INVITED ARTICLE

A thermodynamic description of the adsorption-induced structural transitions in flexible MIL-53 metal-organic framework

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(Received 8 January 2014; accepted 27 January 2014)

We briefly review the concept of temperature-loading phase diagram that we derived from an osmotic statistical ensemble analysis of the adsorption-induced structural transitions observed in the MIL-53 family of metal-organic framework nanoporous materials. We highlight the generic nature of this diagram and comment on the occurrence of breathing transitions depending on the guest fluid, the framework functionalisation and the nature of the metal centre.

Keywords: adsorption; statistical thermodynamics; structural transitions; nanoporous materials

1. Introduction

Among the wide class of metal-organic frameworks and other related open framework hybrid materials, the subclass of soft porous crystals (SPCs) has attracted a lot of attention in the past few years. According to Kitagawa, who introduced this notion, ‘soft porous crystal are defined as porous solids that possess both a highly ordered network and structural transformability. They are bistable or multistable crystalline materials with long range structural ordering, a reversible transformability between states and permanent porosity’ [1]. It has been recently shown that the ‘softness’ of these materials, which was somewhat ill defined up to now, actually stems from a highly anisotropic mechanical (or elastic) behaviour, with some directions of the crystal exhibiting very low Young’s modulus and shear modulus [2].

SPCs exhibit large-amplitude structural deformations induced by various external stimuli such as temperature, mechanical pressure or guest adsorption. Guest-induced structural transitions include the gate adsorption and the breathing phenomena. Gate adsorption typically involves an abrupt structural transition between a nonporous state and a porous crystalline host that is induced by gas adsorption [3,4]. The breathing phenomenon consists of two successive adsorption-induced crystal-to-crystal transformations, from a large pore (lp) state to a narrow pore (np) state and back again to the lp structure [5,6].

In a series of articles, the present authors have investigated the equilibrium thermodynamics of adsorption-induced and pressure-induced breathing transitions using an analytical approach based on the osmotic statistical ensemble. Some key questions were answered, such as the prediction of the occurrence or absence of guest-induced breathing for a given guest–host system [7–9] and the successful derivation of a (temperature–gas pressure) phase diagram for the several gases (xenon, methane and carbon dioxide)/MIL-53 systems [10–12] as well as breathing phase diagram for binary mixtures of methane and carbon dioxide/MIL-53 [13]. The physical mechanism of the breathing transitions was addressed by viewing the adsorption-induced stress exerted on the material as the stimulus that triggers breathing transitions, in a way similar to lp-to-np structural transitions that can be induced by mechanical compression. This new view of the breathing that we proposed implies that the structural transitions in SPCs take place when the stress reaches a certain critical threshold [14,15]. Though the exact chemical origins of this stress have not yet been fully uncovered, it is similar in nature to the elastic limit (or yield strength) in classical mechanics, where the deformation stops being quasistatic. For example, a recent molecular simulation study has shed some light on the pressure-induced amorphisation of Zeolitic Imidazolate Framework ZIF-8 [16]: the amorphisation transition in this material was shown to be the result of pressure-induced softening, until the pressure reached a value at which the crystal was not mechanically stable (Born’s stability criterion no longer hold). Although it has not been unequivocally demonstrated, we envision that a similar mechanism might be in play in the breathing of MIL-53.

This hypothesis of a ‘critical stress threshold’ enabled to explain, at least qualitatively, the hysteresis phenomenon observed in the breathing transitions; when approaching the...
structural transition, the material is in two different phases on the adsorption and desorption branches, whose critical stress need not be equal (it was demonstrated, for example, that other mechanical properties such as the bulk modulus vary between the two phases [15]). Moreover, this concept was used as a basis for building a multiscale dynamic model in order to capture the dynamics of adsorption-induced deformation and structural transformation in MIL-53 based on the coupling of the host–guest adsorption interactions with the elastic response of the three-dimensional framework of a given geometry [17,18]. Finally, the issue of multistability and intermediate structures was recently addressed, using the osmotic potential approach [19].

In this paper, we briefly review the equilibrium temperature-loading phase diagrams (i.e. the \{temperature–gas pressure\} diagrams) that were computed for different guest-MIL-53 systems. We highlight the generic nature of this diagram and comment on the occurrence of breathing transitions depending on the guest fluid, the framework functionalisation and the nature of the metal centre.

2. Temperature-loading diagrams for several guest-MIL-53(Al) systems

We have used a model based on the so-called osmotic ensemble [7], which is the appropriate statistical ensemble to describe fluid adsorption in a flexible porous material. Since the MIL-53 material exhibits clear structural transitions between two metastable framework structures, namely the ‘narrow pore’, np phase, and the ‘large pore’, lp phase (see Figure 1), we were able to use a simplified osmotic sub-ensemble to describe the equilibrium between host structures upon fluid adsorption [7,8]. Langmuir fits of the experimental isotherms served as approximations to the rigid host isotherms in both the lp and np structures. We showed that, at a fixed temperature, the occurrence of breathing (or other structure transitions) upon adsorption could be rationalised by three key parameters with clear physical meaning: the affinity of the fluid for each phase (as described by the Langmuir’s Henry constant), the capacity (or saturation uptake) of fluid in each phase and the free energy difference between the empty phases.

In the first study of this series, performed on the \{Xenon- MIL-53 (Al)\} system [10], we have used stepped isotherms at two temperatures to determine the transition enthalpy and entropy of the empty host material, as well as the free energy difference between the empty lp and the np structures. Not unexpectedly, the lp form was predicted to be the most stable one at room temperature, while the np structure becomes the most stable one below 203 K. One of the interests of the osmotic thermodynamic model is that it enables to compute equilibrium thermodynamic data for the bare host material using thermodynamic adsorption data only.

The osmotic model, with the use of the fits performed on the experimental adsorption isotherms, enables to investigate the full temperature-loading phase diagram of \{Xe, MIL-53(Al)\}. By solving the osmotic thermodynamic equations numerically, we determined for each temperature whether breathing takes place and if so, what the transition pressures are. The predicted temperature–xenon gas pressure diagram is shown in Figure 2.

The lp phase was found to be stable at high temperature and again at lower temperature. There is an intermediate np phase stability domain for xenon pressure lower than a limiting pressure of around 1.6 bar. This result is reminiscent of the re-entrant behaviour observed in some liquid crystals [20]. As noted above, however, the low-temperature
stable phase at zero pressure (empty material) is the np phase. The phase diagrams for the {CO\textsubscript{2}, MIL-53(Al)} and {CH\textsubscript{4}, MIL-53(Al)} are also shown in Figure 2 [12]. All three diagrams have in common the equilibrium np–lp transition temperature of the bare MIL-53(Al) material (203 K in our model, subject to an estimated uncertainty of ±10 K), where the initially empty open structure contracts upon guest molecule adsorption. The fact that this has not been observed in some cases at room temperature simply means that the transition line maximum in this system is below the room temperature. The present findings for methane clearly confirm these predictions.

The above thermodynamic considerations are very general and obviously not limited to the special case of one or the other gas adsorption. The condition \( k_{np}/k_{lp} > 1 \) is expected to hold true for all the simple guest molecules that have been investigated so far. This means that there should be a range of temperatures above the equilibrium np–lp transition temperature of the bare MIL-53(Al) material (203 K in our model, subject to an estimated uncertainty of ±10 K), where the initially empty open structure contracts upon guest molecule adsorption. The fact that this has not been observed in some cases at room temperature simply means that the transition line maximum in this system is below the room temperature. The present findings for methane clearly confirm these predictions.

The difference in the stability domain of the np phase in the three different cases can be qualitatively understood as follows. For each system, there is a temperature \( T_{max} \) (see Figure 3a), above which gas adsorption does not induce the lp–np phase transition anymore. Since the driving force for the closure of the lp structure is the guest–host interaction, which induces the cell contraction, one may simply write \( k \Delta H_{ads,lp} \). The increase in \( T_{max} \) in going from CH\textsubscript{4} to Xe and CO\textsubscript{2} can then simply be explained by the increase in adsorption enthalpy in the lp phase. While \( P_{max} \) is approximately the same for CH\textsubscript{4} and Xe, its value for CO\textsubscript{2} is larger by a factor of \( \sim 3 \). This difference can be accounted for by a larger interaction energy between guest molecules in the case of carbon dioxide, due to their quadrupole moments. This causes a stronger ordering of the CO\textsubscript{2} molecules in the np phase and increases the stability domain of this phase.

In Figure 3b, we sketch the three phase diagrams in reduced units of \((T/T_{max})\) and \((P/P_{max})\). Some sort of a “universal” phase diagram seems to come out of this presentation. This confirms the existence of a generic temperature-loading phase diagram, as long as the adsorbate is a simple gas such as methane, carbon dioxide or xenon. It must be recalled at this stage that the osmotic model predicts the conditions of thermodynamic stability at full equilibrium and does not take into account hysteresis effects. Hysteresis was systematically encountered in all reported MIL-53 experiments and often leads to some complicated mixtures of phases [21]. This model describes what
would happen in a homogeneous system at full equilibrium. The osmotic model is aimed at describing the thermodynamics behind the scene. The hysteresis issue is being addressed in some of our other studies [14–19].

Finally, one should mention that the osmotic model was extended to predict the behaviour of fluid mixtures adsorbing in flexible nanoporous materials by proposing an analytical scheme called OFAST (osmotic framework adsorbed solution theory) [13]. Figure 4 represents the \{CO$_2$/CH$_4$, MIL-53(Al)\} diagrams for different values of the carbon dioxide mole fraction. We can see that, in addition to the re-entrant nature of the phase diagrams themselves in \((T, P)\) space, there is a nonmonotonic evolution of the maximal temperature and pressure of the np phase as a function of the mixture’s composition. This unexpected result, first hypothesised on a purely theoretical thermodynamic basis [9], was later proven true by experimental measurements [13].

3. Temperature-loading phase diagrams for some other guest-MIL-53 materials systems

The osmotic temperature-loading phase diagram can be used to study the effect of changes in the material’s composition on the breathing behaviour. We have performed an experimental and theoretical study of carbon dioxide adsorption in amino-functionalised MIL-53(Al), jointly with the group of Denayer [11]. In Figure 5, the \{CO$_2$, amino-MIL-53(Al)\} diagram is compared with the “regular” MIL-53(Al) diagram. The equilibrium np–lp temperature \(T_0\) is slightly different (203 K for regular MIL-53 and 226 K for amino-MIL-53), and the initial slope of the transition line is higher in the case of the amino-MIL system. Even though the overall shape of the temperature–gas pressure phase diagram is similar, there is a spectacular difference in the stability domain of the np structure, which can be accounted for by the increased stability of this form due to the presence of the amino groups in the structure. The strong affinity of CO$_2$ molecules in the np form leads to a larger value of \(K_{np}/K_{lp}\) for the amino-MIL material compared to the regular MIL-53(Al) and enlarges the stability domain of the np form.

An even more drastic change in the MIL-53 composition consists of replacing the aluminium centre by a gallium atom. MIL-53 (Ga) was synthesised and characterised by the group of Férey [22] and then further investigated by Boutin and co-workers [23]. Breathing transitions were found to take place upon several gas adsorptions [22] but the stable phase at room temperature was found to be the np narrow pore structure [22,23]. A recent quantum chemistry investigation by Coudert and co-workers allowed to understand that np phase was more stable in the case of MIL-53 (Ga), because of the more diffuse orbitals of Ga compared to Al [24]. Thus, the np phase is the stable structure at room temperature (rather than lp as Al-MIL53). The effect of replacing Al by Ga is simply to increase the value of \(T_0\), the np–lp equilibrium phase transition temperature of the empty MIL-53 framework. The whole temperature-loading phase diagram is thus switched to higher temperature.
4. Conclusion

The temperature-loading phase diagram of the flexible MIL-53 family of materials is a useful tool to understand the behaviour of adsorption-induced breathing structural transitions. Whether or not these transitions take place upon adsorption of a particular gas or gas mixture depend on the relative location of the stability regions of the np and lp states in the system’s \((T, P, x)\) space, where \(T\) is the temperature, \(P\) is the adsorbate gas pressure and \(x\) is a mole fraction describing the gas composition. Even though this is just an equilibrium thermodynamic view of the breathing process, which means for instance that it lacks the hysteresis effects that take place in the experiments, this temperature-loading concept has allowed to demonstrate that the breathing effect in MIL-53 is a very general phenomenon, that should be observed in some region of the \((T, P)\) space whatever the guest molecule, since it is expected that the affinity of the guest molecule, since it is expected that the affinity of

Acknowledgements

This short review paper is dedicated to Professor Pierre Turq on the occasion of his 70th birthday. Pierre was a pioneer in introducing statistical mechanics and molecular simulations at all scales in France, in the field of chemistry and physical chemistry, and the French community owes him a lot.

Funding

The authors acknowledge funding from the Agence Nationale de la Recherche under the project ‘SOFT-CRYSTAB’ [grant number ANR-2010-BLAN-0822].

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