▊ **Metal-organic frameworks** |*Hot Paper*|

Cooperative Adsorption by Porous Frameworks: Diffraction Experiment and Phenomenological Theory

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Abstract: Materials science of metal open frameworks is a state-of-the-art field for numerous applications, such as gas storage, sensors, and medicine. Two nanoporous frameworks, γ-Mg(BH$_4$)$_2$ and MIL-91(Ti), with different levels of structural flexibility, were examined with in situ X-ray diffraction guest adsorption–desorption experiments. Both frameworks exhibit a cooperative guest adsorption correlated with a lattice deformation. This cooperativity originates from the long-range interactions between guest molecules, mediated by elastic response of the host porous structure. The observed experimental scenarios are rationalized with a mean field Gorsky–Bragg–Williams (GBW) approach for the lattice-gas Ising model. The adjusted GBW model, in combination with in situ synchrotron powder diffraction, demonstrates an efficient experimental and phenomenological approach to characterize thermodynamics of the adsorption in MOFs not only for the total uptake but also for every specific guest site.

Introduction

Cooperativity is an intriguing phenomenon manifesting itself as a collective response of many (weakly) bound entities on the external stimuli.[1–3] If a response to external stimulus starts locally, its propagation through the system is affected by interactions of the responding units. An example of a cooperative process is given by a spin crossover in molecular crystals, where a local change of the spin state in a spin-active molecule may promote or suppress a similar change in the neighboring unit cells;[4,5] a binding of oxygen to hemoglobin is another archetypal example of cooperativity at a supramolecular level.[6] In the case of spin-crossover, the cooperative response is promoted by long-range intermolecular interactions, while the binding of oxygen to hemoglobin represents an intramolecular cooperativity.

Porous frameworks[7–9] is a blossoming field of research due to a versatile chemistry and great potential for selective adsorption, separation, and storage of guest molecules of interest.[10–12] Their selective properties are predominantly a function of local host-guest binding, however the adsorption also manifests in long-range effects such as a volume change and breathing deformations.[13] Elastic response may mediate correlation of the guest uptake between distant pores and therefore provides inter-pore "interactions" and a cooperativity of the adsorption process; this kind of cooperative response is quite different from an "intra-pore" interaction between guest molecules where the latter form a liquid phase filing empty pores of otherwise rigid host structure. Cooperativity has been observed quite a few times for the gas/molecule adsorption in the recently explored porous frameworks but a systematic experimental examination of this phenomenon together with a theoretical analysis accounting for the host-mediated guest-guest interactions is still missing.

The abrupt response to a tiny external stimulus, promoted by cooperativity, is of a great interest for practical applications. This effect can be used for sensing, switching, and even memory-related applications. A combination of the compositional and structural affluence of porous frameworks, such as MOFs (metal-organic frameworks), with cooperativity, could be a powerful tool for a flexible design of materials with tailored magnetic and dielectric properties, thus expanding potential applications of MOFs far beyond gas storage and separation. There are numerous observations of continuous or step-wise framework deformation conjugated with selectivity of gas adsorption, also linked to polar or non-polar character of the adsorbed molecules.[14] Such collective phenomena clearly indicate that selectivity might depend on cooperative interactions mediated by the framework. A coherent understanding should

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be therefore based on a cooperative thermodynamics of guest uptake in MOFs; this thermodynamics however is still to be formulated.

As a step towards understanding of cooperative phenomena, here we examine with in situ diffraction experiment two nanoporous frameworks, γ-Mg(BH$_4$)$_2$[15] and MIL-91(Ti) (MIL for Materials of the Institute Lavoisier),[16,17] with different levels of structural flexibility and cooperativity of guest adsorption. We parameterize cooperative response with a mean field Gorsky–Bragg–Williams (GBW) approach for the lattice-gas Ising model.[18–20] The adjusted GBW model, in combination with in situ synchrotron powder diffraction, demonstrates an efficient experimental and phenomenological approach to characterize thermodynamics of the adsorption in porous frameworks with a site-specific resolution. A further development of the proposed approach accounting for a distribution of the site-specific thermodynamics parameters and intra-pore guest-guest interactions is also discussed.

Results and Discussion

The results will be presented in three stages. First, we show the necessary experimental information on the structural evolution for two different porous frameworks. Second, the model intended to rationalize experimental observations is derived. Finally, we compare the experimental data with the theoretical

model and give the thermodynamic estimates based on the model.

The crystal structures of two studied porous frameworks have been reported before;[14,15] in this work we give the basic structural information necessary for further understanding. The crystal structures of two microporous materials of γ-Mg(BH$_4$)$_2$ and MIL-91(Ti) are shown in Figure 1, where guests in the pores are indicated as colored spheres. The framework topology of γ-Mg(BH$_4$)$_2$ is isomorphous to a porous zinc imidazolate framework ZIF-72,[21] and MIL-91(Ti), which belongs to Ti piperazine bisphosphonate materials with narrow pores containing free-standing P—OH terminal bonds, is found to be monoclinic, similar to its first reported MIL 91(Al) analogue.[15] Our trial to transform the experimental structure of MIL-91(Ti) in accordance with the recently revised ordered triclinic structure of MIL-91(Al)[22] did not succeed. The ADDSYMM routine from PLATON suggested the previously known $C2/m$ symmetry (86%).[23] The empty voids of γ-Mg(BH$_4$)$_2$ are located in the hexagonal channels along the body diagonal in the cubic structure (Figure 1a), while MIL-91(Ti) is characterized by four different water sites (the spheres are depicted by different colors), where the packing of piperazine organic ligands show main porosity along the b axis (Figure 1b). Thus, there is only one crystallographic pore site in γ-Mg(BH$_4$)$_2$, while the water molecules occupy four independent sites in MIL-91(Ti) (see Figures 1 and 2 for the nomenclature of the guest sites).

No polymorphic transitions associated with change of symmetry have been detected in the 100–450 K temperature range for both compounds. The temperature dependent
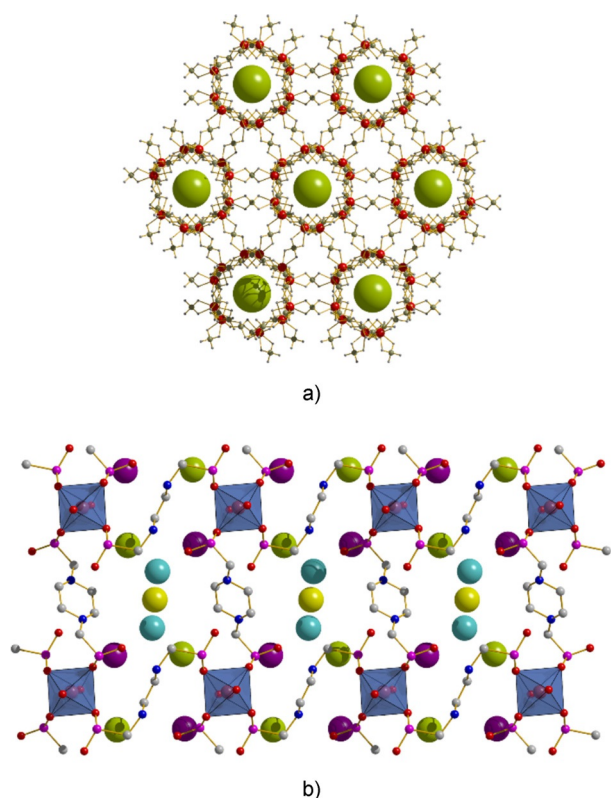

a)

b)

Figure 1. The projections of γ-Mg(BH$_4$)$_2$ (a) and MIL-91(Ti) (b) crystal structures along [1 1 1] and [0 1 0], respectively. The vacant sites are shown as lime spheres in γ-Mg(BH$_4$)$_2$, and the large yellow (O102), lime (O100), aqua (O101), and violet (O103) spheres correspond in MIL-91(Ti) show sites occupied by guest molecules.
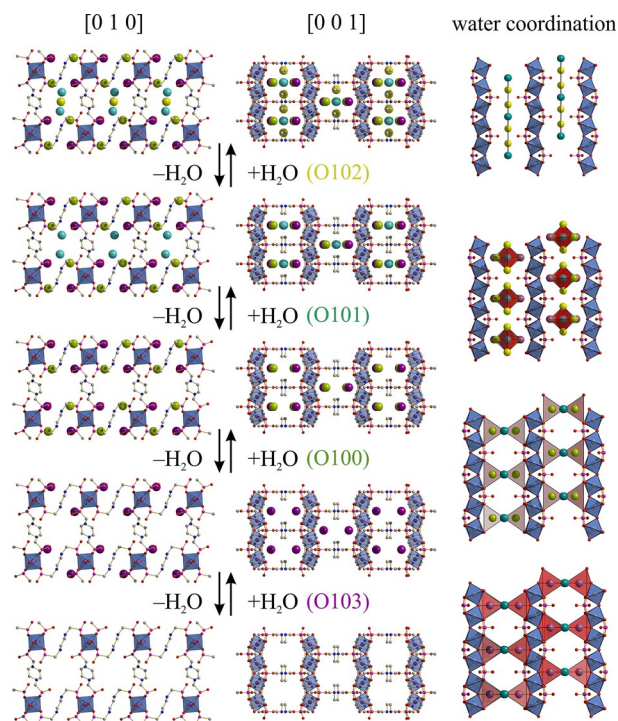

Figure 2. The nomenclature of water occupied guest sites for MIL-91(Ti). The coordination polyhedra of water molecules (spheres depicted by yellow, teal, olive, and violet) are shown in the right column. Color code of the framework atoms: O—red; N—blue, C—grey, P—pink.

evolution of the crystal structures (the unit cell parameters and occupancies of guest sites) are presented in Figures 4 (also in Figure S3 in the Supporting Information) and 5. A characteristic sigmoidal shape is observed for N_2 and ethane in γ-Mg(BH$_4$)$_2$, while a hysteresis behavior is found for three out of four sites for H$_2$O in MIL-91(Ti). A similar response is found for unit cell dimensions indicating a link between occupancies and elastic deformation.

Theoretical model

We propose to parametrize guest adsorption together with observed structural changes with a mean field Gorsky–Bragg–Williams approach for the lattice-gas Ising model. For this model, a filled or empty guest site can be considered as an example of a two level system with energy difference between the levels $2\Delta = E_{full} - E_{empty}$. The state of a guest site can be characterized with a scalar pseudospin variable σ that is set to $+1$ if the site is occupied by a guest molecule, or to -1 if the site is empty. A generic guest-host system can be therefore reduced to a system of interacting bi-stable units. A convenient way to model collective effects in such a system is an Ising-like Hamiltonian [Eq. (1)]:

$$H = \sum_j \sum_i \Delta_i \sigma_{ij} + \sum_i \sum_{i'} \sum_j \sum_{j'} J_{ii'jj'} \sigma_{ij} \sigma_{i'j'} \quad (1)$$

Here, we assign to a guest site i in unit cell j a variable σ_{ij}. The first term in the Hamiltonian sums up the single-site energies while the second term accounts for the interactions between guest sites i and i' located in unit cells j and j'. $J_{ii'jj'}$ is a coupling constant for the corresponding interaction, which is somehow mediated by the flexible porous host framework and its exact microscopic nature is not relevant for this phenomenology.

The Hamiltonian [Eq. (1)] maps adsorption of guest molecules by porous solid to a lattice-gas model and resembles very similar models for spin-crossover phenomena.[24] For the sake of simplicity we neglect intermolecular interactions between the guest molecules within the same pore and interactions between different sites in different pores keeping only same site–different pore terms. Under such an assumption different guest sites can be considered separately. In the mean-field approximation Gibbs free energy is expressed as following [Eq. (2)–(3)]:

$$\Delta G_{tot} \approx \sum_i \Delta G_i \quad (2)$$

$$\Delta G_i = -(\Delta H_i - T\Delta S_i)\gamma_i - TS_{mix} - \Gamma(1 - \gamma_i)\gamma_i \quad (3)$$

Here γ_i is a fraction of the adsorbed guest molecules at the crystallographic site i, $\gamma_i = \frac{1 + \langle \sigma_i \rangle}{2}$. The values of ΔH_i and ΔS_i denote enthalpy and entropy associated with guest adsorption by the site i. S_{mix} is a configurational (mixing) entropy [Eq. (4)]:

$$S_{mix} \approx R[\gamma_i ln\gamma_i + (1 - \gamma_i)ln(1 - \gamma_i)] \quad (4)$$

The sum of enthalpies calculated from occupancies for crystallographically independent guest sites may serve as an estimate for the isosteric heat of adsorption neglecting its dependence on the amount of adsorbate.

The last term in [Eq. (3)] accounts for cooperative interactions between guest molecules, in the next neighbor approximation $\Gamma_i \propto zJ_i$, where z is a number of nearest neighbors. From the equilibrium condition $\frac{\partial \Delta G}{\partial \gamma} = 0$ one derives the following useful expression [Eq. (5)]:

$$T = \frac{\Delta H_i - \Gamma_i(1 - 2\gamma_i)}{\Delta S_i - Rln(\frac{1-\gamma_i}{\gamma_i})} \quad (5)$$

According to this expression, the temperature of a half-filled state gives an estimate of the ratio between entropy and enthalpy [Eq. (6)]:

$$T_{1/2_i} = \frac{\Delta H_i}{\Delta S_i} \quad (6)$$

A few possible scenarios of cooperative adsorption/desorption with different degrees of cooperativity Γ_i can be observed, see Figure 3. Depending on the Γ_i value versus a critical $\Gamma_c = \frac{2R\Delta H}{\Delta S} = 2RT_{1/2}$, the cooperativity is negligible for $\Gamma_i < \Gamma_c$, low if $\Gamma_i \approx \Gamma_c$ and strong if $\Gamma_i > \Gamma_c$ (Figure 3).
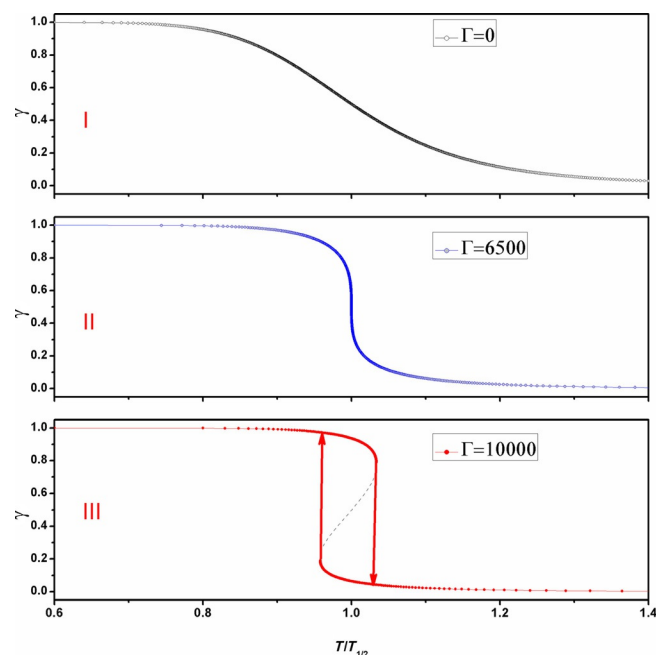

Figure 3. The shapes of the adsorption/desorption curves for $T_{1/2} = 400$ K, depending on different Γ values: $\Gamma < \Gamma_c$ (I), $\Gamma = \Gamma_c$ (II), and $\Gamma_c > \Gamma_c$ (III).

Model versus experiment

Experimental scenarios of nitrogen and ethane adsorption by γ-Mg(BH$_4$)$_2$, together with water uptake by MIL-91(Ti), are shown in Figures 4 and 5. The transition curves have been par-
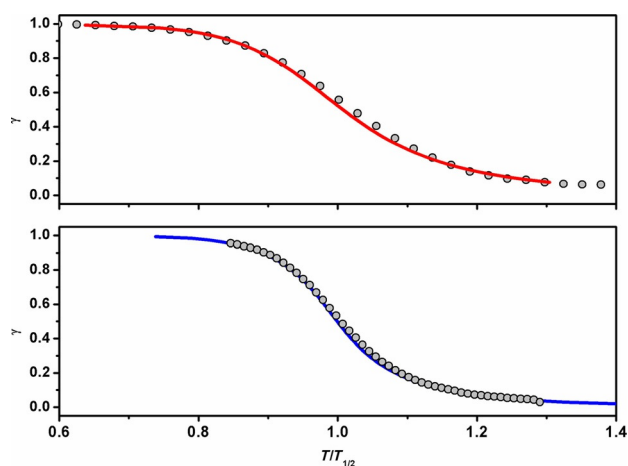
Figure 4. The occupancies of adsorbed nitrogen (red) and ethane (blue) in γ-Mg(BH$_4$)$_2$ (at 0.3 and 0.5 bar, respectively). The solid lines represent the fit with Equation (5), where the calculated $T_{1/2}$ for nitrogen and ethane adsorption are 148 and 264 K, respectively.

ameterized in accordance with Equation (5) and their corresponding parameters are given in Table 1.

The thermodynamic parameters (enthalpy, entropy, and cooperativity parameter) for γ-Mg(BH$_4$)$_2$ can be readily calculated from the synchrotron powder diffraction data with a least-squares fitting procedure (see Figures S1 and S2 in Supporting Information). The GBW model satisfactory maps both cases for nitrogen and ethane adsorption to a gradual crossover between empty and full states. The refined cooperativity parameter for nitrogen is nearly 0 (within 2 standard deviations), and therefore scenario I is realized (see Figure 4). The uptake of ethane shows a certain cooperativity, which is, however, below a critical value; this scenario is somewhat in between the cases I and II.

Water uptake in MIL-91(Ti) serves as an example of scenario number III—a highly cooperative process with a temperature hysteresis; Figure 5. Interestingly, all four water sites show different thermodynamics and one of them also distinctly different cooperativity. In contrast to γ-Mg(BH$_4$)$_2$ with a single guest void, water molecules in MIL-91(Ti) adopt different crystallographic sites and different coordination; Figure 2. Therefore, water molecules, which occupy different sites, perturb the framework in a different manner and their binding energies are not expected to be identical. While average occupancy for water molecules is fully reproducible, a certain irreproducibility is noted the unit cell dimensions ($\approx 2\%$ unit cell volume deviation). The structural mechanism of such small difference is difficult to see, but this difference can be explained by elastic response on a redistribution of water molecules within the framework. In spite of the fact that a special care was taken to minimize the kinetic effects (minimal volume of the sample, waiting between data acquisition for a semi-stationary state), the cooperativity parameter still may be overestimated; nevertheless a cooperative character of the adsorption is clearly seen. Herein, the precise numerical fit was not possible and therefore we limit the analysis by an estimative match of the observed and calculated dependences; see Table 1.

Theoretical consideration of a gas adsorption is naturally based on analysis of the attachment of molecules to the surface of a solid, or to the surface of a pore in a solid; essential ingredients of the theory are Langmuir or modified virial equations.[25] An account for the interactions of the adsorbed molecules with each other can be done, for example, within the Frumkin–Fowler–Guggenheim approach,[26] as a result a sigmoidal adsorption isotherms can be rationalized. Further increase of interactions would lead to formation of a liquid guest phase, and observed hysteresis associates with a vapor-liquid transformation of the guest phase in a porous confinement.[23] However, all these models consider a solid absorbent as a silent spectator. Such an assumption can be valid for very rigid porous materials, but it can hardly be fulfilled for a flexible/breathing MOF. A more complete theory should also account for thermodynamics of structural deformations of the host structure.[27]

First principles calculations may help to scrutinize the reaction of the host structure on the guest uptake, however long-range effects are still difficult to deal with due to the complexity of modelling systems larger than a few hundred of molecules.[1] We therefore perform a combined analysis where an adjustable phenomenological model is used together with the experimental data. Such an approach does not answer the question on the microscopic nature of cooperativity and underlying interactions. Instead, it offers the thermodynamic measures for each adsorption site separately and maps adsorption by MOFs to a broad class of phenomena successfully modelled with Ising and alike statistical models.

Formally, the proposed model is a version of Gorsky–Bragg–Williams mean field approximation, and it is known as the Slichter–Drickamer model for spin-crossovers. An important ingredient of the theory is a cooperative interactions between guests through the host structure. An elementary event of guest occupation in a unit cell of a flexible "breathing" MOF deforms not only the given cell but also, to a certain extent, the neighboring ones. A single unit cell with a guest can, therefore, be seen as an elastic defect in the empty host media. An interaction of such defects through elastic deformation of the host matrix provides a natural basis for cooperativity. As a result, guests occupying different and even distant cells can "talk to each other" through the elastic deformations they induce. A theory that may help to explain the microscopic nature of the cooperativity may be based on an elastic approach accounting for interaction of spherical and dipolar defects[28] or on a more general phonon-mediated mechanism.[29] Further experiments probing elastic moduli and phonon densities of states and dispersions of empty and loaded MOFs are necessary to uncover the role of the host matrix in the interaction between guest molecules.

An elementary event of guest occupation in a unit cell also implies certain guest-host interactions. In our model, we parametrize the energy cost associated with those interactions with enthalpy and entropy estimates for every crystallographically independent guest site. The occupancy of these guest sites observed in our experiments as a function of temperature corresponds remarkably well to what is expected from the
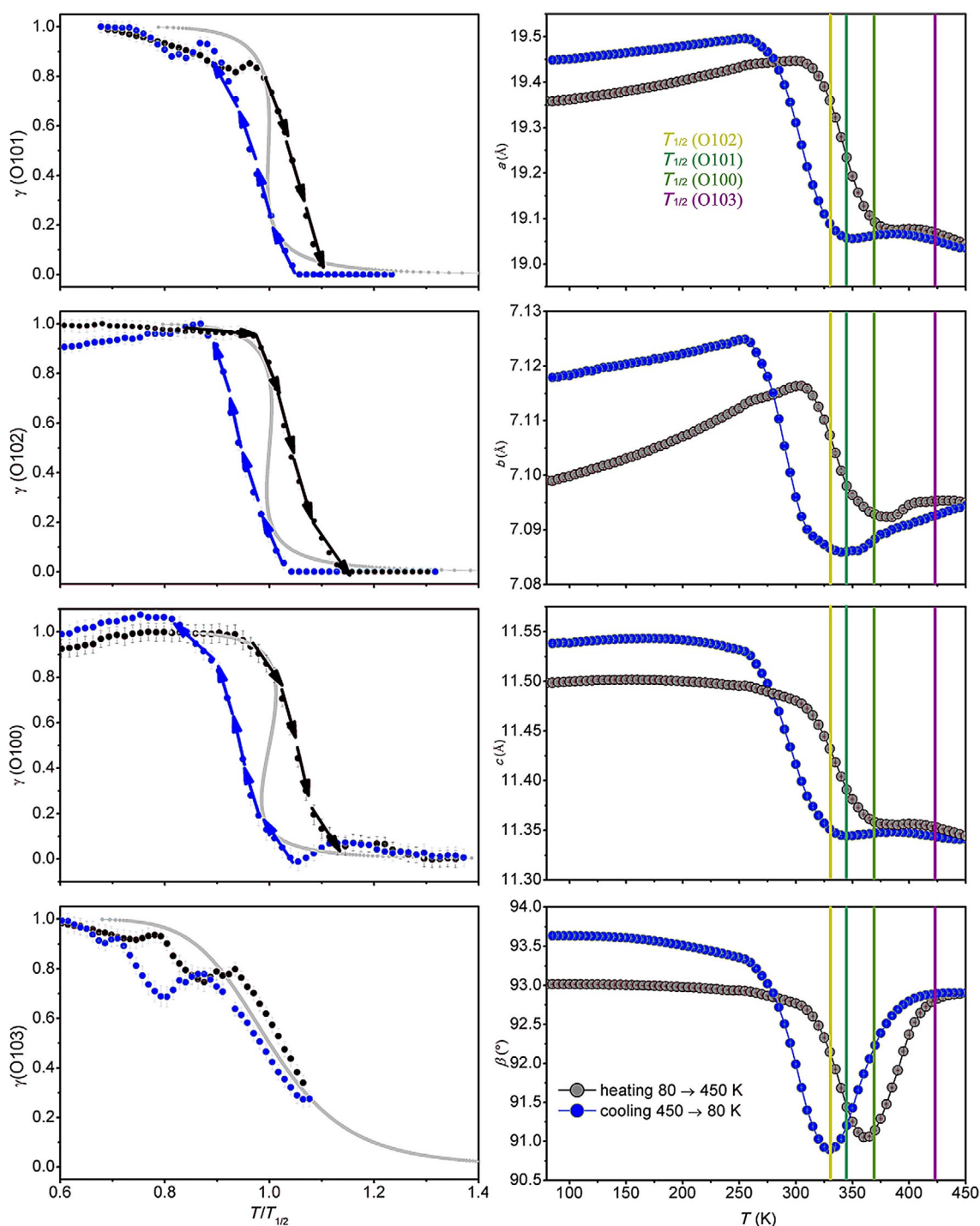
Figure 5. The structure evolution of MIL-91(Ti) upon water release. Left: occupancies as a function of temperature for 4 independent guest sites, solid lines represent theoretical estimate (see text). Right: unit cell dimensions as a function of temperature. The calculated temperatures for the water adsorption to O100, O101, O102, and O103 $T_{1/2}$ crystallographic sites are 331, 369, 345, and 423 K, respectively.

phenomenological model with cooperative interactions. In particular, nitrogen in γ-Mg(BH$_4$)$_2$ shows nearly zero cooperativity, whereas ethane is adsorbed in a cooperative fashion. This difference in cooperativity may be related to a larger size of the ethane molecules (the kinetic diameter of C$_2$H$_6$ is 4.44 versus 3.64–3.80 Å for N$_2$)[30] and therefore larger strain it imposes in the host framework. The difference in size may also serve as a

reason for higher affinity of C$_2$H$_6$ by γ-Mg(BH$_4$)$_2$ as compared with N$_2$; the maximal loading for C$_2$H$_6$ is reached at 0.5 bar (Mg(BH$_4$)$_2$·0.603(2) C$_2$H$_6$) while for N$_2$ it needs 30.6 bar to reach a similar value (Mg(BH$_4$)$_2$·0.63 N$_2$).

Water uptake by MIL-91(Ti) from the atmosphere is more complicated in terms of cooperativity and it correlates with much higher lattice deformation as compared with γ-Mg(BH$_4$)$_2$.

Table 1. The obtained thermodynamic parameters for γ-Mg(BH$_4$)$_2$ and MIL-91(Ti) based on the GBW model.

Guest site	$-\Delta H$ [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]	$T_{1/2}$ [K]	Γ [J mol^{-1} K^{-1}]
γ-Mg(BH$_4$)$_2$				
N$_2$	12.0(9)	81(6)	148	0
C$_2$H$_6$	25.3(3)	96(1)	264	1984(6)
MIL-91(Ti)				
H$_2$O(100)	36.5	110	332	7050
H$_2$O(101)	40.5	110	369	6500
H$_2$O(102)	38.0	110	345	6500
H$_2$O(103)	46.5	110	423	0

Cooperativity of elastic origin assumes a correlation between site occupancy and lattice deformation for a single guest site. A multi-site case is obviously more complicated (Figure 5, the right panel). Four guest sites in MIL-91(Ti) show different behavior that can be tentatively associated with their coordination by the MOF host structure (Figure 2). The most cooperative response is observed for 3 water molecules occupying the central part of a pore; notably filling of these positions correlates with the changes of unit cell size and shape (Figure 5). The last water molecule seems to show higher binding to the host structure (higher $T_{1/2}$) and occupies a pocket in a pore corner; the deformations associated with filling of this position appear to be accommodated by local structural distortions and affect long-range elastic strain to a much smaller extent.

The estimates of thermodynamic parameters, single-site enthalpy, and entropy for N$_2$ in γ-Mg(BH$_4$)$_2$ ($\Delta H = 12.0(9)$ kJ mol^{-1} and $\Delta S = 81(6)$ J mol^{-1} K^{-1}) can be compared, for example, with the adsorption enthalpy and entropy calculated from variable-temperature FTIR spectroscopy data for N$_2$ in protonic zeolite H-ZSM-5; $\Delta H = 19.7(5)$ kJ mol^{-1} and $\Delta S = 125(5)$ J mol^{-1} K^{-1}.[31] For both cases the cooperativity is similarly low and Equation (5) reduces to the van't Hoff equation; Figure S6. For strongly cooperative scenarios the van't Hoff equation is not applicable and one has to use Equation (5) instead. Irrespective to the degree of cooperativity, easily measurable temperature of half-filling $T_{1/2_i} = \frac{\Delta H_i}{\Delta S_i}$ offers safe starting point for the thermodynamic estimates.

In spite of the fact that the proposed model catches well the main features of cooperative adsorption, there is still big room for its further development. In particular, the theory can be easily extended to account for a distribution of the model parameters; such an extension would allow to reproduce a slope of otherwise vertical hysteresis borders.[21]

Here we limit the analysis by isobars only with temperature evolution being solely defined by entropy terms [Eq. (2)]. An analysis of isotherms is another necessary extension of the present theory. At first approximation, enthalpy contribution should be the most sensitive to pressure, assuming $\Delta H \propto p_c$ one easily derives an equation for an isotherm based on Equation (2) where increase of the partial pressure gives a sigmoidal cooperative increase of the absorbed gas. However, physical pressure should favor a low-volume empty host matrix, therefore it would do the opposite—it would suppress the adsorp-

tion. The further development of the theory requires the input from experiments. Diffraction measurements, similar to those presented here, but done at different pressures should help to evaluate pressure and temperature dependence of $T_{1/2}$ and cooperativity parameter and map the pT phase diagram.

Conclusions

We present experimental illustration of different degrees of cooperativity using powder diffraction data for nitrogen and ethane in nanoporous γ-Mg(BH$_4$)$_2$ and 4-site water uptake in MIL-91(Ti). Adsorption scenarios are deduced from the site occupancies; a comparison with conjugated lattice deformation serves as an illustration of elastic nature of the cooperative response. An Ising-like lattice gas model in Gorsky–Bragg–Williams mean field form is applied for the guest-uptake process in the flexible MOF. This approach accounts for cooperative interactions for the guest molecules occupying different pores and interactions are mediated by elastic perturbations induced by guest molecules in the flexible framework structures.

This combination of the phenomenological model and a diffraction experiment offers a simple yet very powerful tool to examine thermodynamics of cooperative adsorption. With only a small set of parameters we are able to reproduce the main characteristics of a variety of adsorption curves, essentially because of the empirical nature of the adjustable parameters.

The phenomenological approach for the adsorption scenario does not depend on the microscopic origin of the underlying intermolecular interactions. These interactions can be traced from diffraction data collected under gas pressure. The powder diffraction technique is a very powerful in situ tool but has its natural limitations, if one has to refine tiny atomic shifts in a large structure. It would be very interesting to see what kind of interactions between the guest and host contributes more to the lattice deformation. This problem may be addressed by an in situ diffraction experiment on a single crystal.

A similarity of cooperative adsorption in flexible porous solids with well-studied collective behavior of bi-state systems promises many new phenomena to be observed for both static and kinetic properties. Phase diagram mapping and search for new ordered phases should be addressed to a single crystal diffraction experiment. A correlation analysis of site-specific thermodynamic parameters and cooperativity with crystal structure and chemistry of ligands and active centers is another direction where our phenomenological approach may offer certain predictive power.

Our observations and analysis suggest one more control parameter to be optimized in a rational design of MOFs—a cooperativity. This property opens new functionalities of MOFs, for example, highly cooperative uptake and release of absorbed gas at well-defined thermodynamic conditions, a controlled switch between "sponge on" and "sponge off" regimes, and even memory effects.

Experimental Section

Powder diffraction experiments at ambient conditions have confirmed the reported crystal structures and proved single phase composition for both powders. The crystal structure data was complimented with temperature and pressure evolution changes, which are associated with adsorption and desorption of the guests into the host frameworks.[32] For that purpose, in situ synchrotron powder diffraction measurements at BM01 station of Swiss-Norwegian Beam Lines at the European Synchrotron Radiation Facility (Grenoble, France) have been performed.[33] The experimental details, data processing, and structural analysis are described in the supporting Information.

Conflict of interest

The authors declare no conflict of interest.

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