Strategies for designing & improving flexible MOFs

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Abstract. Even today, the problem of greenhouse gas emissions and recycling endanger human health continuously. The dynamic structure of the flexible MOFs (metal-organic frameworks) allows them to change their structure in response to external stimuli. And a fresh approach to reducing greenhouse gas emissions comes from using flexible frames for gas absorption, notably in the area of lower energy and highly selective gas separation. This review starting from the design and improvement of flexible MOFs summarizes some excellent cases in carbon dioxide capture. Finally, the potential applications of flexible MOFs are classified and briefly analyzed.

Keywords: MOFs, Flexible Framework, Design, Potential Applications.

1. Introduction

We do not inherit the Earth from our ancestors, we borrow it from our children. Countries have begun to control greenhouse gas emissions since the "Kyoto Protocol" was proposed in 1997. However, plans for transforming their energy-providing resources, can't be carried out smoothly due to energy issues. As a result of those difficulties, global temperatures have been rising in recent years. And it will create serious problems for humans. One way to solve the above problems is to develop a better carbon catcher. Soft Porous Crystals (SPCs), considered third-generation MOFs, can respond to external stimuli. This unique feature of the SPCs, also known as breathing and swelling phenomena, shows the reversible interactions between host and guest. For example, the adsorption capacity of MIL-53(Materials Institute Lavoisier) to CO_2 is up to 31.4% (quality score, at 30MPa and 1℃) after the structural change induced by the binding of MIL-53's hydroxyl group to CO_2 guest molecules [1]. This is far higher than other molecular sieves and activated carbon materials of carbon dioxide adsorption. Besides, functional modification of the MIL-53 framework can overcome the puzzle of poor gas adsorption at low pressure, a difficult problem that widely exists in microporous materials. SPCs might be essential in the adsorption and desorption of CO_2 since they possess characteristics that are not exhibited in other reported substances. Using SPCs as a carbon capture material also provides a new idea for solving greenhouse gas emissions. This paper will focus on the structure and properties of SPCs, as well as their application in different fields, and to sort out the previous research. At the same time, this paper will surround the breathing effect of SPC and its application in greenhouse gas capture. Hoping this work may shed some light on understanding the future direction of the carbon catcher, SPCs.

This article will be divided into five parts. Starting with the second part, a series of relevant literature will be reviewed, some typical modes of flexibility will be introduced, several important factors will be enumerated, and some applications in the gas phase will have analyzed. Finally, the sixth part of the article will have a summary, discussing the limitations of the article and the future directions.

2. Literature review

Flexible MOFs, sometimes called SPCs (Soft Porous Crystals) is a kind of reticular material with a dynamic structure, which is different from ordinary MOFs. SPCs are defined as porous solids that possess both a highly ordered network and structural transformability [2]. The first widely accepted prediction of a flexible frame took place in 1998 [3]. S. Kitagawa [4] discussed functional Porous Coordination Polymers in 2004, which is the beginning of the research. Unfortunately, compared with traditional MOFs, which are widely concerned and studied, there is little research on SPCs, and one of the reasons for this phenomenon is that there are fewer compounds to choose from. Only a few materials have been systematically studied, including MIL-53 and MIL-88 [5]. However, except for a few materials that have been studied in detail, the rest of the field remains blank. On the other hand, Cao et al. [6] analyzed the design, synthesis, and application of MOFs based on flexible linkers in 2014. S. Kaskel and R. A. Fischer [5] believe that in the future, it will be possible to broaden the functional idea of a framework's responsiveness to factors other than host-guest interaction-related stimuli from light, mechanical deformation, thermal, electrical, or magnetic force.

3. Typical modes of flexibility in SPCs

The four main types of flexibility—breathing, swelling, linker rotation, and subnetwork displacement—are generally accepted to exist. The unit cell volume of the breathing effect and the swelling effect both change, but the shape and space group of the unit cell are retained in the swelling effect.

3.1. Breathing effect

As an early research star material, MIL-53(M) family ($[M(bdc)(OH)]_n$ with bdc = 1,4-benzenedicarboxylate, and M = Al, Fe, Cr, Sc, Ga, In) provide so many typical examples. The changing of the unit cells' angles and characteristic distances lead to the space groups of two distinct phases (narrow pore-large pore) transforming mutually. There is a transition from the lp→np phase that can be observed at roughly 125K in vacuo [7]. Then the phase transition is complete at roughly 375K, after which the material progressively changes back to the lp form above 325K which shows the feature of the breathing effect: the change of unit cell index in geometry is accompanied by phase transitions. There is a widely believed point of view, one of the reasons for the flexibility of those MOFs is their high anisotropy. Walker et al. [8] reported that at low temperatures, dispersive interactions lead to stabilizing the np phase. The increased entropy of the revolving linker molecules causes the production of the lp phase as the temperature rises.

3.2. Swelling effect

Although it has been demonstrated that changes in the unit cell characteristics and cell volume strongly correlate with the presence of guests, we should remember that even if an external stimulus may activate SPCs' framework flexibility, the probability of host-guest interactions is not 100 percent. MOF-5($[Zn_4O(BDC)_3]_n$, BDC =1,4-benzenedicarboxylate)[9], which is well known in this field, is one of the archetypal rigid frameworks can show its flexibility without guest molecules.

3.3. Linker rotation

This kind of mode is mainly based on the movements of the rotational linker, and the consequence is the pore windows expanding and bigger molecules adsorbing. By using those characteristics, researchers gained a valuable possibility to design engineering special functions. A good illustration of this is the framework $[Cd_2(pzdc)_2(BHE\text{-}bpb)]_n$ (pzdc = 2,3-pyrazinedicarboxylate; BHE-bpb = 2,5-bis(2-hydroxyethoxy)-1,4-bis(4-pyridyl)benzene)[10], which is made of alkyloxy functionalized pyridyl linkers interconnected with $[Cd_2(pzdc)_2]_n$ layers. The interactions between the OH groups situated on pyridyl pillars and other neighbor OH groups at the end of the pyridyl pillars' alkyloxy side chains, resulted in pore gating. When a polar molecule contacts the gate, the metal centers of the frame are affected, causing the opening of the gate. This provides an accessible strategy to design new frameworks with the selectivity to the guest molecules: modification or pruning of an organic ligand.

3.4. Subnetwork displacement

It is a special phenomenon that only occurs in systems having individual frameworks without interaction by strong chemical bonds. Van der Waals interactions between these systems enable subnets to drift, relocate, or shift concerning one another.

4. Factors that can't be ignored: building a satisfactory framework

4.1. Starting from the linker& organic ligands: an effective measure of enhancing the framework

4.1.1. Choosing a suitable linker for your target. As we all know, when organic compounds interact with light, part of them can alter their conformation or structure. And the framework consists of those molecules that may retain their photoresponsivity. Photoswitches are most frequently introduced by adding them as a functional group to the linker. Unfortunately, only the azobenzene group has so far been introduced into MOFs, even though there are many different types of photoswitchable compounds in labs [5]. Modrow et al. [11] used an azobenzene functionalized bipyridine derivative to synthesize the framework $[Zn_2(2,6\text{-ndc})_2\text{-(azo-bipy)}]_n$ (azo-bipy = 3-azo-phenyl-4,40-bipyridine) which based on pillared-layer. The linker of material can be observed converted from trans to the cis isomer after being triggered by the light of a wavelength of 365 nm. It is a reversible reaction, and reversible switching back may be accomplished either by heat treatment or irradiation with light with a 440 nm wavelength.

4.1.2. Suitable organic ligands provide diversity for the improvement of frame structure& properties. In Cao's work, metal-organic frameworks (MOFs) were regarded as coordination polymers (CPs), which are crystalline materials constructed from metal ions or clusters bridged by organic ligands to form 1D,2D, and 3D networks [6]. By using flexible ligands, Cao et al. [6] were able to produce fresh crystalline framework materials with desirable properties. As for the pillared-layer MOFs, based on the elongation and shortening of the interlayers, the reversible phases may be determined by selecting better flexible pillars.

MOFs have been expected to have a larger pore void ratio for a long time. Many researchers choose elongated ligands to achieve the high capacity of the framework. Wu et al. [12] used 4,4',4”-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris(oxy)tribenzoic acid(H_3ttt) to synthesize a group of flexible ligand MOFs (FL-MOFs) with pore ratios varying from about 21.1% to 50.8%. On the one hand, using longer ligands likely reduces pore voids' solvent accessibility and decreases the porosity of the material because of the potential for interpenetration in the process of synthesis. On the other hand, however, some experts show that even in the absence of framework interpenetration, a high pore volume ratio can also be achieved. There is an outstanding example, NJU-Bai-9. While the pore volume ratio is up to 78.1%, it also has a BET surface area of 4258 m^2g^{-1}[13].

4.2. Activation & enhancement

4.2.1. Choosing better measures to activate the frameworks. It is important to select the correct linkers and ligands for ideal products, but after building target materials we still need to face a serious problem: how to preserve frameworks' porosity once guest solvent molecules are eliminated. There are several research groups have designed and synthesized the flexible tetrapodal octacarboxylate ligand H^{8-} based framework 4,8-connected scu-MOF$[Cu_4X(H_2O)_4]\cdot 7.5DMF\cdot 8H_2O$(square planar and cubical vertices) [14]. After exchanging by mild solvent, the activated sample shows that the BET surface area and pore volume of the material are 1854 m^2g^{-1} and 0.84 cm^3g^{-1}, respectively. However, after being heated directly at 120°C under a dynamic vacuum, the material only provided a BET surface area of 1115 m^2g^{-1} and a total pore volume of 0.612 cm^3g^{-1}. It is obvious that using a suitable treatment could bring such a big difference from another one just getting a simple treatment. To obtain high porosity crystals, Hupp et al. managed to use supercritical carbon dioxide drying (SCD) to activate MOFs [15] which provides a marvelous approach for keeping permanent porosity and surface areas.

FL-MOFs (MOFs based on flexible ligands) $[In_2L]\ [NH_2(CH_3)_2]_2 \bullet (DMF)_4(H_2O)_{16}$ is a kind of highly porous material [16]. Compared with the sample that has been sufficiently separated under 80°C, using SCD could improve the BET surface area (from 752m^2g^{-1} to 1555 m^2g^{-1}) and pore volume (from 0.612cm^3g^{-1} to 0.62 cm^3g^{-1}). Besides, improving the stability of the SPCs is also one of the focuses of many researchers to avoid the collapse or shrink of the framework after moving the solvent.

4.2.2. Framework modification for targeting needs. One of the difficulties in the research of this kind of soft framework is the approach to synthesizing its complex structure. Modifying the components of building units is an important step in the preparation of functional frameworks. Cao et al. argued that the key to improving gas adsorption and selectivity is enhancing gas-binding affinity [6]. They summarized the following strategies for increasing the tendency of MOF to combine with gas: regulating the pore size, integrating open metal sites, employing amines or nitrogen-rich organic linkers into the frameworks, and adding metal cations. And the last two methods are used more frequently in SPCs.

Even though SPCs have many advantages including high specific surface area and high capacity, they do not have a good effect under some conditions. To increase MIL-53's capacity to absorb substances under low pressure, Serre et al. [1] introduced $-NH_2$ on the organic ligand of MIL-53, which increased the CO_2 adsorption capacity by 15%. Introducing other functional groups, such as -Br, -Cl, and $-NO_2$ [17], which can also affect the CO_2 adsorption capacity of MIL-53. Bai et al. have designed FL-MOFs with an amide insertion $\{[Cu_3(cip)_2(H_2O)_5]\ \cdot xGuest\}_n$ (NJU-Bai3, H_3cip = 5-(4-carboxybenzoylamino)-isophthalic acid) [18] which have a strong gas-combining ability for CO_2 (36.5 kJ mol^{-1} at zero coverage) and high CO_2 uptake (22.12 mmol g^{-1} at 273 K and 20 bar). Same to the prediction by IAST for equimolar gas mixtures, NJU-Bai3 demonstrates that the selectivity of CO_2 over N_2 varies between 25.1 and 60.8, while the values of CO_2 over CH_4 are between 13.7 and 46.6 in the 0-20 bar range. Another famous FL-MOF is $\{[Cu_3(tdpat)(H_2O)_3]\cdot 10H_2O\cdot 5DMA\}_n$ (Cu-tdpat) [19] employed nitrogen-rich organic linkers. As one of the leading MOFs materials for CO_2, H_2, and CH_4 storage, the CO_2 adsorption enthalpy of Cu-tdpat is 42.2 kJ mol^{-1} (without any load), and the low-pressure CO_2 uptake is 44.5% (at 1 bar and 273 K).

In contrast to the above example, another idea is to introduce metal cations. By adding metal cations into $\{[Zn_3(tcpt)_2(HCOO)][NH_2(CH_3)_2]\cdot 5DMF\}_n$ (SNU-100, H_3tcpt = 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine) [20], Suh et al. achieved an example with high CO_2 uptake capacity and selectivity. However, some of the functions in frameworks, such as the isosteric heat, absorption capacity, and selectivity of CO_2 adsorption, are affected by the electrostatic interactions between CO_2 and metal ions out of the impregnated extra-framework.

5. Applications

5.1. Potential applications of SPCs in gases

The gas adsorption capacity and selectivity of SPCs have been mentioned many times above. Besides the focus on gas adsorption, SPCs can also be applied in chromatography as a stationary phase to achieve liquid phase separation. Millange et al. reported a case of the effective separation of mixes of xylene isomers using the MIL-53 (Fe) [21]. Although the powder XRD (X-ray diffraction) indicates each isomer has a corresponding full load of MIL-53(Fe), only the para-isomer can be separated from the mixture (at 293K). Recently, the results of selectivity are usually supported by gas sorption isotherms without competition from other gases. However, the one-component method is no longer appropriate because the flexible behavior is very complex. A potentially accessible approach is the quantitative analysis of gas components before and after reversible binding. The information obtained under dynamic equilibrium may be valuable for measuring the gas separation ability and selectivity of a specific gas.

5.2. Biomedical applications

To avoid complications from healthcare-associated infections, using catheters is a necessary and essential part of today's medical practice [22]. One of the simplest strategies for modifying materials is to immerse them in anti-bacterial drugs so that the catheter can release the carried drug and kill the bacteria in vivo. In addition, there are many opportunities to load drugs during the material's preparation. Although the methods of synthesizing the loaded materials are full of diversity, they all have a mutual defeat: how to keep the concentration of the released agents at an effective level. Horcajada et al. [23] managed to load ibuprofen with MIL-53(Fe) and evaluated the process of drug release. Agree with the unit cell of MIL-53-lp phases under the diffraction, the ibuprofen-loaded material releases slowly so that two steps can be observed. The slow release of drugs helps to reduce the toxicity and discomfort during the treatment, so the research on using SPCs as drug carriers may be hot in the future.

5.3. Sensing

During the structure transformation, parts of SPCs are accompanied by a reversible change in color. One of those frameworks, DSB@$[Zn_2(bdc)_2dabco]_n$ (DSB=distyrylbenzene) [24] was shown by Yanai et al. Thanks to the use of DSB@$[Zn_2(bdc)_2dabco]_n$, CO_2 and acetylene can be distinguished depending on the different fluorescence, even though they both have similar physicochemical properties. Besides, SPCs based on the change in material size can be used to monitor the concentration of gases in the system as an alarm. Usually, each soft framework has an independent gate-opening pressure on different types of gas, and this property does not belong to the rigid MOFs. Once the concentration of the target gas in SPCs is high enough to overcome the gate-opening pressure, leading structure changes significantly even into another phase.

5.4. Catalysis

Single Crystal X-ray diffraction (SCXRD) is a direct and rapid method to obtain the structure of frame materials. However, this is a double-edged sword: the accuracy of the X-ray diffraction results is proportional to the stability of the material. And the dynamic characteristics of the SPCs structure make it easy to be affected by small changes in the system state. Based on the low reliability of the test, the employment of flexible MOFs in reaction catalysis is not suitable.

6. Conclusion

In the past decade, the focus of flexible MOFs research has been restricted to gas adsorption and fluorescence sensing. The reasons include that insufficient diversity of materials and the dynamic structure makes it difficult to obtain accurate measurement results. Furthermore, the production of materials with tailor-made breathing and gate-opening properties and the preservation of preferential conformations are both important considerations. Unlike traditional rigid MOFs, SPCs don't have to alter the aperture precisely because of their dynamic structures which allow a broad future applications prospect for SPCs in gas adsorption and sensing.

A design concept for synthesizing complicated SPCs was presented in this work. Following this synthesis route, researchers need to consider three factors, First selecting and synthesizing a base material that can perform the same (or similar) actions as the target MOFs, then modifying the material with suitable linkers (organic ligands) and choosing a better activation method that makes it have higher application value. The product yield following the abovementioned methods is certainly not optimum. Therefore, the highly effective synthesis of complicated frameworks is a critical issue that will be the focus of future research.

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