

Metal Organic Framework for SO₂ Capture

Baizhu Chen^{1, *, †}, Yiqiu Huang^{2, †} and Xinni Wang^{3, †}

¹Hefei Thomas School, Hefei, China

²Hangzhou En el Foreign Language School, Hangzhou, China

³The Affiliated International School of Shenzhe, Shenzhen, China

*Corresponding author: cbzzbc114514@outlook.com

†These authors contributed equally.

Abstract. Metal-organic framework (MOF) is a poriferous 3D framework, composed of organic ligands and central metal ions. The MOFs are often preferred for SO₂ capture due to their ligand function, large pore volume, simplicity of preparation as well as their relatively low cost of reactivation. In this review, the synthesis strategies achieving the formation of MOFs with higher porosity and strengthened reversibility were introduced. The synthesis processes include conventional heating, modulated synthesis, and post-synthetic modification (PSM). Conventional heating is categorized into two different methods, including electric heating and solvothermal synthesis. Electric heating usually involves using temperature change to produce target MOF whereas solvothermal synthesis is defined as reactions in enclosed containers under autogenic pressure past the boiling point of the solvent. Modulated synthesis and PSM also guarantee low by-products and great stability. The mechanisms of SO₂ adsorption were also discussed, which mainly focused on the physisorption that enables the utilizing resources to be efficiently used, as MOFs with physisorption are reusable. The adsorption site including strong hydrogen bonds and the uncoordinated atom with strong electronegativity also determines MOF's ability. In addition, the influencing factors were interpreted to help demonstrate the mechanism of SO₂ adsorption. The SO₂ adsorption in the MOF is influenced by the pore structure, both the pore arrangement and the pore size, the guest binding to the SO₂ and the linkers to the SO₂.

Keywords: Metal-organic frameworks, SO₂ capture, adsorption, mechanism.

1. Introduction

Sulfur dioxide, SO₂, is a well-known gas contaminant. It's pungent and toxic. SO₂ combines with water and then forms sulphurous acid in human respiratory tracts. The membranes there are gradually corroded. People especially children who live near the petrochemical industry, the source of SO₂, easily suffer from respiratory diseases, allergic diseases and asthma [1]. In general, it's generated artificially by vehicles, energy stations and most industries that need materials containing sulfur elements, particularly the steel industry. In the natural world, a volcanic eruption brings out tremendous amounts of SO₂. Environmentally capturing them in time protects the health of all organisms.

With the increased attention to the treatment of SO₂ emission, the mechanisms of SO₂ capture have been largely studied. Capturing SO₂ with the metal-organic framework (MOFs) will be more efficient and has a lower energy cost. Every microcosmic unit of MOFs is in the shape of a 3D or 2D network. Like coordinated compounds, each junction is a specific metal ion surrounded by organic ligands. And these junctions are arranged regularly to form the network. The progress in SO₂ capture highly involves the evolution of synthesis methods such as conventional heating or modulated synthesis and promoted reusability of MOFs suitable for SO₂ adsorption and the deep study of the influencing factors including pore arrangement, pore size and so on. There're varieties of effective MOFs. For instance, MFM-300(In) takes up 8.28 mmol SO₂ per gram at a maximum of 298 K, 1 atm [2].

This review intends to discuss the synthesis strategies of MOFs suitable for SO₂ capture and the mechanisms of the reversible adsorption process of SO₂ by MOFs, as well as the influencing factors

of SO₂ capture efficiency. It is expected to provide the basic information required to know the SO₂ adsorption of MOFs to guide the new design or more efficient use of MOFs in SO₂ capture by discussing existing MOFs to offer the inspirations, which could lead to the appearance of more advanced material in SO₂ capture.

2. Preparations of MOFs

MOF is a porous 3D framework that can have various combinations with different characteristics, which requires being synthesized in different methods [3]. In addition, to compose MOF in a certain form, such as thin film, membrane and so on, which is needed in different applications, the ways of synthesis are varied [4]. Because of the massive number of methods of the synthesis of MOFs, this paragraph mainly gives a brief introduction of some certain steps that are indispensable to producing stable MOFs and some common methods of synthesis of the MOFs which are suitable for adsorption of SO₂.

2.1. Conventional Heating

Conventional heating is the relatively most common method of synthesizing MOFs. This method can categorize into two different methods: electric heating and solvothermal synthesis. In the case of electric heating, it usually involves using temperature change to produce the target MOF [4]. The synthesis of MFM-601 shows an excellent performance in the adsorption of SO₂ gas. Heat a mixture of ZrCl₄, H₄L and benzoic acid as a modulator in dimethylformamide (DMF) at 120 °C for 24 hours. Then, isolate the MOF product as simple, colorless, plate-shaped crystals [5].

Solvothermal synthesis is defined as reactions in enclosed containers under autogenic pressure past the boiling point of the solvent [4]. An example of the solvothermal synthesis of MOF that specializes in the adsorption of SO₂ is NH₂-MIL-53(Al), which is a useful tool in the adsorption of SO₂ in the flue gas. NH₂-MIL-53(Al) is synthesized by mixing AlCl₃·6H₂O, 2-aminoterephthalic acid, DMF and water, and heating the mixture in a Teflon-lined stainless-steel autoclave at 150 °C for 24 hours [3]. However, these two methods usually contain high costs due to the installation of the equipment required to produce the needed MOF without too much yield of by-product [6].

2.2. Modulated Synthesis

Though there is a lot of interest in stable MOFs, which is necessary for practical application in the future, the inert metal-ligand linkages present considerable synthesis hurdles, which means that the process of MOF growth is hard due to the strong bond. To allow sufficient structural rearrangement or defect repair, the crystallization process necessitates a balance between crystal formation and dissolution, but throughout the MOF development process, the strong coordination connections in robust MOFs are difficult to separate. Therefore, it is necessary to carry out the step of modulation which is the process of regulating the coordination equilibrium by using modulators that either compete with metals for coordination or suppress linker deprotonation. Adding solutions like acid, for example, is one way to lower the rate of crystal growth to assist to form highly crystalline MOFs [7]. For instance, Zirconium-fumarate (Zr-Fum) is synthesized by using fumaric acid to modulate the Zr-oxo cluster to have a larger yield with lower costs [5].

2.3. Postsynthetic Modification

The introduction of post-synthetic modification (PSM) to the standard one-pot synthesis of MOFs is critical, as it can reduce the formation of by-products effectively. PSM enables target MOFs to possess an additional advantage because they can survive challenging alteration conditions while keeping their crystallinity and porosity, which enables MOFs to have more space to capture SO₂. This makes it possible to perform a broader range of PSM reactions on stable MOF platforms [7]. As the most common method of PSM, covalent modification can functionalize MOFs to have customized internal surfaces suitable for the specific application. Apart from covalent modification, dative

modification is also an effective way to be applied in post-synthetic metalation [5]. The metal ions exchange is another efficient method to obtain the MOFs that are hard to form. The inert bond in stable MOFs, which is thought to be able to significantly suppress the exchange process of ligands and metal ions, has been proved by researches that the stability of such bond is overestimated. Therefore, the metal ions exchange can be realized to strengthen the stability by substituting the labile metal nodes with more stabilized ones [7].

Zhang et al. reported MOF-808 using PSM. Originally, due to the coexistence of O₂ and water, SO₂ will convert to sulfate, which would lead to poor performance in the adsorption of SO₂. By using ethylene diaminetetraacetic acid (EDTA), the adsorption site of MOF-808 transfers to the N and COOH group in EDTA-MOF-808 that enabling MOF-808 to acquire excellent reversibility and stability to SO₂ [9].

3. The adsorption process of SO₂ in MOFs

Physisorptions are core to successful gas capture. Except for many traditional materials, the adsorptions in some original MOFs are also irreversible. The bonds formed between adsorbents and target molecules are excessively strong, including non-physisorptions and producing extra substance. the MOFs' structures will be permanently changed and the adsorption ability will be weakened. Therefore, Researchers modify these MOFs by shielding open metal sites with organic ligands. Then, a large percentage of desorption and adsorption are easily achieved. Adsorption mainly happens at adsorption sites. The physical interaction here between MOF and gas is strongest and more sites increase the amount of SO₂ uptake. For modifying original MOFs, take the example of MIL-101(Cr) with the empirical formula [Cr₃(O)(BDC)₃(X)- (H₂O)₂], BDC = benzene-1,4-dicarboxylate, X = F or OH depending on synthesis conditions [10]. As open sites in the MOF, Cr³⁺ accepts electrons transferred by O atoms in SO₂. The bond formed in the length of 1.995Å and adsorption enthalpy change -121 kJ·mol⁻¹ is relatively strong. As the result, MOF's structure is damaged: after 10 cycles of removing in a low-temperature vacuum, the SO₂ is removed only by ~60 %. As shown in Fig.1, the amount of gas uptake, equal to desorbed in the last cycle, was finally reduced to 60%. Zhang et al modified this MOF by binding mmen (N,N'-dimethylethylenediamine) to metal sides. Because of the different polarity of N and S atoms, the dipole-dipole interactions were built. Besides, H and O atoms formed hydrogen bonds. Fig. 2 shows the way of binding between SO₂ and two MIL-101. These relatively weaker interactions are accompanied by enthalpy change in -209 kJ·mol⁻¹ and similar lengths. Ultimately, according to experiments, SO₂ adsorbed successfully increased to ~85% (Fig. 1) by physisorptions and stabilized at this value [11].

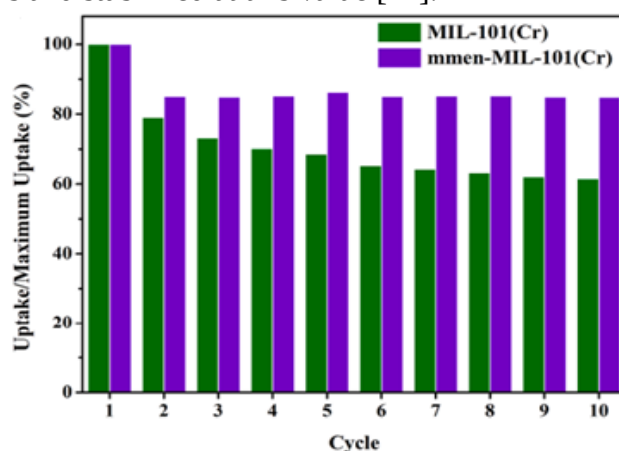


Figure 1. Comparison of SO₂ adsorption-desorption cycling performance for MIL-101(Cr) and mmen-MIL-101(Cr) [11].

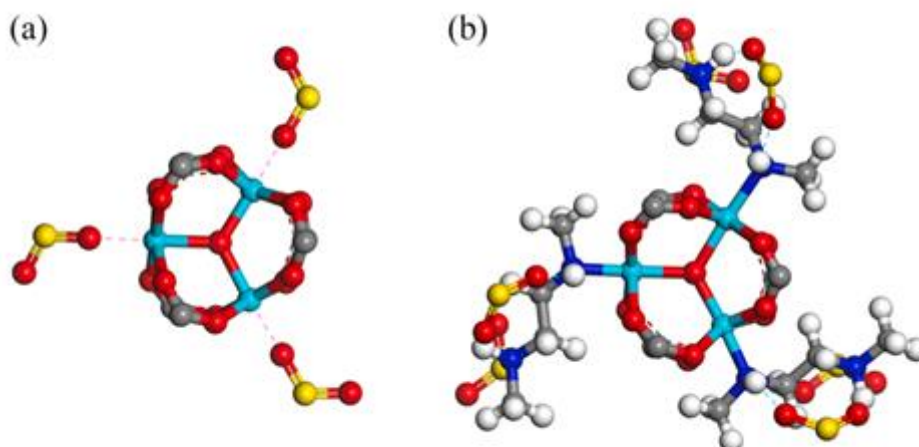


Figure 2. Structures of MIL-101(Cr) (a) and mmen-MIL-101(Cr) (b) when binding with SO₂ [11].

Zhang et al. reported EDTA-MOF-808 and MOF-808 for SO₂ capture. In XPS spectra, they observed the binding energy of 2p orbital in S atoms was between 168.9 and 169.2 eV. The adsorption of SO₂ in MOF-808 is irreversible due to the generation of formic acid when Zr-O clusters chemically bind with SO₂ in MOF-808. The condition was severer with the presence of O₂ because of negative Gibbs free energy (298 K, -136.0 kJ·mol⁻¹). In the SO₂ adsorption field, EDTA-MOF-808 was more advanced. Adding EDTA allowed SO₂ to bind with its N atoms and COOH group instead of the Zr-O cluster inside it. The physisorption was much more reversible and it's supported by Fig. 3: In simulated real fuel gas, the SO₂ uptake stabilized at 3.75 mmol/g⁻¹, 2.55 higher than that of MOF-808. So, EDTA-MOF-808 performs better in both actual flue gas (mix SO₂ with CH₄ and CO₂) and pure SO₂ [12].

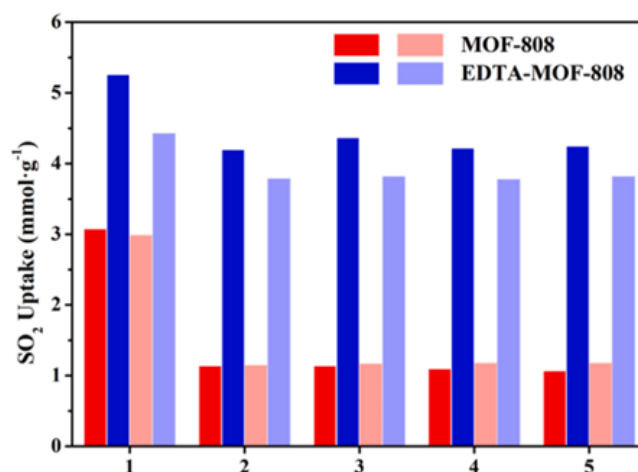


Figure 3. The solid red shows the calculated SO₂ capacity of MOF-808 in pure SO₂ and solid blue shows that of EDTA-MOF-808. Transparent color respectively shows their SO₂ capacities in actual flue gas conditions [12].

Additionally, in the adsorption of SO₂ in MOF, when bond lengths cause similar effects to adsorption, more adsorption sites for one gas molecule lead to better performance for adsorbing that gas. In general, there are two kinds of adsorption sites: strong hydrogen bonds and the uncoordinated atom with strong electronegativity such as nitrogen. Ren et al conducted experiments for adsorption of HBU-20 [Zr₆(μ₃-O)₄(μ₃-OH)₄(CH₃CO₂)₆(L)_{1.5}]·(DMF)₉·(H₂O)₆ L = tetrabenzoic acid, in real fuel gas condition. The capture capability of SO₂ is the best among the three gases. The reason was there were more adsorption sites for SO₂. SO₂ forms more bonds and it's graphically shown in Fig.

4. Besides the acetate ligands which attracted both two gases, some H atoms on phenyls interact with O atom in SO₂ but only μ 3-OH interacts with O in CO₂ [13]. Also, they can be determined by lower binding with DFT calculation [14]. The number of sites will be limited because of atoms existing in different planes in 3D space. Otherwise, if there are multi hydrogen bonds in one plane or multi parts of the target molecule are attracted by forces in different directions, there must be an adsorption site in the position of that target molecule.

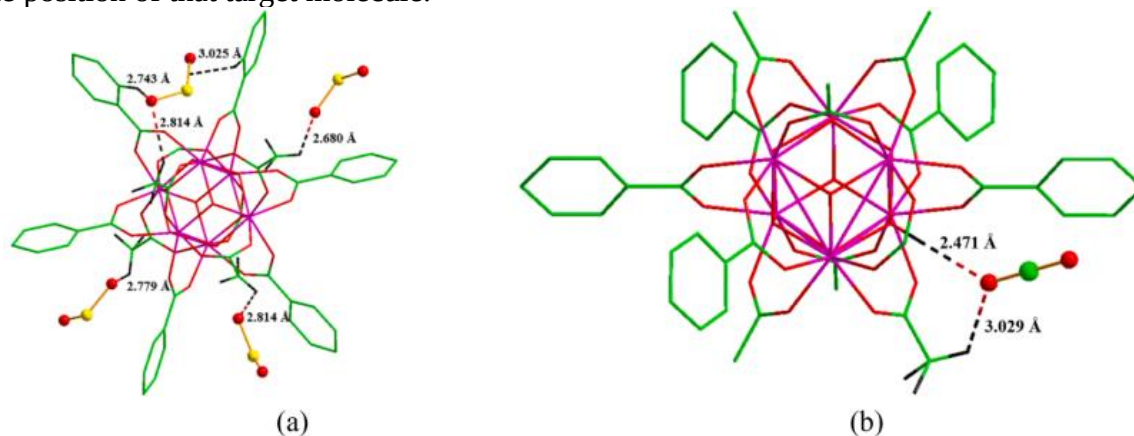


Figure 4. Possible adsorption sites to SO₂ (a), CO₂ (b) [13].

4. Factors for MOFs in SO₂ capture

4.1. Pore Structure

The internal pore structure of MOFs is essential as it determines its flexibility by influencing the overall adsorption process and quality and their adsorption capability and consequently SO₂ capture [15-17]. Considering the high diversity of metals or potential ligands, the number of possible MOF structures is virtually unlimited. Some of the types include UMCM-2, DO-MOF, NOTT-116, Be₁₂(OH)₁₂BTB₄, MIL (101) and ZIF-21. The adsorption of SO₂ is different in these different types of MOF structures. The adsorption of SO₂ differences in these different types of MOF structures. One study indicated that the max adsorption capacity of SO₂ was 51 mg/g for benzothiophene in MOF-5. The adsorption capacity becomes 0.19 mmol/g (35 mg/g) and 0.45 mmol/g (83 mg/g) for dimethyldibenzothiophene (DMDBT) and dibenzothiophene (DBT) respectively while taking UCM-150 [17].

4.1.1 Pore Arrangement.

The arrangement of the pores in a MOF can determine how efficient SO₂ will be removed. It is affirmed that the pore arrangement impacts SO₂ removal and informs the efficiency of the process [15]. In the experiment dealing with a Cu-based MOF, the pore arrangement allowed the dissemination of copper oxide in strategic locations within the MOF allowing the consumption of both stimulated semi-coke and MOF prototypes. Also, the study noted that an arrangement can bring together complementary components, such as in this research's process where a substrate and Cu-BTC were arranged together as the sacrificial model and copper foundation respectively [15]. This arrangement made the MOF obtain a well-developed porous structure equally associated with effective SO₂ removal as elaborated above. With an originally low loading of 0.19 % at Cu⁺ metal cites, the optimized sample shows the breakthrough of SO₂ adsorption capacity of 233.11 mg/g and the stable SO₂ removal efficiency of close to 100%. Also, it's more advanced than coke-base desulfurizers reported previously. A study that reported MOF-5-CXX, associated pore arrangement with the ability to create variance identification that facilitates the capture of minor SO₂ molecules [17]. As their gas adsorption isotherms show, their SO₂ adsorption capacities reached 2.5 mmol/g.

4.1.2 Pore Size.

Various researchers have mentioned the need to use microporous and MOFs with high porosity during SO₂ capture. One study discusses the role of microporous MOF and associates them with efficiency and improved separation capacities [17]. At 298K and 0.002 bar partial pressure of SO₂, SIFSIX-2-Cu-i exhibited distinguished SO₂ capacity as 2.31 mmol/g under mixed gas of N₂ and SO₂, which is equivalent to 2000 ppm SO₂ in the flue gas. It is explained that the pore size influences SO₂ capture as it determines attachments to a specific polar site. In the experiment, 61.2 cm³g⁻¹, a high capacity, combined with outstanding selectivity (10:90 in volume) of SO₂/N₂ (4064), SO₂/CH₄ (871) and SO₂/CO₂ (30) under 298K and 1 bar, was achieved due to the polar sites and pore size [24]. Therefore, the pore size is important in SO₂ removal, including not only flue gas but also other SO₂-containing gases. This efficiency persists despite the combination of gases available or the ambient conditions to which the MOF is subjected since it improves the capture sites.

High porosity is equally a factor since it makes the capture process efficient and generally valuable, like the SO₂/N₂ selectivity illustrated by the used porous materials [24]. The research explains that the pore size can enhance SO₂ capture ability and selectivity. Analysis of adsorption selectivity at 298 K using ideal adsorbed solution theory shows that the transformation of MFM-600 to MFM-601 is accompanied by an increase in selectivity of SO₂ over N₂. Study shows that during SO₂ capture, there is often the tendency to selectively separate the molecules based on their molecular sizes [17]. The MOF pores may influence the type of derivative captured. For instance, when the molecular sizes of thiophen and its derivative are smaller than the MOF pores, the molecules will enter the channels inside MOF and then become temporarily fixed on adsorption sites. In contrast, if the molecular sizes are similar or larger than the pore sizes, spacial hindrances then forbid the molecule to penetrate the framework inside. As the result, adsorption won't take place. Also, some pore sizes may induce region-selective interaction to facilitate SO₂ capture while some may make this impossible, such as mesoporous silica as a possible MOF constituent.

It is explained that the pore size influences the stability of the MOF used in experiments and may encourage research on the separation and capture of SO₂ including where a different small molecule of gases is present [20]. The research designed and synthesized Zr(IV)-MOF (HBU-20). With the BET calculation, it achieves a surface area of 1551.1 m²/g and a considerable pore volume of 0.896 cm³/g. In the condition of 298 K and 100 kPa, it shows an SO₂ adsorption capacity of 6.69 mmol/g. When the volume ratio of SO₂ and CO₂ or CH₄ is 1:99, the experimental selectivities respectively reach 81.1 and 117.6.

4.2. Guest Binding

Guest binding impacts SO₂ capture, particularly through the modulation of the pore environment. One study explains that the modulation of the pore environment can act as an operational tactic when it comes to optimizing guest binding in porous materials, facilitating effective SO₂ capture [19]. Guest binding also determines the circulation of cationic and anionic cores, a process that enhances adsorption capacities and selectivity. Guest binding can also reinforce the realization of SO₂ binding in the respective MOF. Binding interactions, especially with pore surfaces, determine SO₂ capture as they equally influence the binding attraction to other gases within the same spectrum [22]. Similarly, the guest binding ability is critical in SO₂ capture since it influences SO₂ selectivity and capture ability [24]. Guest binding influences region-selective interactions as they determine the pore channels through which SO₂ capture occurs [17]. Studies also show that the guest binding energy equally influences SO₂ capture by reinforcing its selectivity [20]. Guest binding Influenced the performance of MOF adsorption of SO₂. Because of numerically dense CF₃SO₃⁻ groups which contain SO₂ adsorption sites, not only the SO₂ capture ability, capacity, is enhanced to 61.2 cm³g⁻¹ but also the selectivity (10:90 in volume, at 1 bar, 298K) of SO₂ between CO₂ and SO₂ between CH₄ increase to 30 and 871 respectively [24].

4.3. Linkers

Linkers are essential in functionalizing MOFs as various researches elaborate, a critical element in the capture of SO₂. Missing linkers improve pore convenience in terms of access and interaction boost [21]. There is increased SO₂ capture and variance in the applied processes. It is equally easier to identify malfunctioning constituents associated with possible original non-defective ones as they are connected to the missing linkers. Linkers are associated with improved interaction between SO₂ and the MOF, influencing its capture [24]. The research explains that dynamic breakthrough experiments have associated aromatic linkers with regeneration stability and excellent separation performance improvement. Linkers, similar to modulators enhance host-guest interactions [23]. The research explains that the coordinating linkers improve SO₂ reaction and its resulting capture. With the existence of an alkyne ligand rather than only a phenylene one, both the surface area and pore volume are increased. Take the typical example of Cu₃(BHEHPI). The impact of linkers on adsorption is attributed to their effect on the pore size and structure of MOFs. Enhancing the pore volume and surface area involves using longer organic ligands to expand the MOF structure but remaining underlying topology as same [21]. The longer linkers are associated with larger volumes of unit cell and pores. In an experiment to investigate the desulfurization abilities of adsorbents DBT and 4,6-DMDBT, it is indicated that HKUST-1 illustrated a 17.4 smaller cell volume than MOF-399 due to shorter linkers [21]. Thus, it indicated an adsorption desulfurization capacity of 0.15 mmol/g (83 mg/g than HKUST-1).

5. Conclusion

With the increased concerns about the environmental influences of SO₂, studies on SO₂ have largely arisen. As one of the potential porous nanomaterials, MOFs have been discussed as an effective solution in the application of SO₂ capture in the last few years. Constant endeavors have been made to develop advanced MOFs in SO₂ adsorption under different circumstances. In this article, the synthesis strategies including conventional heating, modulated synthesis and post-synthetic modifications of MOFs were introduced in this review. The adsorption process, including non-physisorptions and producing extra substances, was discussed. This process changes the MOF structures permanently, possibly weakening the adsorption ability. The research acknowledges the ability of physisorptions to increase the successful removal of SO₂. Adsorption sites are crucial since bond lengths cause similar effects to adsorption, more adsorption sites for one gas molecule lead to better performance for adsorbing that gas. In general, there are two kinds of adsorption sites including strong hydrogen bonds and the uncoordinated atom with strong electronegativity such as nitrogen. Furthermore, different factors influence the SO₂ adsorption process, namely pore structure which influences MOF performance in terms of the adsorption process, capabilities and quality, pore arrangement determines how efficient SO₂ will be removed, pore size linked to efficiency and improved separation capacities, exposure factors like water vapor and acidic gases associate with improved stability, guest binding particularly through the modulation of the pore environment, host-guest interaction for efficiency and quality of the capture process, and linkers which improve pore convenience in terms of access and interaction boost.

The recent concern about the practical application of MOFs fitting for SO₂ adsorption is the high cost caused by the installation and operation, which could be one respect that should be focused on in the future study. However, although many challenges have not been settled for practical application yet, the appealing porosity and storage capacity and astonishing diversity of structure of MOF suggest that the application of MOF has extremely large potential to be eventually feasible.

References

- [1] Chiang.T.Y., Yuan.T.H., Shie.R.H., Chen.C.F., Chan.C.C. Increased incidence of allergic rhinitis, bronchitis and asthma, in children living near a petrochemical complex with SO₂ pollution. *Environment International* 96 (2016) 1-7.
- [2] Mathew. S., Yongqiang C., Timothy L., et.al Selective Adsorption of Sulfur Dioxide in a Robust Metal-Organic Framework Material. *Adv. Advanced Materials*, 28, (2016) 8705–8711.
- [3] Lei, J., Qian, R., Ling, P., Cui, L., & Ju, H.. Design and sensing applications of metal–organic framework composites. *TrAC Trends in Analytical Chemistry*, 58, (2014) 71-78.
- [4] Stock, N., & Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chemical Reviews*, 112(2), (2011) 933–969.
- [5] Brandt, P., Xing, S.-H., Liang, J., Kurt, G., Nuhnen, A., Weingart, O., & Janiak, C.. Zirconium and Aluminum MOFs for Low-Pressure SO₂ Adsorption and Potential Separation: Elucidating the Effect of Small Pores and NH₂ Groups. *ACS Applied Materials & Interfaces*, 13(24), (2021) 29137-29149.
- [6] Reinsch, H., & Stock, N. Synthesis of MOFs: a personal view on rationalisation, application and exploration. *Dalton Transactions*, 46, (2017) 8339-8349.
- [7] Yuan, S., Feng, L., Wang, K., Pang, J., Bosch, M., Lollar, C., Zhou, H.-C. Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. *Advanced Materials*, 1704303, (2018).
- [8] Carter, J. H., Han, X., Moreau, F. Y., da Silva, I., Nevin, A., Godfrey, H. G. W., Schröder, M. Exceptional Adsorption and Binding of Sulfur Dioxide in a Robust Zirconium-Based Metal-Organic Framework. *Journal of the American Chemical Society. J. Am. Chem. Soc.* 140, (2018) 15564-15567
- [9] Zhang, Z., Yang, B., Wu, Y., Zhang, W., & Ma, H. Post modification of Oxo-clusters in robust Zirconium-Based metal-organic framework for durable SO₂ capture from flue gas. *Separation and Purification Technology*, 276, (2021) 119349.
- [10] Tan.B., Luo.Y., Xiang H., Wang S., Gao X., Zhang Z., Fang Y. Mixed-Solvothermal Synthesis of MIL-101(Cr) and Its Water Adsorption/Desorption Performance, *Industrial & Engineering Chemistry Research*, 58, 8, (2019) 2983-2990
- [11] Zhang Z., Yang B., Ma H. Aliphatic amine decorating metal-organic framework for durable SO₂ capture from flue gas, *Separation and Purification Technology*, 259, (2021) 118164.
- [12] Zhang Z., Yang B., Wu Y., Zhang W., Ma H. Post modification of Oxo-clusters in robust Zirconium-Based metal-organic framework for durable SO₂ capture from flue gas, *Separation and Purification Technology*, 276, (2021) 119349.
- [13] Ren Y., Xu H., Gang S., Gao Y., Jing X., Du J. An ultra-stable Zr(IV)-MOF for highly efficient capture of SO₂ from SO₂/CO₂ and SO₂/CH₄ mixtures, *Chemical Engineering Journal*, 431, (2022) 134057.
- [14] Li Y., Wang G., Shi W., Hou L., Wang Y., Zhu Z. Efficient C₂H_n Hydrocarbons and VOC Adsorption and Separation in an MOF with Lewis Basic and Acidic Decorated Active Sites, 12,37, (2020) 41785-41793.
- [15] Duan, R., Feng, Y., Gu, J., Wang, M., He, B., Liu, L., ... & Wang, X. Ultralow loading of Cu₂O/CuO nanoparticles on metal-organic framework-derived carbon octahedra and activated semi-coke for highly efficient SO₂ removal. *Journal of Cleaner Production*, 341, (2022) 130823.
- [16] Kan, S., Huang, Y., Watanabe, T., Nair, S., Walton, K. S., Sholl, D. S., & Meredith, J. C. MOF stability and gas adsorption as a function of exposure to water, humid air, SO₂, and NO₂. *Microporous and mesoporous materials*, 173, (2013) 86-91.

- [17]Kampouraki, Z. C., Giannakoudakis, D. A., Nair, V., Hosseini-Bandegharai, A., Colmenares, J. C., & Deliyanni, E. A. Metal-organic frameworks as desulfurization adsorbents of DBT and 4, 6-DMDBT from fuels. *Molecules*, 24(24), (2019) 4525.
- [18]Li, L., Da Silva, I., Kolokolov, D. I., Han, X., Li, J., Smith, G., ... & Schroder, M. Post-synthetic modulation of the charge distribution in a metal–organic framework for optimal binding of carbon dioxide and sulfur dioxide. *Chemical science*, 10(5), (2019) 1472-1482.
- [19]Lin, R. B., Xiang, S., Xing, H., Zhou, W., & Chen, B. Exploration of porous metal–organic frameworks for gas separation and purification. *Coordination chemistry reviews*, 378, (2019) 87-103.
- [20]Ren Y., Xu H., Gang S., Gao Y., Jing X., Du J. (2022) An ultra-stable Zr(IV)-MOF for highly efficient capture of SO₂ from SO₂/ CO₂ and SO₂/CH₄ mixtures, *Chemical Engineering Journal*, 431 (2022) 134057.
- [21]Rodríguez-Albelo, L. M., López-Maya, E., Hamad, S., Ruiz-Salvador, A. R., Calero, S., & Navarro, J. A. Selective sulfur dioxide adsorption on crystal defect sites on an isorecticular metal organic framework series. *Nature communications*, 8(1), (2017) 1-10.
- [22]Savage, M., Cheng, Y., Easun, T. L., Eyley, J. E., Argent, S. P., Warren, M. R., ... & Schröder, M. Selective adsorption of sulfur dioxide in a robust metal–organic framework material. *Advanced materials*, 28(39), (2016) 8705-8711.
- [23]Walton, I., Chen, C., Rimsza, J. M., Nenoff, T. M., & Walton, K. S. Enhanced sulfur dioxide adsorption in UiO-66 through crystal engineering and chalcogen bonding. *Crystal Growth & Design*, 20(9), (2020) 6139-6146.
- [24]Zhang, Y., Zhang, P., Yu, W., Zhang, J., Huang, J., Wang, J., ... & Deng, S. Highly Selective and Reversible Sulfur Dioxide Adsorption on a Microporous Metal–Organic Framework via Polar Sites. *ACS applied materials & interfaces*, 11(11), (2019) 10680-10688.