Design of Metal-Organic Frameworks with High Low-pressure Adsorption Performance of CO2

Yilian Zheng 1, Xiaolu Xu 2, Xu Zhang 1, Lei Qin 1, Yin Lu 2, * and Guoliang Zhang 1, *

1 Institute of Oceanic and Environmental Chemical Engineering, Zhejiang University of Technology, Hangzhou, China
2 College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou, China

*Corresponding author e-mail: guoliangz001@126.com; luyin_zjsru@aliyun.com

Abstract. Reducing the concentration of carbon dioxide (CO2) in the atmosphere has momentous significance for alleviating global warming and protecting human health. Attractively, metal-organic frameworks (MOFs), as a novel class of porous materials, have held enormous potential in the field of CO2 adsorption in virtue of their unique features such as ultrahigh specific surface area, adjustable channels, and high-density active sites. Considering that the CO2 capture in practical applications is often performed at low pressure, it is more practical to design and develop MOFs with high low-pressure CO2 adsorption performance. In this contribution, the strategies for improving low-pressure CO2 adsorption performance of MOFs have been introduced and compared, and the relationship between the structure and adsorption capacity of MOFs as CO2 adsorbents has been analyzed.

1. Introduction
Carbon dioxide (CO2), one of the primary greenhouse gases, has made enormous contribution to more and more severe global warming, posing a daunting threat to sustainable development of the world. Reducing the emission and lowering the concentration of atmospheric CO2 have been regarded as one of the most pressing environmental issues at present. In addition, the capture of CO2 in confined spaces and the adsorptive separation of CO2 from CH4 for natural gas upgrading are both of essential significance to the manufacture and living of our society. Consequently, it's exceedingly imperative to design and fabricate advanced materials with high performance for selective adsorption and separation of CO2. Metal-organic frameworks (MOFs), as a class of emerging crystalline porous materials, are self-assembled by the bonding of inorganic metal ions with organic ligands and have aroused great concern and interest from researchers [1-4]. On account of their large specific surface area, high porosity, tailorable pore structures and highly dispersed active sites, MOFs have been widely applied in many fields [5-7]. Remarkably, selective adsorption and separation of gas mixture, especially CO2 from other gases, has been one of the most intriguing research areas in the applications of MOFs over past two decades, which could be demonstrated by the number of publications presented in Figure 1 [8-10].
Since Yaghi and co-workers [11] first attested the viability of CO₂ sorption in MOF-2 in 1998, tremendous efforts have been made to explore new MOFs for efficient adsorption of CO₂. For instance, the research group synthesized MOF-177 in 2005 and found that the MOFs exhibited a CO₂ adsorptive capacity of 1470 mg/g at room temperature and 35 bar, equivalent to 9 times its own volume when there was no other adsorbent [12]. Subsequently, they claimed that the CO₂ uptake values in MOF-200 and MOF-210 were both 2400 mg/g at 298 K and 50 bar, far more than that of other MOFs ever reported, ascribed to their ultrahigh specific surface areas [13]. Similarly, Hupp’s group [14] obtained NU-100 with a specific surface area of 6143 m²/g via De novo synthesis and the sorption experiments manifested that the material had a storage capacity of 2315 mg/g for CO₂ at room temperature and 40 bars.

As is well known, the larger the specific surface area of MOFs, the stronger their ability to capture CO₂. However, taking actual applications into account, the adsorption and separation of CO₂ is generally conducted in a low-pressure multi-component gas system, thus the adsorption property of MOFs for CO₂ may be markedly influenced when exposed to multi-component gaseous mixture under dynamic conditions. Hence, investigating CO₂ adsorption performance of MOFs at low pressure is a much more meaningful topic.

2. Strategies to improve low-pressure adsorptive capability of CO₂ in MOFs

2.1. Adjustment of pore structures

In comparison with high pressure, the interaction between MOFs and CO₂ at low pressure is relatively weaker, rendering low-pressure CO₂ adsorption capacity of MOFs poorer. Studies have shown that the adsorption capability of CO₂ on MOFs at low pressure is related to the adsorption heat [15, 16]. Fortunately, the introduction of new metal centers with smaller radius can decrease the pore size of MOFs to some extent, thereby increasing CO₂ adsorption heat of MOFs. For example, Lau et al. [17] revealed that the CO₂ uptake of UiO-66(Zr) increased by 81% with a 10 kJ/mol enhancement in isosteric adsorption heat via post-synthetic exchange with Ti(IV) ions over the wide range from low pressure to
ordinary pressure at 273 K. The contrastive experiments interestingly indicated that enhanced performance of CO$_2$ uptake could be attributed to smaller pore size in Ti-exchanged UiO-66 (Figure 2). Alternatively, the fabrication of interpenetrating structures can be an effective option for MOFs to boost their adsorption capability of CO$_2$ at low pressure. For instance, Kim and coworkers [18] synthesized catenated CuTATB-60 and non-catenated CuTATB-30 by a controllable sonochemical method. The experimental results showed that the adsorption value of the as-obtained CuTATB-60 for CO$_2$ could reach 189 mg/g, which was higher than that of CuTATB-30 (156 mg/g). Besides, CuTATB-60 also exerted an exceptional selectivity of CO$_2$ over N$_2$ (>20:1) at normal temperature and pressure, testifying that the catenated structures in CuTATB-60 played a key role in CO$_2$ adsorption.

![Figure 2](image_url)

**Figure 2.** Structures of (a) UiO-66 and (b) Ti-exchanged UiO-66.

### 2.2. Introduction of coordinatively unsaturated metal sites into MOFs

In principle, coordinatively unsaturated metal sites in the structure of MOFs bring about strong interaction between MOFs and CO$_2$, endowing MOFs with outstanding CO$_2$ adsorption performance at low pressure. Previous work [19, 20] have manifested that metal sites with unsaturated coordination mode in MOFs could be obtained by removing coordinated certain molecules like solvent and ligands with poor coordination ability. Yaghi et al. [21] reported that Mg-MOF-74 with coordinatively unsaturated magnesium ions, as shown in Figure 3, could adsorb 8.9 wt. % CO$_2$, equal to 0.44 mol of CO$_2$ molecules per metal ion, while its structural analog Zn-MOF-74 adsorbed merely 0.35 wt. % of CO$_2$, which implied different metal ions played different roles in determining CO$_2$ adsorption performance of MOFs. Furthermore, they attributed the exceptional capacity of Mg-MOF-74 to the interaction between CO$_2$ molecules and the open metal ions in the structure of Mg-MOF-74. Analogously, Wang and co-workers [22] fabricated a novel Co(II)-based MOF, {[Co$_2$(tzpa)(OH)(H$_2$O)$_2$] ·DMF}, employing tetrazolyl-carboxyl as bifunctional ligand followed by the removal of coordinated water molecules. The gas sorption experiments suggested that the Co(II)-based MOF displayed an excellent CO$_2$/CH$_4$ selectivity of 31.8 for the mixtures containing 50% CO$_2$ at room temperature and atmosphere pressure. X-ray crystallographic measurements suggested that multiple coordinatively unsaturated metal centers in the as-prepared MOF created by removing coordinated water molecules acted as active Lewis acid sites, resulting in eminent adsorption property and prominent selectivity for CO$_2$.

As a matter of fact, the presence of moisture is inevitable in the mixture of CO$_2$ and other gases, which poses a major obstacle to the CO$_2$ adsorption performance of MOFs. For this reason, it is of practical significance to develop moisture-resistant MOFs as high-efficiency CO$_2$ adsorbents. For example, UTSA-16 was synthesized by Masala et al. [23] and activated under high vacuum. The experimental statistics illustrated that the CO$_2$ working capacity (0.94 ± 0.04 mol/kg) of UTSA-16 in humid conditions was only slightly lower than that of dry conditions (1.30 ± 0.02 mol/kg), which demonstrated that high-density coordinatively unsaturated metal centers were more likely to interact with CO$_2$ than water, making the as-obtained MOF a promising candidate for efficient CO$_2$ capture even under wet operating conditions.
2.3. Functionalization of MOFs with Lewis base

As is noted, when Lewis base such as nitrogenous groups of amines is introduced into the structure of MOFs, the interaction between the local dipole of the nitrogenous groups and the quadrupole moment of CO$_2$ molecule will induce the dispersion force and electrostatic force between MOFs and CO$_2$, consequently enhancing the CO$_2$ adsorption capability of MOFs [24-26]. For example, Milner et al. [27] successfully prepared 2,2-dimethyl-1,3-diaminopropane-grafted Mg$_2$(dobpdc) (Figure 4) by means of post modification. The experimental data suggested that the diamine-functionalized MOF could uptake 90% CO$_2$ from coal flue gas at 313 K at about 15 mbar and the adsorption between CO$_2$ and amine functionalized MOF was responsible for the exceptionally high CO$_2$ uptake from dilute streams.

3. Conclusion

With the urgent demand for energy-saving separation techniques, the exploration of new adsorbents for CO$_2$ is therefore gaining big momentum, of which MOFs have shown great potentialities and wide prospects owing to their unique properties. Studying the adsorptive separation performance of MOFs for CO$_2$ under actual production and living conditions, in particular at low pressure, is of vital significance for promoting MOFs from the laboratory scale to the practical use. Several useful strategies on how to effectively improve the low-pressure CO$_2$ adsorption performance of MOFs have been developed, including the adjustment of pore structures, the introduction of coordinatively unsaturated
metal sites into MOFs and the functionalization of MOFs with Lewis base. Although some progress has been made in the field of low-pressure adsorptive separation of CO$_2$ in MOFs, intense efforts still need to be made to further improve its performance and promote its industrial application. Moreover, the development of reliable approaches to achieve MOFs with high stability and reproducibility for CO$_2$ adsorption remains an arduous mission.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (21736009, 21506193 and 21476206). Zhejiang Public Welfare Research Project (2016C32022) and National Natural Science Foundation of Zhejiang Province (GB18041260092).

**References**

[1] W. Li, Y. Zhang, Z. Xu, Q. Meng, Z. Fan, S. Ye, G. Zhang, Assembly of MOF microcapsules with size-selective permeability on cell walls, Angew. Chem. Int. Ed. 128 (2016) 967-971.

[2] L. Qin, Z. Li, Z. Xu, X. Guo, G. Zhang, Organic-acid-directed assembly of iron-carbon oxides nanoparticles on coordinatively unsaturated metal sites of MIL-101 for green photochemical oxidation, Appl. Catal. B-Environ. 179 (2015) 500-508.

[3] W. Li, Y. Zhang, Z. Xu, A. Yang, Q. Meng, G. Zhang, Self-assembled graphene oxide microcapsules with adjustable permeability and yolk-shell superstructures derived from atomized droplets. Chem. Commun. 50 (2014) 15867-15869.

[4] F. Tan, M. Liu, K. Li, Y. Wang, J. Wang, X. Guo, G. Zhang, C. Song, Facile synthesis of size-controlled MIL-100(Fe) with excellent adsorption capacity for methylene blue, Chem. Eng. J. 281 (2015) 360-367.

[5] W. Li, Z. Yang, G. Zhang, Z. Fan, Q. Meng, C. Shen, C. Gao, Stiff metal-organic framework-polyacrylonitrile hollow fiber composite membranes with high gas permeability, J. Mater. Chem. A 2 (2014) 2110-2118.

[6] L. Qin, Z. Li, Q. Hu, Z. Xu, X. Guo, G. Zhang, One-pot assembly of metal/organic-acid sites on amine-functionalized ligands of MOFs for photocatalytic hydrogen peroxide splitting, Chem. Commun. 52 (2016) 7110-7113.

[7] X. Cheng, M. Liu, A. Zhang, S. Hu, C. Song, G. Zhang, X. Guo, Size-controlled silver nanoparticles stabilized on thiol-functionalized MIL-53(Al) frameworks, Nanoscale 7 (2015) 9738-9745.

[8] G. Zhang, J.H. Zhang, P.C. Su, Z.H. Xu, W.B. Li, C. Shen, Q. Meng, Non-activation MOF arrays as coating layer to fabricate stable superhydrophobic micro/nano flower-like architecture, Chem. Commun. 53 (2017) 8340-8343.

[9] P. Su, W. Li, C. Zhang, Q. Meng, C. Shen, G. Zhang, Metal based gels as versatile precursors to synthesize stiff and integrated MOF/polymer composite membranes, J. Mater. Chem. A 3 (2015) 20345-20351.

[10] W. Li, P.C. Su, Z.J. Li, Z.H. Xu, F. Wang, H. Ou, J.H. Zhang, G. Zhang, E. Zheng, Ultrathin metal-organic framework membrane production by combination of sol-gel and vapor-deposition, Nat. Commun., 8 (2017) 406-413.

[11] H. Li, M. Eddaoudi, T.L. Groy, O.M. Yaghi, Establishing micro porosity in open metal-organic frameworks: gas sorption isotherms for Zn(BDC) (BDC = 1,4-Benzenedicarboxylate), J. Am. Chem. Soc. 120 (1998) 8571-8572.

[12] A.R. Millward, O.M. Yaghi, Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature, J. Am. Chem. Soc. 127 (2005) 17998-17999.

[13] H. Furukawa, N. Ko, Y.B. Go, N. Aratani, S.B. Choi, E. Choi, A.O. Yazaydin, R.Q. Snurr, M.O. Keefé, J. Kim, O.M. Yaghi, Ultrahigh porosity in metal-organic frameworks, Science 329 (2010) 424-428.
[14] O.K. Farha, A.Ö. Yazaydin, I. Eryazici, C.D. Malliakas, B.G. Hause, M.G. Kanatzidis, S.T. Nguyen, R.Q. Snurr, J.T. Hupp, De novo synthesis of a metal-organic framework material featuring ultrahigh surface area and gas storage capacities, Nat. Chem. 2 (2010) 944-948.

[15] J. Li, J. Yu, W. Lu, L. Sun, J. Sculley, P.B. Balbuena, H. Zhou, Porous materials with pre-designed single-molecule traps for CO$_2$ selective adsorption, Nat. Commun. 4 (2013) 1538-1545.

[16] O. Shekhah, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil, M. Eddaoudi, Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture, Nat. Commun. 5 (2014) 4228-4234.

[17] C.H. Lau, R. Babarao, M.R. Hill, A route to drastic increase of CO$_2$ uptake in Zr metal organic framework UiO-66, Chem. Commun. 49 (2013) 3634-3636.

[18] J. Kim, S.T. Yang, B.C. Sang, J. Sim, J. Kim, W.S. Ahn, Control of catenation in CuTATB-n metal-organic frameworks by sonochemical synthesis and its effect on CO$_2$ adsorption, J. Mater. Chem. 21 (2011) 3070-3076.

[19] W. Li, Y. Zhang, C. Zhang, Q. Meng, Z. Xu, P. Su, Q. Li, Q. Shen, Z. Fan, L. Qin, G. Zhang, Transformation of metal-organic frameworks for molecular sieving membranes, Nat. Commun. 7 (2016) 11315-11323.

[20] W. Li, G. Zhang, C. Zhang, Q. Fan, C. Gao, Synthesis of trinity metal-organic framework membranes for CO$_2$ capture, Chem. Commun. 50 (2014) 3214-3216.

[21] D. Britt, H. Furukawa, B. Wang, T.G. Glover, O.M. Yaghi, Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites, P. Natl. Acad. Sci. USA 106 (2009) 20637-20640.

[22] H. Wang, L. Hou, Y. Li, C. Jiang, Y. Wang, Z. Zhu, Porous MOF with highly efficient selectivity and chemical conversion for CO$_2$, ACS Appl. Mater. Interfaces 9 (2017) 17969-17976.

[23] A. Masala, J.G. Vitillo, G. Mondino, C.A. Grande, R. Blom, M. Manzoli, M. Marshall, S. Bordiga, CO$_2$ capture in dry and wet conditions in UTSA-16 metal organic framework. ACS Appl. Mater. Interfaces 9 (2017) 455-463.

[24] M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel, D. Farrusseng, Generic postfunctionalization route from amino-derived metal-organic frameworks, J. Am. Chem. Soc. 132 (2010) 4518-4519.

[25] L. Kong, R. Zou, W. Bi, R. Zhong, W. Mu, J. Liu, R.P.S. Han, R. Zou, Selective adsorption of CO$_2$/CH$_4$ and CO$_2$/N$_2$ within a charged metal-organic framework, J. Mater. Chem. A 2 (2014) 139-142.

[26] T.M. McDonald, J.A. Mason, X. Kong, E.D. Bloch, D. Gygi, A. Dani, V. Crocella, F. Giordanino, S. Odoh, W.S. Drisdell, B. Vlaisavljevich, A.L. Dzubak, R. Poloni, S.K. Schnell, N. Planas, K. Lee, T. Pascal, L.F. Wan, D. Prendergast, J.B. Neaton, B. Smit, J.B. Kortright, L. Gagliardi, S. Bordiga, J.A. Reimer, J.R. Long, Cooperative insertion of CO$_2$ in diamine-appended metal-organic frameworks, Nature 519 (2015) 303-318.

[27] P.J. Milner, R.L. Siegelman, A.C. Forse, M.I. Gonzalez, T. Runčevski, J.D. Martell, J.A. Reimer, J.R. Long, A diaminopropane-appended metal-organic framework enabling efficient CO$_2$ capture from coal flue gas via a mixed adsorption mechanism, J. Am. Chem. Soc. 139 (2017) 13541-13553.