Characterization of Gas Adsorption Sites and Behaviors in Metal-Organic Frameworks

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In this paper, we start with a short introduction to the research background of gas adsorption in the metal-organic frameworks (MOFs) field, and then we highlight the gas adsorption sites and behaviors with the aid of various characterization methods, among which we discuss mainly infrared absorption and Raman scattering, as well as X-ray diffraction and neutron diffraction. In addition, we introduce briefly X-ray spectroscopy because they also play a crucial role in understanding MOFs' gas adsorption. On the other hand, computational simulations, which can reveal underlying adsorption and working mechanism in microscale, are also discussed. Finally, comprehensive kinetic studies are briefly summarized based on these advanced characterization methods.

Keywords metal-organic frameworks, gas storage, characterization methods

Introduction

Metal-organic frameworks (MOFs) are crystalline networks constructed from metal clusters/ions and organic linkers through self-assembled process. The permanent porosity, high surface area and tailorable structures are the signatures that provide MOFs with great potential in gas storage and separations in terms of energy and transport efficiency, which have been the primary focuses in research fields and widely studied for MOFs' applications.^[1-3] MOFs, which could be dated back to 1990s,^[4] have been potentially applicable in luminescence, catalysis, gas storage and separation, and so on.^[5-8] The hallmark of MOFs is superior surface areas with adjustable pore sizes, which simulate the development of applications in sustainable energy-related gas storage and separation. Rational design of frameworks with high storage capacity or separation becomes a mainstream in the past twenty years. As a result, hundreds of MOFs have been developed for gas storage or separation, in particular for hydrogen,^[9-12] methane,^[5,13-17] and carbon dioxide.^[18-23] For instance, one of the best materials for methane storage is HKUST-1 (HKUST=Hong Kong University of Science and Technology),^[13] which exhibited a total volumetric capacity of 230 cc(STP)/cc and 270 cc(STP)/cc (STP: standard temperature and pressure, 273.15 K, 1 atm) at 35 and 65 bar, respectively, with a working capacity of 190 cc(STP)/cc in a recent report, which turns out good for commercialization in powering auto vehicles. Nowadays, it becomes commercial available.^[24] However, the industrial application of those MOFs stalls due to the their easy poisoning by sulfur oxides among the natural gas pipelines and as well as packing problems.^[16] Therefore, studying the detailed gas adsorption process in order to ultimately design new MOFs with better stability and

higher gas uptake properties is in great demand.^[25] Nevertheless, such studies are quite scarce due to the lack of attention.^[26] Considering the interactions between MOFs and guest molecules play a key role in gas storage and separation, we aim to review briefly recent discoveries about interactions between MOFs and gaseous guests with the expectation to benefit future design that meet the commercial application. Herein, studies about various characterization methods for MOFs' gas sorption properties, including infrared absorption and Raman scattering, X-ray diffraction, neutron diffraction, and X-ray spectroscopy, and computational simulations will be outlined. At the end, comprehensive kinetic studies will be further highlighted.

Infrared absorption and Raman scattering

The major interactions between MOFs and gas molecules are electrostatic interactions and van der Waals (vdW) forces. As the experimental studies on those interactions rely highly on the bonding configurations of guest molecules within the framework, it could be generally characterized by the vibrational spectroscopy, such as IR adsorption and Raman scattering.^[27,28] In this section, we will focus on using IR and Raman to probe the interactions between guest molecules and surface of MOFs. Studies about the vibrational changes in the adsorption studies of H₂,^[29-31] SO₂,^[32] CH₄,^[33] CO,^[34-37] and CO₂^[38-43] using IR absorption and Raman scattering will be discussed.

Infrared absorption spectroscopy (IR)

The vibrational frequency of bonding of guests or frameworks always shifts during the kinetically diffusion and adsorption process. In this regard, those shifts could be clearly observed using IR absorption spectroscopy. Taking CO₂ as an

example, the linear molecule has four vibrational normal modes but three fundamental vibration frequencies due to the degeneracy of two bending modes (Figure 1).^[44,45] In the adsorption process of CO₂ within MOFs, both the bending ν_2 and asymmetric stretching ν_3 modes of CO₂ are perturbed when interacting with framework, which change usually the dipole moment and consequently gives rise to the frequency shifts in the IR spectra. Meanwhile, the symmetric stretching ν_1 of CO₂ becomes Raman active due to the altered polarizability.^[45] In the following examples, studies using IR absorption spectroscopy will be outlined based on the different causes—structural change of MOFs, functionalization on organic linkers and direct influence from metal secondary building units (SBUs).

Structural change of MOFs

Vimont and coworkers^[38] reported that the carbon atom of CO₂ interacts with the oxygen atoms of hydroxyl groups in MIL-53(Cr) as an electron-acceptor with the spectroscopic evidence for formation of electron-donor-acceptor (EDA) Complex between the CO₂ and hydroxyl group in framework. The IR spectra of MIL-53(Cr) demonstrated a redshift of the ν_3 band (from 2335 to 2349 cm⁻¹ with increasing amount of CO₂). A splitting of ν_2 mode (662 and 650 cm⁻¹) was also observed due to the symmetry lowering of the absorbed CO₂ (Figure 2). Along with a significant perturbation for the corresponding IR band of μ -OH of the oxo-chromium (III) SBUs, the authors ascribed the splitting to the interactions between the oxygen of μ -OH and carbon atom of CO₂. A similar splitting of ν_2 has also been reported by Férey and coworkers.^[46] In addition to the ν_2 splitting and the significant perturbation of the ν (OH) band, IR spectra revealed that the band at 1022 cm⁻¹ for the dehydrated sample shifted to 1017 cm⁻¹ under 1 bar of CO₂ and progressively returned to its initial position with an increasing pressure to 10 bar during an adsorption-desorption cycle. This shift could be directly attributed to the structural changes of MIL-53 from the opening forms (1022 cm⁻¹) to the closed form (1017 cm⁻¹), which enabled us to evaluate the ratio of the open and closed structures upon CO₂ adsorption (Figure 3). Noticeably, a new ν_2 band appeared at 659 cm⁻¹ at higher CO₂ pressure, which could be a sign of a small perturbation of the hydroxyl groups caused by the opening structure. In addition to the hydroxyl groups, amine grafting has been approved to improve the CO₂ capture significantly.^[47,48] Eli Stavitski and coworkers^[39] studied the N-H stretching of NH₂-MIL-53 using IR. They found the N-H stretching region was only slightly affected upon CO₂ exposure, which was in contrast to the previous published result.^[49] However, it should be considered of high importance for the overall performance of the adsorbents, since full regeneration might be achieved under very mild conditions.

Functionalization on organic linkers

Functionalization on the organic linkers with polar groups is another prospective method to provide extra adsorption sites for CO₂. After the perturbation of polar group linker Br and Cl, the perturbed δ (OH) at 890 cm⁻¹ was surprisingly identical to that of free MIL-53(Fe). Since only one perturbed OH component existed in the IR spectra, the researcher concluded there was no direct interaction between the polar groups and CO₂ in

those cases.^[50] Moreover, the retained N-H stretching frequency of NH₂-MIL-53 and the persisted δ (OH) of other functionalized MIL-53 implied that the polar groups tended generally to break the hydrogen bonds with the μ -OH instead of direct interacting with CO₂.

Figure 2 IR spectra of activated MIL-53(Cr) with increasing CO₂ pressure to (a) 1066 Pa, (b) 2400 Pa, (c) 3850 Pa, (d) 5000 Pa, e) 5850 Pa. Inset: perturbation of δ (OH) mode upon adsorption. Reprinted with permission from Ref. [38]. Copyright 2007 Royal Society of Chemistry.

Figure 3 Bottom (2D IR Map): a) Variation in the intensities of MIL-53LP (1017 cm⁻¹) and MIL-53HP (1022 cm⁻¹) bands and b) in the ν_2 CO₂ bands (653, 662 cm⁻¹ MIL-53LP; 659 cm⁻¹ MIL-53HP) versus CO₂ pressure. Top: hysteresis phenomenon observed during an adsorption-desorption cycle. Curves were obtained from the quantitative analysis of the corresponding IR spectra. Reprinted with permission from Ref. [46]. Copyright 2007 Wiley-VCH.

Figure 1 Three vibrational frequencies of four vibrational normal modes of CO₂. Reprinted with permission from Ref. [44]. Copyright 1992 Elsevier.

Open metal sites and metal centers

The direct coordination of metals to CO₂ was firstly reported on the open metal site of CPO-27, which was isostructural to MOF-74.^[51] The IR component at 2341 cm⁻¹ with a shoulder at 2329 cm⁻¹ significantly increased upon a progressive decreased CO₂ pressure, which corresponded to a perturbed ν_3 mode with formation of Ni²⁺...O=C=O adducts (Figure 4). Meanwhile, the ν_2 mode of CO₂ was also perturbed in the evidence of an intense doublet at 659 and 651 cm⁻¹. Similar perturbations on ν_2 and ν_3 modes were also noticeable in the series of M(II)-MOF-74 (M = Mg, Zn, Co, Ni).^[52] Interestingly, the open Zn centers had the strongest redshift influence on the ν_3 frequency, while the Mg center had almost no effect. In this case, it could be summarized that the interactions between the adsorbed CO₂ and the 3d electrons led to the different ν_3 frequency.

Figure 4 Spectra of CPO-27-Ni at decreasing CO₂ pressure. Inset: the CO₂ bending region. Reprinted with permission from Ref. [51]. Copyright 2008 Royal Society of Chemistry.

Raman scattering

In the same manner of IR absorption spectra, Raman scattering also provides detailed information on the bond breaking and formation during the adsorption process. Herein, we will discuss a typical case study for water adsorption. In the examination of moisture stability of a series of paddle wheel-based frameworks M(bdc)(ted)_{0.5} (M = Cu, Co, Ni, Zn; H₂bdc = 1,4-benzenedicarboxylate; ted = triethylenediamine), Chabal and coworkers^[53] noticed significant changes of two Raman bands (Figure 5). One Raman band was associated with the mixing of the lone pair of the nitrogen with the C-C of the organic linkers (ν_4), and the other band was associated with the metal-metal interaction in the paddle wheels. Although the activated MOFs all adopted the signature IR frequency bands, distinct Raman bands were observed upon hydration. The ν_4 band persisted in case of the Cu-, Co-, and Ni-based MOFs, while a redshift occurred in the Zn-based MOF due to the dissociation of nitrogen of the ted linkers from the Zn cluster. Furthermore, the metal-metal vibration was highly metal-dependent, as it persisted in the Ni-based MOF, vanished in the Zn-based MOF, combined to a single band with a new band at 268 cm⁻¹ in the Cu-based MOF, or completely disappeared in the Co-based MOF. All the Raman shifts provided direct evidence of the critical dependence of the moisture stability on the metal ions in this isostructural MOFs.

X-ray diffraction

Single Crystal X-ray Diffraction (SCXRD)

Among all the characterization methods in the sorption

study of MOFs, SCXRD can provide direct visualization of MOF-guest interactions.^[54] Early gas sorption studies using SCXRD focused on the structural changes and the phase transitions caused by the adsorbed gas molecules.^[36, 55-57] Kitagawa and coworkers^[58] reported the first observation of porous to nonporous phase transition of a flexible open framework. In their study, the 2D bilayer flexible open Cu-framework showed sponge-like dynamic behavior with bond breaking and formation triggered by hydration and dehydration. With the aid of structural determination by SCXRD, the gate-opening and gate-closing phenomenon could be directly evidenced and attributed to the MOF-guest interactions. Observations on phase transitions by SCXRD were also noted by the Moggach's group,^[59] the Takamizawa's group,^[60] and the Morries's group.^[61] The guest dependence of interaction sites were later studied in details by Wright and coworkers.^[62] The measurements of adsorption of CO₂, CH₄, and C₂H₆ on a microporous MOF, ScBDC, provided the proof of well-defined and gas-specific adsorption sites. Both CH₄ and C₂H₆ had similar adsorption sites in the framework channels, whereas the CO₂ molecules interacted with the aromatic H atom of the framework in an end-on fashion along with a cavity a formation as three phenyl rings of the ligands rotated close to CO₂.

Functionalization on the surface of MOFs has approved as a subject of increasing MOF-guest interaction sites.^[23, 63-67] Zhang and Chen^[68] reported *in situ* SCXRD studies on loading CO₂ into MAF-2 (MAF = metal azolate framework), a MOF of copper and 3,5-diehy-1,2,4-triazole. The SCXRD study revealed the CO₂ molecules were well embedded in the pocket

Figure 5 Raman spectra of activated MOF before and after hydration. Reprinted with permission from Ref. [53]. Copyright 2012 American Chemical Society.

with a distance of 3.41 Å, which were significantly larger than the van der Waals radii of CO₂ (3.25 Å), indicating the coordinated nitrogen atoms of MAF-2 served as an electronegative site (Figure 6). In another example of MAF-X7,^[69] partially coordination between triazolate nitrogen atoms and CO₂ was evident by a shorter distance between the carbon of CO₂ and the nitrogen of the triazolate linkers. Moreover, the CO₂ molecules were also directed towards the H⁺ cation through oxygen of DMF, and a weak hydrogen bond was formed between the pyridyl ring and a CO₂ molecule. Therefore, the cooperative effect of the partially uncoordinated nitrogen, the anionic framework, the cation inside the channel, and the suitable pore size/shape all contributed to the strong CO₂ binding in MAF-X7. Meanwhile, Shimizu and coworkers^[70] conducted X-ray diffraction experiments by loading CO₂ into [Zn₂(Atz)₂(ox)], a MOF constructed from amino-functionalized 1,2,4-triazoles (Atz), oxalate ligands, and Zn, at different temperatures. A loading of 1.2 CO₂ per MOF formula unit could be optimized, which was in agreement with the gravimetric adsorption measurements. SCXRD study revealed that two CO₂ molecules were crystallographically located inside the pore. The distance between the carbon of CO₂ molecules and the nitrogen atoms of the amino group was 3.151 Å, and the H atom of the amino group was out of the plane of the triazole (Figure 7). These two observations indicated the lone pair electrons of the nitrogen were responsible for CO₂ binding. Moreover, gas adsorption study on MAF-23 exhibited an even shorter N-C distance of 3.011 Å, and each of the two CO₂ molecules interacted simultaneously with a pair of uncoordinated N donor like a molecule claw.^[71] Therefore, a narrower N···N claw angle demonstrated a higher CO₂ affinity.

Powder X-Ray Diffraction (PXRD)

Observation of structural change

In MOF field, there are enormous reports investigating the relationship between structural change and gas adsorption from the *in situ* PXRD data.^[37,40,42,63,72-74] One of the novel isostructural series, MIL-53(M(III)), possesses a pressure-responsive behavior, which is termed “breathing”.^[75] This breathing phenomenon often occurs in the MOF materials possessing 1D or 2D metal moieties decorated on the structural tunnels. Férey’s group had crystallographically studied the framework response *in situ* by synchrotron PXRD. It was found that anhydrous MIL-53(Cr) possesses a reversible cycling property upon CO₂ addition ranging from 0 to 10 bar (Figure 8).^[46] The tunnel structure adopted the low-pressure form (MIL-53LP) below 4 bar, then it transformed to the high-pressure form (MIL-53HP) above 5 bar. The high-pressure form could further be converted to the low-pressure version upon CO₂ exhaust with a hysteresis. This structural evolution upon CO₂ loading resolved by PXRD analysis gave a visualized image of the breathing effect. Further *in situ* PXRD studies on MIL-53 with various metal clusters (Fe, Cr, Al)^[76] and different functional groups (-Cl, -Br, -CH₃) were thoroughly investigated with various hydrocarbon adsorbates.^[77,78]

Zhou’s group^[79] published an interesting stimuli-responsive MOF, PCN-123, which possessed reversible alteration of guest molecule adsorption upon photo irradiation or thermal treatment. The working principle was to introduce a photo-sensitive functional group, azo-phenyl ring, into the organic linkers of PCN-123. As azo-phenyl rings can switch its conformations from *trans*-isomer to *cis* by external stimulation, the resulting MOF is able to present structural change. In order to experimentally observe the structural change, envelope analysis method was applied through PXRD experiments.^[80-82] As shown in Figure 9 (Middle), the electron density difference ex-

Figure 6 A CO₂ molecule trapped inside the pocket (a) and six molecules collected in the cage (b) of MAF-2. Reprinted with permission from Ref. [68]. Copyright 2009 American Chemical Society.

Figure 7 CO₂ molecular binding with Zn₂(Atz)₂(ox) at 173 K. Reprinted with permission from Ref. [70]. Copyright 2010 American Association for the Advancement of Science.

tracted from PXRD data corresponded to the orientation of azo-benzene groups. Before UV irradiation, it showed less electron density around the metal clusters but more nearby the ligands in the *trans*-isomer. In contrast, electron density around metal clusters was increased after UV irradiation. It experimentally demonstrated the flip response of azo-benzene groups with photo/heat stimulation. Besides, it could be seen that the space for CO₂ molecules to adsorb was affected by the steric hindrance caused by azo-benzene groups. As a result, different amounts of CO₂ molecules could be controlled by the *trans/cis* isomerization, as experimentally observed by the PXRD analysis.

Figure 8 Left: *In situ* powder XRD patterns of MIL-53(Cr) collected under various pressures of CO₂ at 293 K. Right: The corresponding structural changes with CO₂ pressures. Reprinted with permission from Ref. [46]. Copyright 2007 Wiley-VCH.

Figure 9 Top: Trans-cis isomerization of the ligand of PCN-123 induced by UV irradiation and thermal treatment reversibly. Middle: The electron density differences of PCN-123 generated from *in situ* powder XRD analysis. Bottom: Simulated CO₂ uptake was illustrated in PCN-123-*trans* and PCN-123-*cis*. Reprinted with permission from Ref. [79]. Copyright 2011 American Chemical Society.

Neutron diffraction

Neutron diffraction and X-ray diffraction differ in the way to be scattered by matters but are similar in the analytical techniques. Neutrons interact with atomic nuclei, while X-rays disturb the electron clouds of the samples. It has been understood that X-ray produces stronger interference signals when hitting atoms possessing larger electron numbers. As compared with cross sections of X-ray scattering, which is proportional to Z^2 (Z = atomic number), those of neutron scattering show little systematic tendency with Z . Moreover, neutron diffraction distinguish one element from another, and more precisely, from one isotope of an element to another as well.^[83]

As complementary methods, X-ray diffraction and neutron diffraction have different sensitivities for different elements. It

has been approved that neutron diffraction is an irreplaceable tool for scientists to analyze H₂ adsorption sites in the MOFs. The nuclei ¹H and ²H are more detectable by neutron diffraction, as they are stronger scatterers for neutrons. Therefore, neutron diffraction studies have been desirable to obtain accurate positions of H₂, which is typically impossible using X-ray diffraction. The H atoms possess large incoherent scattering cross section in neutron diffraction experiments, as caused knotty difficulties in positional identification, deuterium (D₂) has been a substituent instead.^[63]

Single crystal neutron diffraction (SCND)

The first study to elucidate the hydrogen adsorption sites using single crystal neutron diffraction was reported by Spencer and coworkers.^[84] The adsorption sites were determined according to the neutron Laue data collected on MOF-5 at 120, 50, 30, and 5 K. The α -sites were found over the shared vertex of ZnO₄ units, which were fully occupied under 50, 30, and 5 K (Figure 10). Another adsorption site was located on a site of 3m symmetry over the face of a ZnO₄ tetrahedron at 5 K.

Figure 10 (a) The location of the hydrogen absorption sites at 5 K relative to the framework atoms. (b) Space-filling diagram of one of the framework cavities at 5 K. Reprinted with permission from Ref. [84]. Copyright 2006 the Royal Society of Chemistry.

Powder neutron diffraction (PND)

Positional identification of H₂/D₂

Peterson and Kepert *et al.*^[85,86] reported six stable D₂ adsorption sites in HKUST (Figure 11). They designed this *in situ* PND experiments by loading various volumes of D₂ into a capillary line packed with HKUST-1 at 77 K and then collected the PND patterns. Fourier analyses revealed that the H₂ molecules initially preferred site D₂ (1), which was located at the unsaturated axial sites of the Cu paddle wheels, and then occupied D₂ (2) and D₂ (6) (top panel of Figure 11). It gave direct evidence that the Coulomb-type electrostatic interactions between the exposed metal sites and D₂ played a key role in the overall storage. Other adsorption sites were sequentially occupied with the pores size from the smallest to the largest. Remarkably, it followed concentration-dependent arrangements, which were competitively determined by D₂-D₂ and D₂-framework interactions (bottom panel of Figure 11).

NIST (National Institute for Standards and Technology Center for Neutron Research) had also made endeavors on a special phenomenon of hydrogen storage in MOF-5 and ZIF-8.^[87,88] Six adsorption sites were obtained from the Fourier difference analyses after Rietveld refinements in ZIF-8, while four sites were found in MOF-5 in a similar manner (Figure 12). Interestingly, it revealed that the adjacent D₂ molecules were apart with a distance of 3.0 Å under low temperature and high concentration, constructing interlinked molecular nanocages. Different D₂ nanocages could be formed with distinguishable topologies by varying the D₂ loadings (Figure 13). It suggested that MOF lattices could be used as a template to build artificial

Figure 11 D₂ sites in HKUST-1: site 1 is the axial Cu sites; site 2, 3, 5 viewed along [111] in the small octahedral pores; site 4, 6 viewed along [100] in the large cuboctahedral cages. Reprinted with permission from Ref. [85, 86]. Copyright 2006 and 2011 American Chemical Society.

Figure 12 The real-space Fourier-difference scattering-length density superimposed with (left) the MOF-5 and (right) ZIF-8 structures. Reprinted with permission from Ref. [87, 88]. Copyright 2005 American Physical Society and 2007 American Chemical Society.

Figure 13 Different D₂ nanocages in MOF-5 (blue and green spheres) obtained at (a) 34 and (b) 46 D₂ per unit loading, respectively. Reprinted with permission from Ref. [87]. Copyright 2005 American Physical Society.

hydrogen nanoclusters, which might possess unique quantum natures and confinement effects.^[87] As a future perspective, it points out a direction for this important theoretical research.

Positional identification of guest molecules

Synchrotron-based or neutron-based powder diffraction is widely used for probing the favored locations of various guest molecules, including CH₄, CO₂ and noble gases.^[67,89] In this type of research, structure details can be determined by X-ray and/or neutron diffraction data, which could potentially elucidate the fundamental understanding of the adsorption mechanisms and reveal a direction towards advanced MOF designs.^[15] For instance, Wu and colleagues^[90–92] determined the CH₄ binding sites or several prototypical MOFs. It was found that CH₄ adsorption was initiated from the coulomb interactions with coordinately unsaturated metals and multiple vdW interactions with open metal sites, window openings, cage centers and cage corner sites. Bases on this study, it can be found that the accessibility and compatibility of pore volume for different guest molecules are favorable structural features for methane storage. The Hulvey's investigation of noble gases (Xe, Kr, Ar, Ne) adsorption in HKUST-1 gave a parallel conclusion that dominant binding sites are located in and around the small tetrahedral cages instead of the open Cu(II) sites (Figure 14).^[93] Similar effects using the Fourier technique have been applied to other gases.^[72,92,94,95]

Figure 14 Adsorption sites for (a)Xe (orange atoms) and (b)Ar (green atoms) in HKUST-1 using analysis through synchrotron X-ray and neutron powder diffraction. Reprinted with permission from Ref. [93]. Copyright 2013 American Chemical Society.

X-ray spectroscopy

As we discussed before, X-rays hit a crystalline sample, it can produce stronger interference signals that uncover structure information of the crystal. In fact, part of X-rays could simultaneously be absorbed and disturb the electronic structure of crystalline materials (including MOF), which can provide direct observation of changes occurring in the crystals at the molecular orbital level. For example, one *in situ* measurement at the Mg K-edge of Mg-MOF-74 using X-ray spectroscopy demonstrated distinct pre-edge absorption features associated with the unique and open Mg coordination in Mg-MOF-74.^[96] The mixing of Mg 3p and 3s characters resulted in a strong pre-edge absorption peak for the activated Mg-MOF-74 (Figure 15). However, this signature feature disappeared in the pres-

ence of CO₂, which was the proof of coordination of CO₂ to the open metal sites. Moreover, a blue shift of the pre-edge peak with an increased intensity was noted after introducing CO₂ to Mg-MOF-74.

Figure 15 (a) Mg K-edge spectra of Mg-MOF-74 under vacuum, with increasing gas pressure. (b) Difference spectra generated by subtracting the initial vacuum spectrum from all subsequent spectra. Reprinted with permission from Ref. [96]. Copyright 2013 American Chemical Society.

Computation simulations

Experimentally, it would be difficult and time-consuming to address detailed information, which could be critical to the macroscopic properties that underlying adsorption mechanisms in MOFs. Molecular modeling, by comparison, may provide a valuable complement to experimental studies.^[97] During the past decades, great efforts have been made to apply all kinds of computational approaches to investigate properties of MOFs, such as quantum chemistry calculation and molecular simulation.^[98–115] Furthermore, several advanced methodologies with respect to this class of novel porous materials, have been developed.^[116–118] All these information can help to obtain a deeper and more thorough understanding of the features of MOFs. For adsorption, the main contributions of computational studies are determining adsorption sites and revealing adsorption mechanisms in general.^[119,120]

Determination of adsorption sites

Hydrogen storage

Hydrogen storage is one of the earliest research topics in MOFs area.^[3,121,122] In 2004, Sagara and coworkers^[123] investigated the binding energy of H₂ in MOF-5 using quantum chemistry calculations for the first time. Then, Zhong and Yang^[124] performed systematic molecular simulations, including Grand Canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations, on the adsorption and diffusion of H₂ in IRMOFs in 2005. The results indicated that metal-oxygen clusters are preferential adsorption sites for H₂, and with the increase of pressure the effect of the organic linkers becomes evident. On the basis of these information about adsorption

sites, Zhong and Yang^[125] further studied the adsorption of H₂ in MOFs using a combined GCMC simulation and density functional theory (DFT) calculation. Several locations and orientations of H₂ within MOFs were tested around Cu₂(CO₂)₄ unit in MOF-505,^[126] and the strongest adsorption configuration is observed to locate in the direction of open metal sites, as shown in Figure 16. H₂ molecule is inclined to expose the negative lobe of its quadrupole to the Cu atom. In addition, they further examined the snapshots of the structures of MOF-505 with adsorbed H₂ at various pressures. Typical ones shown in Figure 17 illustrated that the sequence of H₂ adsorption is as follows: firstly, H₂ molecules occupy the center regions of the smaller pores, which formed by six inorganic Cu₂(CO₂)₄ units (Figure 17a); then, they begin to be adsorbed at the corners of the larger pores with the increase of pressure (Figure 17b); H₂ molecules finally are adsorbed mainly around the organic units with further increasing pressure (Figure 17c).

Figure 16 Close-up view of the DFT calculated configurations of an adsorbed molecule around the inorganic Cu₂(CO₂)₄ unit in MOF-505. Reprinted with permission from Ref. [125]. Copyright 2006 American Chemical Society.

Methane storage

Motivated by energy applications, for example, natural gas vehicles, methane adsorption in MOFs have received substantial attention.^[3,15,127–129] Zhong and Wang^[130] studied the adsorption sites, conformation and the adsorption energies of CH₄ in MOF-5 using DFT calculations. Through a systematic structure optimization, the Zn₄O clusters are identified as the preferential adsorption sites (I, II position in Figure 18), and O-Zn narrow area (I position in Figure 18) shows the largest adsorption energy for CH₄. Herein, C-H bond in CH₄ molecule is in the position of pointing to O atom in the framework. Zhou and coworkers^[92] investigated CH₄ adsorption sites in several typical MOFs by performing GCMC simulations in combination with DFT calculation as well as neutron powder diffraction (NPD) method. For example, in HKUST-1, the window site of the small octahedral cage is considered as another primary CH₄ adsorption site, besides the open metal site as conventionally known. The distance between an adsorbed CH₄ molecule and O atoms in framework is in the range of 2.7–3.2 Å, inducing strong interaction of CH₄ around these window sites. In PCN-11, it is found that the large cage corner sites also provide major adsorption sites and contribute significantly to a remarkable total CH₄ uptake of 194 cm³ (STP) cm⁻³ at 298 K and 35 bar.

Carbon dioxide capture

Compared to H₂ and CH₄, the adsorption of carbon dioxide molecules in MOFs is more complicated due to their quadrupole moments.^[97] By analyzing the center of mass (COM)

Figure 17 Snapshots of the structures of MOF-505 with adsorbed H_2 at various pressures. Reprinted with permission from Ref. [125]. Copyright 2006 American Chemical Society.

Figure 18 The adsorption sites of CH_4 near the Zn_4O cluster: (I) O-Zn narrow area and (II): O-Zn wide area. Reprinted with permission from ref.[130]. Copyright 2006 Chinese Chemical Society.

probability distributions of CO_2 extracted from GCMC simulations carefully, Zhong and coworkers^[131] believed the preferential adsorption sites of CO_2 in chemical Li-modified MOF-5 (chem-2Li) was different from those in the original material as well as the physical Li-modified one (phys-2Li), attributed mainly to the stronger charge-quadrupole interaction. The statistical results from simulation illustrate that CO_2 molecules tend to bridge between two ligands instead of pointing to the metal clusters in phys-2Li. While in chem-2Li the CO_2 molecules are not parallel to the O-Li dipoles, the most probable distribution of the angle is about 45° .

Adsorption mechanism

More recently, considerable efforts have been made to explore the adsorption mechanism fully utilizing the irreplaceable advantage of computational methods. Classical simulations with quadratic Feynman-Hibbs (FH) effective potential indicated that quantum effect plays a significant effect on the H_2 adsorption especially at low temperature, due to their unique characters.^[132-134] On the basis of this effect, quantum sieving can be used to separate the hydrogen isotope mixtures efficiently, which takes place on the condition that the difference between molecular size and pore size becomes comparable to the de Broglie wavelengths of hydrogen. The difference in the zero point energy (ZPE) induces that heavier isotopes are confined less than lighter ones in the pore.^[135] With the aid of various computational tools, it can be predicted that MOFs are suitable candidates for the separation of hydrogen isotopes through quantum sieving, including path integral Monte Carlo,^[136] proposed novel concept like “quantum effective pore size” (QEPS).^[137] This has been verified by recent direct measurement in experiment.^[138] MOF-74,^[139] as one of benchmark MOFs with a high density of open metal sites, has received special attention because of their fast and specific CO_2 adsorption. Several groups focused on performing calculations to provide insights into the nature of the strong binding of CO_2 with the framework and try to understand the adsorption mechanisms, which are critical for the rational design of improved MOFs.^[140-142] Thonhauser and coworkers^[117] incorporated van der Waals forces self-consistently in DFT in the form of a van der Waals density functional (vdW-DF) to analyze CO_2 adsorption in MOF-74. The calculation results indicate fully occupied semi-core 3d electrons in Zn have a significant effect on the interaction with the adsorbed CO_2 molecules. Furthermore, it is found that there is a depletion of electrons around Zn atom upon adsorbed CO_2 , while this depletion was not existed for Mg-MOF-74, by applying a charge-density analysis. The depletion of charge is an effect of the Zn d orbitals that also affects the charge distribution in the adsorbed CO_2 molecules. This can be used to explain computational and experimental findings that the binding energy of CO_2 molecule in Mg-MOF-74 is larger than that in Zn-MOF-74.^[52] Jung and coworkers^[141] performed a series of quantum chemistry calculations and predicted that Ti- and V-MOF-74 should have an enhanced affinity of CO_2 compared to Mg-MOF-74, which may be attributed to the formation of additional weak coordination bonds with CO_2 through forward donation. Smit, Gagliardi, and coworkers^[143] characterized the reactive adsorption of CO_2 in the amine-functionalized $\text{Mg}_2(\text{dobpdc})$ by quantum-chemical calculations. It is believed that there is the formation of a hydrogen-bonded complex involving two carbamic acid moieties during the adsorption process, and the proposed mechanism is as shown in Figure 19.

Comprehensive kinetic studies in gas sorption

Kinetic studies of gas adsorption process can reveal molecular transport/diffusion behaviors inside porous materials, thus help to guide the design of new materials targeting for certain gas storage or separation applications.^[144-146] To date, research regarding this topic is still relatively rare, presumably due to the difficulties in observing the transport behaviors of gas molecules with traditional characterization techniques.

In the research of MOFs for methane storage applications, Lucena and coworkers^[147] reported firstly a “methane transport” phenomenon in PCN-14. The simulations showed that there was no energy barrier between weak and strong adsorption sites, suggesting the methane molecules are guided from open

Figure 19 The proposed mechanism of CO₂ adsorption in an alkylamine-functionalized Mg₂(dobpdc). (left) First CO₂ uptake; (right) second CO₂ uptake. Reprinted with permission from Ref. [143]. Copyright 2013 American Chemical Society.

metal sites to other adjacent adsorption sites inside this MOF (Figure 20). This kinetic transport phenomenon of methane molecules inside PCN-14 is very interesting, but it was only confirmed by computational studies in their work. In 2015, the Zhou group^[148] did a systematic study on methane storage in several MOFs and discovered similar kinetic behaviors of methane molecules inside these MOFs. Combining three tools: experimental observations, simulations and *in situ* PXRD technique, they studied gas dynamics and the distribution of guest molecules under various conditions in MOFs. In this study, *in situ* PXRD characterization technique was utilized to study the kinetic behaviors of gas molecules in MOFs for the first time. Using synchrotron radiation source, the PXRD patterns of MOFs loaded with methane were measured, respectively. The electron density distribution was then obtained from a few reflection peaks in the diffraction pattern of both samples. Structure envelop surface can be generated from the electron density distribution information.^[81,82,149,150] Comparison of the structure envelope surfaces in the activated and methane loaded MOFs gives the information of adsorption sites inside the MOFs. By measuring the *in situ* PXRD of MOFs at different temperatures, they confirmed experimentally the “methane migration” mechanism, which is the methane molecules migrate from open metal sites to “window” structure in the adsorption process. Essentially, *in situ* PXRD detects the electron density difference in activated sample and gas loaded sample at a certain temperature or time. Using this method to detect the gas adsorption sites at different temperatures or time gives insight into the kinetic information in gas adsorption process (Figure 21).

Combining simulation and *in situ* characterization, Canepa and coworkers^[140] studied the transport mechanism of small molecules in Mg-MOF-74. Simulation was firstly employed to predict the diffusion behaviors of gas molecules in the MOF. Instead of *in situ* PXRD, they used time-resolved *in situ* IR, which measures the changes in asymmetric modes of gas molecules. The asymmetric stretch modes of CO₂ and H₂O, which was obtained from *in situ* IR spectroscopy, indicate two consecutive steps involved in a typical gas loading process of Mg-MOF-74. The gas molecules were firstly adsorbed in nanopores on the surface of the MOF, resulting in a very high loading in those nanopores thus limiting diffusion of more approaching molecules. The increasing lateral interactions between adsorbed molecules could lead to a redshift, which was observed from *in situ* IR. As time progresses, the *in situ* IR showed a blueshift indicating the asymmetric modes went back to its original location. Accordingly, this change indicated the diffusion of the gas molecules from high-loaded pores to low-

Figure 20 (a) Contour plot of the calculated potential energy of methane molecules in the xz plane that goes from the copper atoms of a $\text{Cu}_2(\text{CO})_4$ cluster, crossing the center of the basket partial structure. $\varepsilon_{\text{Cu}} = 0.006$ kcal/mol. (b) Contour plot of the potential energy for $\varepsilon_{\text{Cu}} = 3.81$ kcal/mol. Reprinted with the permission from Ref. [147]. Copyright 2011 American Chemical Society.

Figure 21 DED snapshots illustrate the evolution of CH₄ equilibrium states in PCN-306. The CH₄-loaded crystals were diffracted at (a) 295K, (b) 200 K, and (c) 150 K. The right-side images, viewed along the a-axis. Reprinted with the permission from Ref. [148]. Copyright 2015 American Chemical Society.

loading pores that located further inside the MOF. The frequency shifts in *in situ* IR was a direct evidence of the two-stage mechanism in the gas diffusion process. More of such typical studies could be found in the review paper by Thonhauser and coworkers.^[117]

Conclusions

Gas storage and separations, including methane, carbon dioxide and hydrogen, are very important for people's existence

and development. The discovery of materials with high gas storage capacity or outstanding separation capacity has been a hot and challenging topic.^[151,152] As a kind of typical porous material, MOFs, one of the candidates for gas storage and separations, catch people's eyes.^[153,154] However, when it comes down to the real application, the investigation of MOFs as potential sorbents for gas storage presents significant challenges from raw to ready. Therefore, a prospective approach to address this difference is to establish the adsorption process with various methods simultaneously and cooperatively. Fortunately, the aforementioned studies have demonstrated the convenience and precision in determining the adsorption sites and showcase the importance of the metal units, organic linkers, the pore size, and the gas molecule itself with the help of different characterization methods. Integration of the knowledge gained from those methods will certainly promote an insight about the gas sorption process and definitely be tailored to the design of new generation of MOFs. In brief, we believe that a successful implementation in the application of MOFs as gas sorbents lies heavily on the understanding of routine gas sorption process, and such studies will continue to not only make contributions to the application of MOFs but also drive the development of individual technologies to new frontiers.

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Author Contributions

† X.-J. H. and X. W. contributed equally to this work.

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