metal sites that can enhance the heat of adsorption without compressing the gas into the regime of too high pressures. Isosteric heat of hydrogen adsorption in the range of 15-25 kJ/mol is also recommended for achieving the DOE 2017 targets to store hydrogen gas at about 30 bar and to release at about 1.5 bar [20]. The supports from computer simulations allow predicting and designing new MOFs that can significantly improve the room-temperature performance in recent years [36].

2.1.2. Methane storage

Methane gas is one of the most important hydrocarbon fuels that can provide high energy density together with low carbon emission after combustion process due to its great hydrogen-to-carbon ratio.

The idea of methane storage in MOFs was first established from the pioneer research of Kitagawa group [37]. They synthesized the coordination polymers with 3D frameworks and large cavities, which were used to adsorb significant amount of CH_4 by the diffusion of the gas into the cavities [37]. Afterward, many MOFs were studied for methane storage, for example, MOF-6 (IRMOF-6) exhibited the highest methane storage capacity of 155 v(STP)/v (or 240 cm^3/g) at 298 K and 36 atm, greater than that of any other MOFs and porous materials at that time [38]. New MOFs have been synthesized with a variety of important factors such as high surface areas, ligand functionalization, open metal sites, *etc.*, which have leaded to the significant improvements in the methane adsorption capacity. Several MOFs have the uptake values of CH_4 that have already reached the DOE target (180 v(STP)v at ambient temperature and pressure under 35 bar) [39]. In addition, computational simulations by first-principles methods have indicated that the creating of open metal sites within MOFs can increase the binding strength of methane with the metals by high affinity created at these metal areas [40-41]. Most recently, research of Yildirim group has examined on six promising MOFs for methane storage including PCN-14, UTSA-20, HKUST-1, Ni-MOF-74 (Ni-CPO-27), NU-111 and NU-125. The result showed in Figure 4 that HKUST-1 has highest volumetric uptake of methane that is 230 cc(STP)/cc at 298 K, 35 bar and 270 cc(STP)/cc at 298 K, 65 bar, which holds the record of methane uptake to date and meets the new volumetric target recently set by the DOE that is 263 cc(STP)/cc at 298 K and 65 bar [42]. Meanwhile, other MOFs such as NU-111, Ni-MOF-74 and PCN-14 have reached up to 70% of the new DOE gravimetric and volumetric targets (see Figure 4 upper panel) [42]. The gravimetric target is 0.5 grams of methane per gram of sorbent (see Figure 4 lower panel).

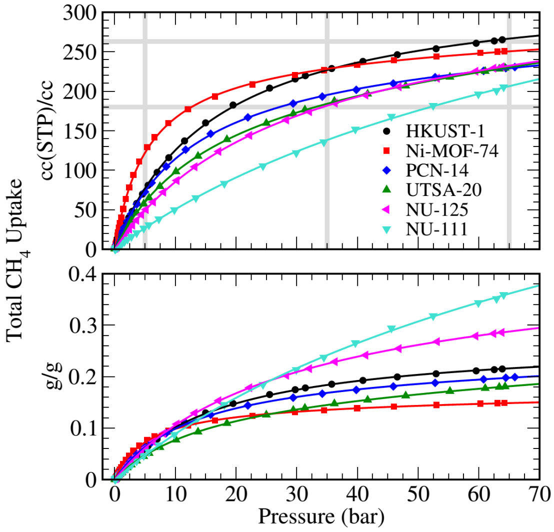


Figure 4. Volumetric (upper panel) and gravimetric (lower panel) uptakes of MOFs. The gray horizontal lines show the old and new DOE targets for volumetric methane storage. Reprinted with permission from Ref. 42. Copyright 2013 American Chemical Society.

In general, the storage of hydrogen and methane in MOFs has been extensively studying and achieved significant results. Several MOFs exhibit a remarkable capability of adsorption of a large quantity of hydrogen and methane. The DOE′s targets for methane storage have been reached but further development is required for more economical competence while the targets for hydrogen storage are currently unreachable. However, many strategies to enhance the hydrogen storage capacity have been developed such as the creation of open metal sites, doping with metal ions, fabrication of metal nanoparticles to utilize the spillover effect, functionalization of the ligands, and catenation/interpenetration of the frameworks. These strategies have shown a considerable improvement of the storage capacity of the gases that makes MOFs becoming the leading material for hydrogen and methane storage.

2.2. Gas capture for environmental issues

The emission of carbon dioxide and other toxic gases due to the escalation in global population and combustion of fossil fuels for energy demand has resulted in massively negative impacts to the environment and human′s health. The concern of global warming and air pollution has drawn special public attention to capture and reduce CO_2 and other toxic gases. It has been proven that MOFs are the forefront for this purpose because of their advanced structural properties [43-45].

2.2.1. CO_2 capture

For the capture of CO_2 in MOFs at high pressures, in 2005, the first systematic study was carried out with a series of MOFs in order to find out the relationship between the surface area and CO_2 uptake capacity [5]. Nine MOFs with various structural geometries were selected including square channels (MOF-2), pores decorated with open metal sites (MOF-505 and $Cu_3(BTC)_2$), hexagonally packed cylindrical channels (MOF-74), interpenetrated (IRMOF-11), amino- and alkyl-functionalized pores (IRMOFs-3 and IRMOFs-6) and the ultra-high porosity frameworks (IRMOF-1 and MOF-177). The results from gravimetric and volumetric measures showed that the saturated CO_2 uptake capacities are qualitatively correlated with the surface areas of the MOFs. They found that MOF-177 has the highest Langmuir surface area of 5640 m^2/g and the CO_2 uptake of 33.5 mmol/g at 35 bar and ambient temperature, which surpass any reported porous materials including the benchmark of zeolites (13X) and activated carbon (MAXSORB) [5]. Recently, Furukawa *et al.* successfully synthesized the ultrahigh porosity MOFs which are assembled from $Zn_4O(CO_2)_6$ unit and one or two organic linkers [4]. Among them, MOF-200 and MOF-210 showed the CO_2 uptake approximately 2400 mg/g at 298 K and 50 bar and set a new record for the adsorption capacity of CO_2 among all porous materials (see Figure 5) [4].

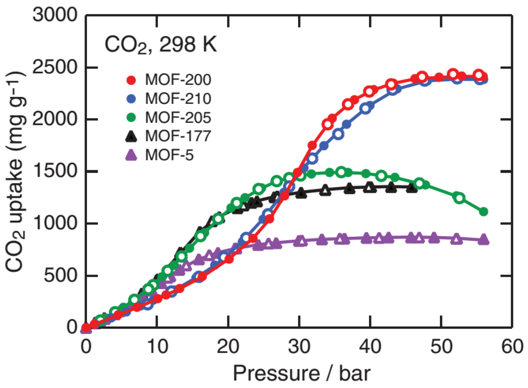


Figure 5. CO_2 uptake capacities of MOFs at 298 K. Reprinted with permission from Ref. 4. Copyright 2010 American Association for the Advancement of Science.

The capture of CO_2 at low pressures is related to the separation of this gas from power-plant flue gas where the partial pressure is much lower than atmospheric pressure. At these conditions, the storage capacity of CO_2 within MOFs is more dominantly governed by the MOF-CO_2 interactions. It was proved that MOFs with a high density of open metal sites could dramatically strengthen the MOF-CO_2 interactions and accordingly increases the CO_2 uptake capacity because of the high affinity attraction from these unsaturated sites. The best performance recorded to date is Mg-MOF-74 or Mg/DOBDC with open Mg^{2+} sites with CO_2 uptake capacity of 35.2 wt% at 298 K and 1 bar [46]. Most recently, Fletcher *et al.* found that new MOFs with nitrogen-rich ligands, which act as Lewis base functionalities, can create an affinity toward CO_2 and demonstrate potential for CO_2 capture technology [47]. There are also a huge number of MOFs which are able to adsorb significant amounts of CO_2 at different temperatures and pressures such as NU-100, MOF-74, MIL-101, and HKUST-1 [48-50].

2.2.2. CO, H_2S and SO_2 capture

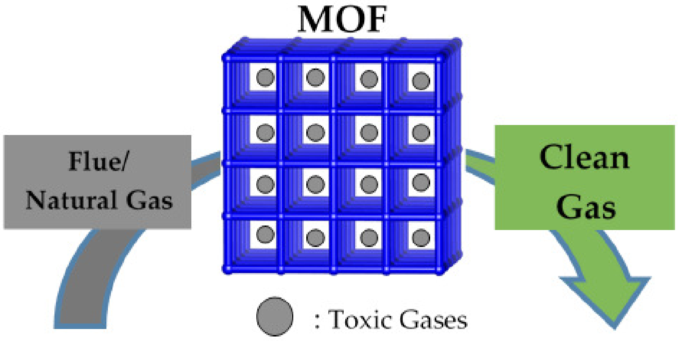


Figure 6. Schematic description of gas purification by using MOFs.

MOFs have also been investigated for the removal of other toxic gases such as CO and SO_2 for the purification of flue gas and the reduction of harmful gases in the environment [44-45, 51-52]. For air purification, it was noted that, low concentration of the toxic gases in applications must be considered; therefore, the designated MOFs must show the preferential adsorption toward the targeted gas over a mixture of gases. A schematic description of selective adsorption of toxic gases in the gas mixture is presented in Figure 6. Indeed, MOFs containing coordinatively unsaturated sites (CUSs) have been developed for this requirement. Britt *et al.* performed the experiment for a series of isoreticular metal–organic frameworks (IRMOFs) with various linker lengths as well as chemical functional groups, including MOF-5, IRMOF-3, MOF-177, IRMOF-62, Zn-CPO-27 and $Cu_3(btc)_2$. They found that these selected MOFs proved the high capability of capture and removal of various harmful gases and vapor contaminants such as sulfur dioxide, ammonia, chlorine tetrahydrothiophene, benzene, dichloromethane, and ethylene oxide [51]. MOF-74 series constructed from different alternative open metal sites of Mg, Ni, Co, and Zn exhibits the remarkable ability of capturing carbon monoxide, nitrogen oxides and sulfur-containing compounds. Cu-BTC and MIL-series have been studied for the removal of CO in principle of the coordination between metal ions and CO to form carbonyl complexes. The computational results showed that electrostatic interactions between CO and Cu-BTC framework atoms are the main factor dominating the CO adsorption while MIL-series with significantly large cages compared to the size of CO is not the ideal option for the adsorption of large quantity of CO at relatively low pressure [44, 53]. For the removal of sulfur-containing compounds, the series MIL-53(Al, Cr), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) have been explored for the adsorption of H_2S in which MIL-47(V) and MIL-53(Al, Cr) with small pore sizes exhibited the reversibility under H_2S pressure [53]. In addition, many MOFs such as M(bdc)(ted)$_{0.5}$ (M stands for the substituted metals), MOF-74, NOTT-300, and HKUST have been tested for the capture and removal of SO_2, where Ni(bdc)(ted)$_{0.5}$ has been proven to be the best candidate with a significant SO_2 uptake of 9.97 mol/kg at room temperature and 1.13 bar [54]. The summary of selected MOFs with high uptake capacities toward three toxic gases CO, H_2S and SO_2 is listed in Table 2.

Table 2. Uptake capacities of selected MOFs for CO, H_2S and SO_2.

Adsorbed gas	MOF	BET surface area (m^2/g)	Capacity (mmol/g)	Conditions		Ref.
				Temperature (K)	Pressure (bar)	
CO	Cu-BTC	1500	11	298	40	[55]
	Zn-MOF-74	1900	8	298	40	[55]
	IR-MOF-1	3362	7.5	298	40	[55]
	MIL-101(Cr)	2471	1.13	288	1.13	[56]
			1.0	303	1.13	[56]
	MOF-177	4500	4.2	298	10	[57]
	DMOF-1	1863	2.0	294	10	[58]
H_2S	Ni-MOF-74 (Ni-CPO-27)	1193	6.4	298	0.05	[59]
	MIL-47	1222	1.5	303	0.3	[53]
	MIL-53 (Fe)		2.5	303	30	[53]
	Cu-TDPAT		1.25	298	30	[60]
SO_2	Ni(bdc)(ted)$_{0.5}$	1925	9.97	298	1.12	[54]
	Zn(bdc)(ted)$_{0.5}$	1794	4.41	298	1.01	[54]
	Mg-MOF-74	1525	8.60	298	1.02	[54]
	NOTT-300	1370	8.1	273	1	[61]
	$M_3[Co(CN)_6]_2$	870	2.5	298	1	[62]
	FMOF-2	378	2.19	298	1	[63]

Through this section, one can see that MOFs with ultrahigh surface area and porosity such as MOF-210 and MOF-200 are the best choices for the capture of CO_2 at high pressure. Meanwhile, the using of MOFs with coordinatively unsaturated metal sites is the most effective solution to increase the adsorption capacity of CO_2 and the harmful gases at low pressures.

2.3. Gas and drug storage for biomedical applications

Nowadays, medical treatment using drug is the most popular therapy. Two of main administrations are oral and injected ways. By these ways, the drug takes effects on whole body that causes side effects and over dosages. However, these drawbacks can be eliminated by using new carriers for drug delivery toward the targeted organs. Therefore, the development of new drug carriers which enhance therapeutic efficiency and reduce side effects is necessary.

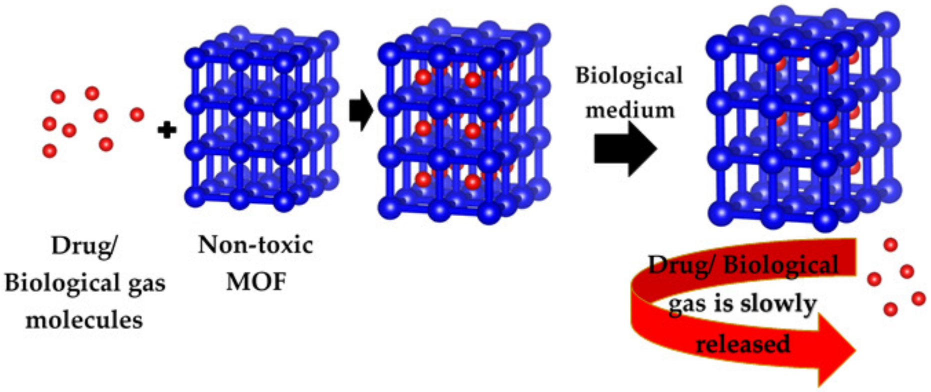


Figure 7. Schematic diagram of the drug and biomedical gas delivery by MOFs.

Nanoscaled liposomes constructed from polymers, amorphous silica and zeolites have been widely used for drug delivery; however, there are still many limitations such as low drug storage, rapid drug release, and high toxicity due to containing toxic metals. The enormous pore volume of MOFs together with high flexibility in the selection of the organic and inorganic components offer MOFs to be the most suitable carriers for drug delivery (Figure 7) that attains the following features [64]: (1) low toxicity by using the biocompatible metals; (2) biodegradability; (3) switching of hydrophilicity/hydrophobicity; (4) highly desirable uptake of drugs; (5) the controllable release and the elimination of “burst effect”. The vast storage of drugs can reduce the amount of its carrier despite of using high dosage. The combinations of non-toxic metals with adjustable linkers make MOFs become attractive carriers for biological small gas and drug molecules.

2.3.1. Biological small gas delivery

Small gases such as nitric oxide (NO), carbon monoxide (CO), and hydrogen sulfide (H_2S) are particularly interested in biological signals as gasotransmitters which are freely permeable to cell membranes and play important roles for human organs. These gases are known as harmful gases; however, they are endogenously produced by human organs with an extremely small quantity for biological processes [64-67]. The storage and control of the release of the gases in human body make the gases localized only at the targeted organ in a long-term medical treatment and reduce the over dosage [64-67]. Moreover, the biological gas delivery enhances therapeutic efficiency of gases.

NO plays an important role as the signaling gas in the regulation of blood pressure and the biological processes in the neuronal, immune, and vascular systems. The dosage of NO depends on the desired treatment. A higher dosage is required for antibacterial applications while a lower dosage at biological level (*threshold is 10 parts per billion NO released per minutes* [68]) is used for antithrombotic treatments and regulation of vascular vessel [69]. The control of the release of NO becomes very important for different purposes, which can be performed through using MOFs. Morris's group used MOFs as NO carriers and tested the toxicity of the NO-loaded MOFs [69]. They introduced Co-, Ni-, and Cu- and Cr-based MOFs which were activated to create open metal sites before loading gaseous NO. However, those selected metals are not biocompatible. Therefore, designing of MOFs from biocompatible metals becomes much more attractive. MIL family such as MIL-53, MIL-88, MIL-100, MIL-101, MIL-127 constructed from non-toxic metals is a very promising candidate for biomedical applications [65, 67]. Besides, Ca-based MOF (BioMIL-3) was also tested for carrying of NO. This MOF offered a significant loading but very slow release [70]. The series of MIL-88s (Fe) was found to be the best candidate for the adsorption and delivery of NO at the moment [71].

The release of NO from the MOF carrier can be triggered by using pressure, temperature, light, and chemicals. However, the trigger by water is the most crucial method because it does not require an external energy and works extremely well in the medium of organs. In these biological media, water molecules displace NO from the MOF carrier and make NO released purely. Therefore, NO-loaded MOFs must be protected in dry conditions during the storage to eliminate unexpected release of NO. Studies for the release of NO were experimentally performed for BioMIL-3, MIL-88s, HKUST-1, and CPO-27-M (M = Ni, Co) [70-73]. It was found that the release of NO was very limited. HKUST-1 exhibited a few µmol/g of NO released after one hour [72]. Similar behavior to that of HKUST-1 was also obtained for MIL-88B and BioMIL-3 [70-71]. In particular, MIL-88A performed 0.12 µmol/g of NO released after 16 hours (Figure 8) [71]. With this released amount of NO, MIL-88A provided dosage at the biological level within 16 hours after starting. Up to now, only CPO-27-M (M = Ni, Co) exhibits the completely releasing ability of the adsorbed gas within 14 hours by water trigger [73]. Other strategies to enhance NO storage and control of NO delivery are functionalization of linkers and metal doping. OH/NO_2 functionalized MIL-88B releases 14% of total adsorbed NO while the amount of NO released from MIL-88A is only 5% of overall loaded gas [71]. Cattaneo indicated that the Ni doped CPO-27-M (M= Mg, Zn) provided wide range of released gas depending on proportion of Ni dopant [74]. Depending on the particular desired use of NO, some non-toxic MOFs have provided good selections for NO release that make them the best candidates for this application, see Table 3 for more information.

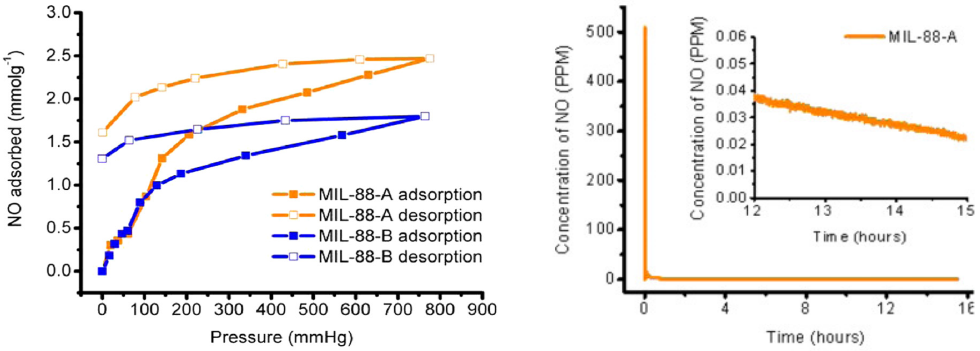


Figure 8. Left side: NO adsorption isotherm of MIL-88 at 303K. Right side: Kinetics of NO release from MIL-88A at 298 K under water trigger. Inset was included to highlight the NO delivery at biological level. Reprinted with permission from Ref. 71. Copyright 2013 American Chemical Society.

Table 3. Summary of NO storage and delivery in non-toxic MOFs constructed from Fe and Ca metals. NO release was measured under water trigger (nitrogen gas with 11% relative moisture). Experiments were performed at the pressure of 1 bar.

MOF	Total amount of adsorbed NO (mmol/g)	Total amount of released NO under wet trigger (mmol/g)	Temperature of release experiment (K)	% released NO	Ref.
MIL-88A	2.5	0.12	303	5	[71]
MIL-88B	1.6	0	303	0	[71]
MIL-88B-NO_2	1	0.14	303	14	[71]
MIL-88B-2OH	1	0.12	303	12	[71]
BioMIL-3	0.8	0.005	303	1	[70]
MIL-100 (Fe^{III})	2.7	0.35	298	13	[68]
MIL-100(Fe^{III}/Fe^{II})	4.5	0.55	298	12	[68]
MIL-127 (Fe^{III})	1.2	0.2	298	17	[68]
MIL-127(Fe^{III}/Fe^{II})	2.2	0.5	298	22	[68]
$Fe_2(NO)_2$(dobdc)	6.21	4.0	310	64	[75]

H_2S and CO also play important roles in many systems of the human body as vasodilator [65, 67]. However, they are less attractive to be used as medicine agents because the biological activity of H_2S is lower than NO, while the toxicity of CO is very high [65, 67]. Morris group used Ni- and Zn-based MOFs for H_2S delivery and *in vitro* toxicity test. In their study, a slight loss of H_2S storage after six months and lower biological activity than that of NO implied some disadvantages [59]. The delivery of CO gas in MOFs as pharmacological and therapeutic agents is also less attractive due to its high toxicity. The existence of the gas in the blood stream reduces the ability of oxy-hemoglobin binding which is required for transporting gaseous oxygen, and thus causes the lack of oxygen for the tissues. Up to now, only Ma and co-workers reported NH_2-MIL-88B and MIL-88B for the load and release of CO under human-blood-simulated medium [76]. To our knowledge, there are not yet *in vitro* biological tests for CO-loaded MOFs.

2.3.2. Drug delivery

Ibuprofen is used for relieving pain, and reducing fever and inflammation. A high ibuprofen uptake was achieved up to 1.38 gram over 1 gram of MIL-101(Cr) [77] that is 9 times and 4 times higher than that of zeolite (Fau) and mesoporous silica (MCM-41), respectively [77]. A complete release of ibuprofen takes 6 days for MIL-101(Cr) while it takes 7 days for zeolite and 2 days for mesoporous silica. It is known that chromium is a toxic element for the human body. Low-toxic element such as Fe is preferred for biomedicine. The Fe-based MIL such as MIL-53(Fe) was investigated and the result showed that it can store 0.21 gram of ibuprofen per gram of MIL [78]. The time of fully release was achieved after 3 weeks.

Other important drugs of concerns are busulfan and doxorubicin for antitumor treatment, and azidothymidline triphosphate and cidofovir for antiviral treatment [65]. These drugs encounter the vital drawbacks such as high solubility and low stability in the biological aqueous medium that lead to their short half-life, low bioavailability and limitation in natural barriers bypass. The delivery of the drugs from the iron and carboxylate ligand MOFs can solve these drawbacks. Busulfan has been widely used in high-dose chemotherapy for leukemia. However, it has low stability in aqueous medium and high toxicity owing to its crystallization in the hepatic microvenous systems. The previous carriers can store busulfan up to 6 wt% [65, 79]; however, the release of busulfan from these carriers is too fast [80]. Gref and co-workers found that the delivery of busulfan by using MOFs constructed from iron and carboxylate ligands could improve the storage of busulfan up to 25% [81]. Furthermore, MOFs not only protect busulfan against the reduction of its quality but also eliminate its crystallization. Azidothymidine triphosphate, which used for the treatment of HIV/AIDS infection and cidofovir, is antismallpox agent with the drawbacks similar to busulfan. Furthermore, they have very limited abilities in intracellular penetration because of their highly hydrophilic property. Only a few researches have been tested the delivery of the drugs from MOFs, which showed the promising results [65, 82-84].

The non-toxic porous MOFs are potential candidates for drug and gas delivery. However, only a few of MOFs have been studied for this application, where biological properties such as biocompatibility, biodegradability, and toxicity must be tested for successful applications in practice.

3. Conclusions

In summary, MOFs have exhibited as promising novel adsorbents for a wide range of gases assigned for various purposes. Although applications require further investigations of many aspects such as interaction mechanisms, environmental compatibility, water durability etc., the demands of using such state-of-the-art material for capture and storage of large quantities of gases have led to different strategies to dramatically improve the adsorption capacity and other drawbacks.

Much progress has been made in terms of the characteristics of the materials such as exceptionally high surface area, ultrahigh porosity, addition of open metal sites as well as high-pressure durability, flexible reversibility, and gas storage capacity. However, vital challenges remain unsolved. Therefore, next phase of researches should focus on the following problems: (1) enhance hydrogen uptake capacities at ambient condition (room temperature and pressures below 100 bar) to achieve the DOE 2017 targets, (2) capture and remove multiple toxic gases at once using the same structure of MOF in order to improve the performance and reduce the cost for the removal of toxic gases, (3) design and search for biocompatible MOFs which offer a high drug loading and a controllable release of stored drugs.

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References

[1] H.-C. Zhou, J. R. Long, and O. M. Yaghi, Introduction to Metal-Organic Frameworks, Chem. Rev. 112 (2012) 673.

[2] R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Younga, D. Yuan, D. Zhao, W. Zhuang, and H. C. Zhou, Potential applications of metal-organic frameworks, Coor. Chem. Rev. 253 (2009) 3042.

[3] H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, Nature 402 (1999) 276.

[4] H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, and E. Choi, Ultrahigh Porosity in Metal-Organic Frameworks, Science 329 (2010) 424.

[5] A. R. Millward and O. M. Yaghi, Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature, J. Am. Chem. Soc. 127 (2005) 17998.

[6] O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. B. T. Nguyen, A. Ö. Yazaydin, and J. T. Hupp, Metal-organic Framework Materials with Ultrahigh Surface Areas: Is the Sky the Limit? J. Am. Chem. Soc. 134 (2012) 15016.

[7] P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill and M. J. Styles, MOF positioning technology and device fabrication, Chem. Soc. Rev. 43 (2014) 5513.

[8] X. Ma, H. Yang, L. Yu, Y. Chen and Y. Li, Preparation, Surface and Pore Structure of High Surface Area Activated Carbon Fibers from Bamboo by Steam Activation, Materials 7 (2014) 4431.

[9] J. García-Martínez, M. Johnson, J. Valla, K. Li and J. Y. Ying, Mesostructured zeolite Y—high hydrothermal stability and superior FCC catalytic performance, Catal. Sci. Technol. 2 (2012) 987.

[10] P. T. S. Nam, V. H. L Phuong, N. T. Tung, Expanding applications of copper-based metal–organic frameworks in catalysis: Oxidative C–O coupling by direct C–H activation of ethers over Cu2(BPDC)2(BPY) as an efficient heterogeneous catalyst, Journal of Catalysis 306 (2013) 38.

[11] L. T. M. Hoang, L. H. Ngo, H. L. Nguyen, C. K. Nguyen, B. T. Nguyen, Q. T. Ton, H. K. D. Nguyen, K. E. Cordova, T. Truong, Azobenzene-Containing Metal-Organic Framework as an Efficient Heterogeneous Catalyst for Direct Amidation of Benzoic Acids: Synthesis of Bioactive Compounds, Chem. Commun. 51 (2015) 17132.

[12] Y.-B. Zhang, H. Furukawa, N. Ko, W. Nie, H. J. Park, S. Okajima, K. E. Cordova, H. Deng, J. Kim, and O. M. Yaghi, Introduction of Functionality, Selection of Topology, and Enhancement of Gas Adsorption in Multivariate Metal-Organic Framework-177, J. Am. Chem. Soc. 137 (2015) 2641.

[13] P. T. K. Nguyen, H. T. D. Nguyen, H. Q. Pham, J. Kim, K. E. Cordova, and H. Furukawa, Synthesis and Selective CO_2 Capture Properties of a Series of Hexatopic Linker–Based Metal-Organic Frameworks, Inorg. Chem. 54 (2015) 10065.

[14] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, and O. M. Yaghi, Hydrogen storage in microporous metal-organic frameworks, Science 300 (2003) 1127.

[15] O. Hüber, A. Glöss, M. Fichtner, and W. Klopper, On the interaction of di-hydrogen with aromatic systems, J. Phys. Chem. A 108 (2004) 3019.

[16] S. S. Han, J. L. Mendoza-Cortés, and W. A. Goddard, Recent advances on simulation and theory of hydrogen storage in metal-organic frameworks and covalent organic frameworks, Chem. Soc. Rev. 38 (2009) 1460.

[17] T. Sagara, J. Klassen, and E. Ganz, Computational study of hydrogen binding by metal-organic framework-5, J. Chem. Phys. 121 (2004) 12543.

[18] Q. Yang and C. Zhong, Molecular simulation of adsorption and diffusion of hydrogen in metal-organic frameworks, J. Phys. Chem. B 109 (2005) 11862.

[19] G. Garberoglio, A. I. Skoulidas, and J. K. Johnson, Adsorption of gases in metal organic materials: Comparison of simulations and experiments, J. Phys. Chem. B 109 (2005) 13094.

[20] M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, Hydrogen storage in metal-organic frameworks, Chem. Rev. 112 (2012) 782.

[21] L. Schlapbach and A. Züttel, Hydrogen-storage materials for mobile applications, Nature 414 (2001) 353.

[22] J. L. C. Rowsell and O. M. Yaghi, Strategies for hydrogen storage in metal-organic frameworks, Angew. Chem. Int. Ed. 44 (2005) 4670.

[23] L. Pan, M. B. Sander, X. Huang, J. Li, M. R. Smith, E. W. Bittner, B. C. Bockrath, and J. K. Johnson, Microporous metal organic materials: Promising candidates as sorbents for hydrogen storage, J. Am. Chem. Soc.126 (2004) 1308.

[24] Y. Li, L. Xie, Y. Liu, R. Yang, and X. Li, Favorable hydrogen storage properties of M(HBTC)(4,4'-bipy).3DMF (M) Ni and Co, Inorg. Chem. 47 (2008) 10372.

[25] B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, and W. Lin, Highly interpenetrated metal-organic frameworks for hydrogen storage, Angew. Chem., Int. Ed. 44 (2005) 72.

[26] Q.-R. Fang, G.-S. Zhu, M. Xue, Q.-L. Zhang, J.-Y. Sun, X.-D. Guo, S.-L. Qiu, S.-T. Xu, P. Wang, D.-J. Wang, and Y. Wei, Microporous metal-organic framework constructed from heptanuclear zinc carboxylate secondary building units, Chem.-Eur. J. 12 (2006) 3754.

[27] D. Yuan, D. Zhao, D. Sun, and H.-C. Zhou, An isoreticular series of metal-organic frameworks with dendritic hexacarboxylate ligands and exceptionally high gas-uptake capacity, Angew. Chem. Int. Ed. 49 (2010) 5357.

[28] K. Sumida, M. R. Hill, S. Horike, A. Dailly, and J. R. Long, Synthesis and hydrogen storage properties of $Be_{12}(OH)_{12}$(1,3,5-benzenetribenzoate)$_4$, J. Am. Chem. Soc. 131 (2009) 15120.

[29] M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, and J. R. Long, Hydrogen storage in a microporous metal-organic framework with exposed Mn^{2+} coordination sites, J. Am. Chem. Soc. 128 (2006) 16876.

[30] H. Chun, H. Jung, G. Koo, H. Jeong, and D.-K. Kim, Efficient hydrogen sorption in 8-connected MOFs based on trinuclear pinwheel motifs, Inorg. Chem. 47 (2008) 5355.

[31] Y. Li and R. T. Yang, Gas adsorption and storage in metal-organic framework MOF-177, Langmuir 23 (2007) 12937.

[32] Y. Wang, P. Cheng, J. Chen, D.-Z. Liao, and S.-P. Yan, A heterometallic porous material for hydrogen adsorption, Inorg. Chem. 46 (2007) 4530.

[33] H. J. Park, D.-W. Lim, W. S. Yang, and T.-R. Oh, and M. P. Suh, A highly porous metal-organic framework: Structural transformations of a guest-free MOF depending on activation method and temperature, Chem. Eur. J. 17 (2011) 7251.

[34] K. Sumida, C. M. Brown, Z. R. Herm, S. Chavan, S. Bordiga, and J. R. Long, Hydrogen storage properties and neutron scattering studies of Mg_2(dobdc) – a metal-organic framework with open Mg^{2+} adsorption sites, Chem. Commun. 47 (2011) 1157.

[35] X.-S. Wang, S. Ma, K. Rauch, J. M. Simmons, D. Yuan, X. Wang, T. Yildirim, W. C. Cole, J. J. López, A. de Meijere, and H.-C. Zhou, Metal-organic frameworks based on double-bond-coupled di-isophthalate linkers with high hydrogen and methane uptakes, Chem. Mater. 20 (2008) 3145.

[36] L. J. Murray, M. Dincă and J. R. Long, Hydrogen storage in metal–organic frameworks, Chem. Soc. Rev. 38 (2009) 1294.

[37] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, and S. Kitagawa, Three-DimensionalFramework with Channeling Cavities for Small Molecules: $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4].xH_2O\}_n$ (M = Co, Ni, Zn), Angew. Chem. Int . Ed. EngI. 36 (1997) 1725.

[38] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O. M. Yaghi, Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage, Science 295 (2002) 469.

[39] S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan, and H-C. Zhou, Metal-Organic Framework from an Anthracene Derivative Containing Nanoscopic Cages Exhibiting High Methane Uptake, J. Am. Chem. Soc. 130 (2008) 1012.

[40] H. Wu, W. Zhou, and T. Yildirim, High-Capacity Methane Storage in Metal-Organic Frameworks M2(dhtp): The Important Role of Open Metal Sites, J. Am. Chem. Soc. 131 (2009) 4995.

[41] S. Ma and H-C. Zhou, Gas storage in porous metal–organic frameworks for clean energy applications, Chem. Commun. 46 (2010) 44.

[42] Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, and T. Yildirim, Methane Storage in Metal–Organic Frameworks: Current Records, Surprise Findings, and Challenges, J. Am. Chem. Soc. 135 (2013) 11887.

[43] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T-H. Bae, and J. R. Long, Carbon Dioxide Capture in Metal–Organic Frameworks, Chem. Rev. 112 (2012) 724.

[44] J. B. DeCoste and G. W. Peterson, Metal–Organic Frameworks for Air Purification of Toxic Chemicals, Chem. Rev. 114 (2014) 5695.

[45] J. Yu, Y. Ma, and P. B. Balbuena, Evaluation of the Impact of H2O, O2 and SO2 on Postcombustion CO_2 Capture in Metal-Organic Frameworks, Langmuir 28 (2012) 8064.

[46] Y. Liu, Z. U. Wang, and H-C. Zhou, Recent advances in carbon dioxide capture with metal-organic frameworks, Greenhouse Gas Sci Technol. 2 (2012) 239.

[47] E. Dooris, C. A. McAnally, E. J. Cussen, A. R. Kennedy, and A. J. Fletcher, A Family of Nitrogen-Enriched Metal Organic Frameworks with CCS Potential, Crystals 2 (2016) 14.

[48] J. Park, H. Kim, S. S. Han, and Y. Jung, Tuning Metal–Organic Frameworks with Open-Metal Sites and Its Origin for Enhancing CO_2 Affinity by Metal Substitution, J. Phys. Chem. Lett. 3 (2012) 826.

[49] B. Supronowicz, A. Mavrandonakis, and T. Heine, Interaction of Small Gases with the Unsaturated Metal Centers of the HKUST-1 Metal Organic Framework, J. Phys. Chem. C 117 (2013) 14570.

[50] H. Wu, J. M. Simmons, G. Srinivas, W. Zhou, and T. Yildirim, Adsorption Sites and Binding Nature of CO_2 in Prototypical Metal-Organic Frameworks: A Combined Neutron Diffraction and First-Principles Study, J. Phys. Chem. Lett. 1 (2010) 1946.

[51] D. Britt, D. Tranchemontagne, and O. M. Yaghi, Metal-organic frameworks with high capacity and selectivity for harmful gases, PNAS 105 (2008) 11623.

[52] F. Bonino, S. Chavan, J. G. Vitillo, E. Groppo, G. Agostini, C. Lamberti, P. D. C. Dietzel, C. Prestipino, and S. Bordiga, Local Structure of CPO-27-Ni Metallorganic Framework upon Dehydration and Coordination of NO. Chem. Mater. 20 (2008) 4957.

[53] L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. Férey, and G. De Weireld, 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 (2009) 8775.

[54] K. Tan, P. Canepa, Q. Gong, J. Liu, D. H. Jonhson, A. Dyevoich, P. K. Thallapally, T. Thonhauser, J. Li, and Y. J. Chabal, Mechanism of preferential adsorption of SO2 into two microporous paddle wheel frameworks $M(bdc)(ted)_{0.5}$, Chem. Mater. 25 (2013) 4653.

[55] J. R. Karra, and K. S. Walton, Molecular Simulations and Experimental Studies of CO_2, CO, and N2 Adsorption in Metal–Organic Frameworks, J. Phys. Chem. C 114 (2010) 15735.

[56] K. Munusamy, G. Sethia, D. V. Patil, P. B. S. Rallapalli, R. S. Somani, H. C. Bajaj, Sorption of carbon dioxide, methane, nitrogen and carbon monoxide on MIL-101(Cr): Volumetric measurements and dynamic adsorption studies, Chem. Eng. J. 195-196 (2012) 359.

[57] L. Wang, L. Wang, J. Zhao, and T. Yan, Adsorption of selected gases on metal-organic frameworks and covalent organic frameworks: A comparative grand canonical Monte Carlo simulation, J. Appl. Phys. 111 (2012) 112628.

[58] P. Mishra, S. Mekala, F. Dreisbach, B. Mandal, and S. Gumma, Adsorption of CO_2, CO, CH_4 and N2 on a zinc based metal organic framework, Sep. Purif. Technol. 94 (2012) 124.

[59] P. K. Allan, P. S. Wheatley, D. Aldous, M. I. Mohideen, C. Tang, J. A. Hriljac, I. L. Megson, K. W. Chapman, G. De Weireld, S. Vaesen, and R. E. Morris, Metal–organic frameworks for the storage and delivery of biologically active hydrogen sulfide, Dalton Trans. 41 (2012) 4060.

[60] Z. Li, Y. Xiao, W. Xue, Q. Yang, and C. Zhong, Ionic Liquid/Metal-Organic Framework Composites for HS Removal from Natural Gas: A Computational Exploration, J. Phys. Chem. C 119 (2015) 3674.

[61] S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang and M. Schröder, Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host, M. Nat. Chem. 4 (2012) 887.

[62] P. K. Thallapally, R. K. Motkuri, C. A. Fernandez, B. P. McGrail, and G. S. Behrooz, Prussian Blue Analogues for CO_2 and SO_2 Capture and Separation Applications, Inorg. Chem. 49 (2010) 4909.

[63] C. A. Fernandez, P. K. Thallapally, R. K. Motkuri, S. K. Nune, J. C. Sumrak, J. Tian, and J. Liu, Gas-Induced Expansion and Contraction of a Fluorinated Metal–Organic Framework, Cryst. Growth Des. 10 (2010) 1037.

[64] P. Horcajada, C. Serre, R. Gref, and P. Couvreur, "Porous Metal–Organic Frameworks as New Drug Carriers," in Comprehensive Biomaterials, 1st edition, Oxford: Elsevier, 2011.

[65] P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris, and C. Serre, Metal-Organic Frameworks in Biomedicine, Chem. Rev. 112 (2012) 1232.

[66] S. Keskin and S. Kızıle, Biomedical Applications of Metal Organic Frameworks, Ind. Eng. Chem. Res. 50 (2011) 1799.

[67] C. He, D. Liu and W. Lin, Nanomedicine Applications of Hybrid Nanomaterials Built from Metal–Ligand Coordination Bonds: Nanoscale Metal–Organic Frameworks and Nanoscale Coordination Polymers, Chem. Rev. 115(2015) 11079

[68] J. F. Eubank, P. S. Wheatley, G. Lebars, A. C. McKinlay, H. Leclerc, P. Horcajada, M. Daturi, A. Vimont, R. E. Morris, and C. Serre, Porous, rigid metal(III)-carboxylate metal-organic frameworks for the delivery of nitric oxide, APL Mat. 2 (2014) 124112.

[69] N. J. Hinks, A. C. McKinlay, B. Xiao, P. S. Wheatley, and R. E. Morris, Metal organic frameworks as NO delivery materials for biological applications, Micropor. Mesopor. Mat. 129 (2010) 330.

[70] S. R. Miller, E. Alvarez, L. Fradcourt, T. Devic, S. Wuttke, P. S. Wheatley, N. Steunou, C. Bonhomme, C. Gervais, D. Laurencin, R. E. Morris, A. Vimont, M. Daturi, P. Horcajada, and C. Serre, A rare example of a porous Ca-MOF for the controlled release of biologically active NO, Chem. Commun. 49 (2013) 7773.

[71] A. C. McKinlay, J. F. Eubank, S. Wuttke, B. Xiao, P. S. Wheatley, P. Bazin, J.-C. Lavalley, M. Daturi, A. Vimont, G. D. Weireld, P. Horcajada, C. Serre, and R. E. Morris, Nitric Oxide Adsorption and Delivery in Flexible MIL-88(Fe) Metal−Organic Frameworks, Chem. Mater. 25 (2013) 1592.

[72] B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas, and R. E. Morris, High-Capacity Hydrogen and Nitric Oxide Adsorption and Storage in a Metal-Organic Framework, J. Am. Chem. Soc. 129 (2007) 1203.

[73] A. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megson, and R. E. Morris, Exceptional Behavior over the Whole Adsorption-Storage-Delivery Cycle for NO in Porous Metal Organic Frameworks, J. Am. Chem. Soc. 130 (2008) 10440.

[74] D. Cattaneo, S. J. Warrender, M. J. Duncan, C. J. Kelsall, M. K. Doherty, P. D. Whitfield, I. L. Megson, and R. E. Morris, Tuning the nitric oxide release from CPO-27 MOFs, RCS Adv. 6 (2016) 14059.

[75] E. D. Bloch, W. L. Queen, S. Chavan, P. S. Wheatley, J. M. Zadrozny, R. Morris, C. M. Brown, C. Lamberti, S. Bordiga, and J. R. Long, Gradual Release of Strongly Bound Nitric Oxide from $Fe_2(NO)_2$(dobdc), J. Am. Chem. Soc. 137(2015) 3466.

[76] M. Ma, H. Noei, B. Mienert, J. Niesel, E. Bill, M. Muhler, R. A. Fischer, Y. Wang, U. Schatzschneider, and N. Metzler-Nolte, Iron metal-organic frameworks MIL-88B and NH_2-MIL-88B for the loading and delivery of the gasotransmitter carbon monoxide, Chem. Eur. J. 19 (2013) 6785.

[77] P. Horcajada, C. Serre, M. Vallet-regí, M. Sebban, F. Taulelle, and G. Férey, Metal–Organic Frameworks as Efficient Materials for Drug Delivery, Angew. Chem. Int. Ed. 45 (2006) 5974.

[78] P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle, and G. Férey, Flexible Porous Metal-Organic Frameworks for a Controlled Drug Delivery, J. Am. Chem. Soc. 130 (2008) 6774.

[79] A. Layre, R. Gref, J. Richard, D. Requier, and P. Couvreur, Nanoparticules polymériques composites, FR 04 (2004) 07569.

[80] A. Layre, P. Couvreur, H. Chacun, J. Richard, C. Passirani, D. Requier, J. P. Benoit, and R. Gref, Novel composite core-shell nanoparticles as busulfan carriers, J. Controlled Release 111 (2006) 271.

[81] T. Chalati, P. Horcajada, P. Couvreur, C. Serre, G. Maurin, and R. Gref, Porous metal organic framework nanoparticles to address the challenges related to busulfan encapsulation, Nanomedicine 6 (2011) 1683.

[82] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P. -N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, and R. Gref, Porous metal-organic-framework nanoscale carriers as a potential platform for drug delivery and imaging, Nat. Mater. 9 (2010) 172.

[83] P. Horcajada, C. Serre, G. Férey, R. Gref, and P. Couvreur, Solide hybride organique inorganique a surface modifiee, French patent application 102573/FR filed the 1/10/2007 PCT/FR2009/001367, 01/10/08.

[84] P. Horcajada, C. Serre, G. Férey, R. Gref, and P. Couvreur, Nanoparticules hybrides organiques inorganiques a base de carboxylates de fer, French patent application 100936/FR filed the 1/10/2007, PCT/FR2008/001366, 01/10/08.

List of abbreviations

No.	Abbreviation	Definition
1	BET	Brunauer-Emmett-Teller
2	BDC/bdc	1,4-benzenedicarboxylate
3	bipy	Bipyridine
4	BPDC	BTE/biphenyl-4,4′-dicarboxylate
5	BTB	1,3,5-benzenetribenzoate
6	BTC	1,3,5-benzenetricarboxylate (H_3BTC)
7	BTE	Benzene-triyl-tris(ethyne-2,1-diyl)tribenzoate
8	btei	5,5′,5″-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate)
9	BTT	1,3,5-enzenetristetrazolate
10	CCDC	The Cambridge Crystallographic Data Centre
11	$Co(CN)_6$	Cobalt(II) cyanid
12	CPO	Coordination Polymer of Oslo
13	dabco	1,4-diazabicyclo[2.2.2]octane
14	dcbBn	6,6'-dichloro-2,2'-dibenzyloxy-1,1'-binaphthyl-4,4'-dibenzoate
15	dcdEt	6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-dibenzoate
16	DFT	Density Functional Theory
17	DMF	N,N′-dimethylformamide
18	DOBDC/dobdc	Dihydroxuterephthalic
19	DOE	United States Department of Energy
20	GCMC	Grant Canonical Monte Carlo simulations
21	HBTC	1,3,5-tri(4-carboxyphenyl)benzene (H_3BTC)
22	hfipbb	4,4′-(idene hexafluoroisopropylidene)-dibenzoate
23	HKUST	Hong Kong University of Science and Technology
24	IRMOF	Isoreticular Metal – Organic Framework
25	MCP	Microporous coordination polymer
26	MIL	Materials from Institut Lavoisier
27	MOF	Metal – Organic Framework
28	MP2	Second order Møller-Plesset perturbation theory
29	NDC	2,6-naphthalenedicarboxylate
30	ntei	5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)-tris(ethyne-2,1-diyl))triisophthalate
31	NU	Northwestern University
32	OPLS	Optimized Potential for Liquid Simulations

33	OPLS-AA	Optimized Potential for Liquid Simulations – All Atoms
34	oxdc	oxydiacetate
35	PCN	Porous Coordination Network
36	pda	p-phenylenediacylate
37	ptei	5,5′-((5′-(4-((3,5- dicarboxyphenyl)ethynyl)phenyl)-[1,1′:3′1″-terphenyl]-4,4″-diyl)-bis(ethyne-2,1- diyl))diisophthalate
38	SBTC	5-sulfonyl-1,2,4-bezenetricarboxylic acid
39	SNU	Seoul National University
40	STP	Standard Temperature and Pressure
41	TCBPA	tris(4-carboxybiphenyl)amine
42	TDPAT	2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine
43	TED/ted	Triethylenedianime
44	UFF	Universal force field
45	UTSA	University of the Texas at San Antonio
46	ZMOFs	Zeolite-like metal organic frameworks