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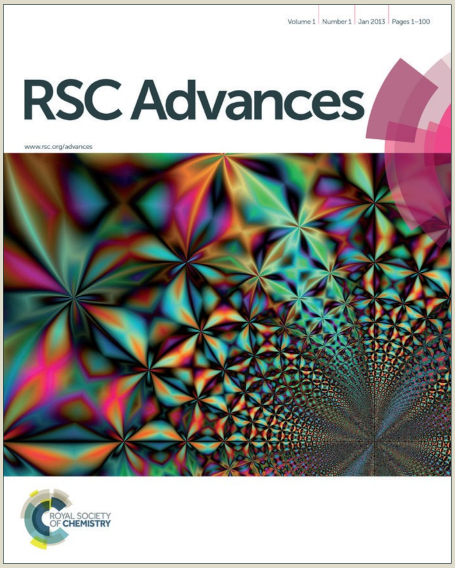

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Stability of Zeolitic Imidazolate Frameworks: Effect of forced water intrusion and framework flexibility dynamics

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Stability of Metal-Organic Frameworks is one of the central issues for their successful usage in the increasingly wide range of applications. Particularly Zeolitic Imidazolate Frameworks (ZIFs) are known for their high stability. Herein we use two most stable representatives ZIF-8 and ZIF-67 to show that concomitant effect of pressure and temperature upon water intrusion/extrusion cycles is strikingly higher compared to separate effect of either pressure or temperature and leads to previously unobserved irreversible structural changes. We also explore the effect of compression-decompression speed on the pronounced breathing effect of indicated ZIFs as part of high-pressure operation and show that framework relaxation time may be very long and should be taken into account for potential applications.

Pronounced porosity and high stability of Metal Organic Frameworks (MOFs) and particularly their subclass Zeolitic Imidazolate Frameworks (ZIFs) attract increasing attention in many fields of science and technology [1]. Applications include gas separation [2], catalysis [3], drug delivery [4], mechanical energy storage (taking advantage of their reversible high flexibility [5,6] or non-wetting liquid intrusion-extrusion [7-9]), systems with negative thermal expansion [10] and others. For all these applications in-depth understanding of the stability conditions of MOFs is obviously very important. Previously reported investigations on the stability of ZIFs include high-pressure and high-temperature tests. For example Chapman et al. reported that for ZIF-8 the critical hydrostatic pressure after which irreversible amorphisation takes place is □0.34 GPa [11]. Hu et al. demonstrated that if applied pressure is non-hydrostatic, even higher values of 1.6 GPa are necessary for irreversible modification of the structure of ZIF-8 [12]. According to Bennett et al. the structure of ZIF-4 can be changed only by pressure of about 6.5 GPa [13]. ZIFs also exhibit pronounced stability in high-temperature tests up to 500°C for ZIF-8 [14] and up to 350°C for ZIF-67 [15].

Recently we demonstrated that by performing water intrusion-extrusion cycles on hydrophobic ZIF-8 metal organic framework, it was possible to provoke irreversible changes of its structure changing the symmetry from cubic to orthorhombic [9], even though such cycles were performed at pressures (about 30 MPa) and temperatures (near 90°C) much lower than the ones reported previously for having any irreversible effect on the structure of ZIF-8 (that is respectively 0.34 GPa [11] and at least 500°C [14]). In this paper we explore the effect of water intrusion-extrusion cycles on another hydrophobic Zeolitic Imidazolate Framework, ZIF-67, offering a different perspective for MOFs stability testing. High-pressure water intrusion-extrusion cycles also constitute the usual operational cycles for {porous materials + a non-wetting liquid} systems to store mechanical energy. The non-wetting condition eliminates the spontaneous penetration of the liquid into the pores of the matrix. By increasing the pressure of the system to some critical value (intrusion pressure P_{int}) the liquid can be forced into the pores; the mechanical energy necessary to break the intermolecular bonds of the liquid during intrusion is supplied to the system during the intrusion process and is associated with the 'solid – liquid' interface development. On the *PV*-diagram this process corresponds to an intrusion plateau and is associated to a significant increase of the compressibility of the system (Fig. 1): the corresponding plateau stands until the pores of the matrix are completely filled. Since lyophobic pores constitute an energetically unfavorable environment for molecules of the non-wetting liquid, the decrease of the pressure in the system down to some critical value (extrusion pressure P_{ext}) leads to the extrusion of the liquid from the pores of the matrix, which is followed by the release of mechanical energy (large expansion of the system, see Fig. 1) and renewal of intermolecular bonds of the liquid. Hence, such a system acts as a Molecular Spring (MS) and can be used for energy storage [7,9,16,17].

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Electronic Supplementary Information (ESI) available: XRD and FTIR data; *PV*-isotherms of the {ZIF-8 + water} system at different compression-decompression speeds. See DOI: 10.1039/x0xx00000x

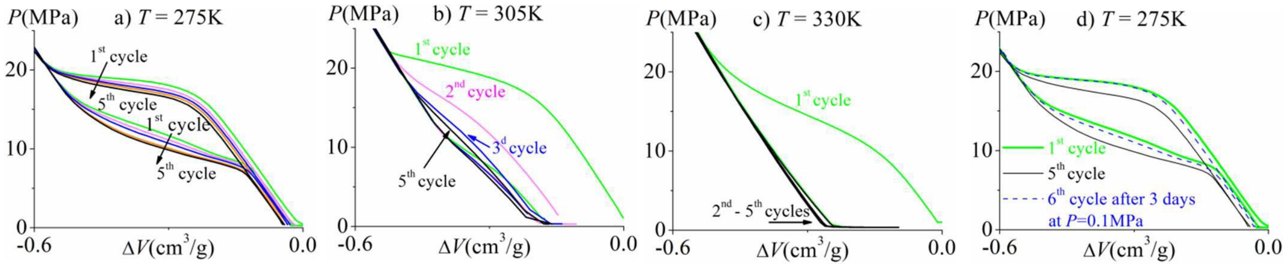

Figure. 1. PV-isotherms of {ZIF-67 + water} system a), b) and c) effect of temperature; d) effect of pause after successive cycling.

The high specific energy which the system stores/restores during the intrusion/extrusion process can be obtained by using porous materials with a large specific surface area (400–2000 m^2g^{-1}) possessing a large specific volume change (mechanical energy) during intrusion/extrusion processes. In this sense MOFs with their large surfaces are attractive candidates for that matter.

Particularly ZIF-67 and ZIF-8 used in this work have specific surfaces of ~1500m^2g^{-1} and ~1800m^2g^{-1} respectively [14,15].

Testing ZIF-67 as a component of HLS with water and its stability upon water intrusion-extrusion at different temperatures follows successful tests of {ZIF-8 + water} [7,9] and {ZIF-71 + water} [8] systems for energy applications.

It is important to note that such mentioned systems were tested in slow (quasi static) operational regimes, while real applications may require much faster compression-decompression (intrusion-extrusion) cycling. For example, HLS based on grafted silica gels and water demonstrates striking operational frequencies up to 22Hz [18,19] and potentially much higher [20], but to our knowledge the effect of compression/decompression speed on the characteristics of HLSs based on MOFs has never been reported. In this paper we also make a first step in investigating such effect for {ZIF-67 + water} and {ZIF-8 + water} systems; in particular the effect of speed of compression/decompression and the framework relaxation time of these ZIFs are discussed.

For this work ZIF-67 ($Co(Hmim)_2$, Hmim = 2-methylimidazole) was purchased from MOF Technologies. ZIF-8 ($Zn(Hmim)_2$) was purchased from Sigma Aldrich as Basolite Z1200. ZIF-67 is isostructural to ZIF-8, which has sodalite (SOD) topology and is formed by bridging 2-methylimidazolate anions and zinc cations. Both materials have pore opening of only 3.4 Å and cages of 11.6 Å [21]. Distilled water was used as non-wetting liquid for both MOFs.

A ST-7M transitiometer (BGR-Tech) was used to obtain the PV-isotherms of the investigated systems in the 275 - 360 K temperature and 0.1 – 30 MPa pressure ranges at different speeds ranging from 0.01 $MPa{\cdot}min^{-1}$ to 5.5 $MPa{\cdot}min^{-1}$ according to the procedure described elsewhere [17].

Compression-decompression cycles of {ZIF-67/ZIF-8 + mercury} systems were recorded using an AutoPore IV 9500 mercury porosimeter in the 0.004 – 100 MPa pressure range.

XRD patterns of pristine MOFs and of MOFs submitted to intrusion/extrusion cycles were recorded on an X'Pert Pro PANalytical diffractometer θ–θ geometry, using Cu Kα radiation (λ = 1.54184 Å) at room temperature in the interval of 3° < 2θ < 120°, with a step size of Δ2θ=0.0167° and a counting time of 119 s for each data value. A total counting time of about 200 min was used for each sample. XRD data were systematically investigated by Rietveld refinement using the FullProf program to check the cubic symmetry, extract the lattice parameters and the quantitative analyses.

FTIR spectra were recorded in the transmission mode using the KBr pellet technique with a Nicolet 5700 spectrometer from Thermo Scientific.

First five successive intrusion-extrusion cycles (performed with compression-decompression rate of 5.5 MPa min^{-1}) for the {ZIF-67 + water} system at different temperatures are presented in Figure 1. It can be seen that each successive cycle provokes changes in *PV*-isotherms: decrease of both intrusion/extrusion pressures and intrusion/extrusion volume. Such changes lower the value of stored/restored energy per one compression-decompression cycle and this effect is much more pronounced at higher temperatures; at 275K the stored/restored energy of the system decrease by about 20% compared to the first cycle, at 330K it is almost 100%, while at 350K there is no extrusion (no restored energy) after the 1st cycle. This result correlates with the degradation of the energetic characteristics of {ZIF-8 + water} system only at temperatures higher than 330K as reported previously: water intrusion-extrusion cycles only at temperatures higher then c.a. 330K provoke irreversible changes in the structure of ZIF-8 and lowers its symmetry from cubic to orthorhombic [9].

In order to understand the reasons for the {ZIF-67 + water} system's degradation, the XRD and FTIR characterization methods were similarly exerted to the reference ZIF-67 and to the modified ZIF-67 after intrusion-extrusion cycles at different temperatures (Fig.1S). The XRD results reveal that water intrusion-extrusion cycling at temperatures of 330K and higher result in formation of new phase, which is cobalt hydroxide $Co(OH)_2$ (see broad diffraction peaks in Fig. 1Sa indicating very small coherent domain size). The amount of $Co(OH)_2$ after first 5 intrusion-extrusion cycles is proportional to the temperature at which such intrusion-extrusion takes place for 305 – 350K temperatures, but doesn't change after cycling at 275K; there is also continuously decrease of unit cell volume with increasing operational temperature (Table 1S), which suggests that not only new phase being formed, but the structure of remaining ZIF-67 also undergoes irreversible changes. The FTIR spectra confirm such dependence (Fig. 1Sb): for all the powders which have undergone intrusion-extrusion cycles in the 305 – 350K temperature range there is a pronounced increase of OH stretching vibration at around 3500cm^{-1}, while broad peak around 3000 cm^{-1} correspond to water in the pores. Such results are interesting since ZIF-67 was proven to be stable to much higher temperatures (in fact it was stable after 5 days boiling in water and 5 days in toluene [15]). Considering the pressure impact, as far as we know, there are no results of high-pressure test of ZIF-67 in the literature.

It is obvious that ZIF-67 is being destructed by water intrusion-extrusion cycles at temperatures from room temperature to higher ones, while such cycling at 275K seems not affecting its stability (Fig. 1S). Thereby the reasons for the degradation of the energetic characteristics of {ZIF-67 + water} system at 275K (Fig.1a) are not clear. In order to clarify this point, additional intrusion-extrusion experiments were performed for this HLS under different dynamics (Fig. 1d).

First a new {ZIF-67 + water} sample was submitted to 5 intrusion-extrusion cycles after which it was kept in the measuring cell at atmospheric pressure for 3 days. Remarkably, after this long pause the 6th compression-decompression cycle demonstrates the recoverability of the energetic characteristics of the system (Fig. 1d): the intrusion pressure is equal to intrusion pressure at the first cycle, while extrusion pressure and volume of intruded water correspond to those of the a second cycle (even for most stable HLSs, which undergo millions of cycles it is typical that the first cycle is different from all following ones [22,23]). Similar sets of experiments were performed with shorter pause at atmospheric pressure and it was found that full recovery period is rather long and for example 2 days at atmospheric pressure is not enough. Such result is rather striking because even though the delay in non-wetting liquid extrusion from the pores is known and was investigated, it is naturally observed for HLSs with very pronounced hysteresis (such HLSs are used for mechanical energy dissipation [18,22,23]), for which extrusion pressure is nearly equal to atmospheric pressure [24]. But for the {ZIF-67 + water} HLS extrusion takes place at rather high pressure (from about 15 to 7 MPa) and the end of this process is rather well marked (Fig. 1d). Perhaps the reason for such long relaxation period of the system is not the slow expulsion of water from the pores, but rather the relaxation of the structure of this MOF, which are known for their high flexibility [5, 6].

In order to check this hypothesis one needs to separate the volume variations due to the pressure induced flexibility of ZIF-67 from the volume variation resulting from the water intrusion-extrusion during a compression-decompression cycle. One of the ways to achieve that is to use a pressurizing fluid with molecules too big to enter the pores or with the surface tension high enough to prevent intrusion in the required pressure range. In fact such experiments were proposed by Beurroies et al. to be used in order to take advantage of the huge flexibility of MIL-53 MOF for mechanical energy applications [5]. Here we followed this approach and performed compression-decompression cycles of {ZIF-67+mercury} system in the 0.004 – 100 MPa pressure range for investigating the flexibility of ZIF-67 and ZIF-8. High surface tension of mercury prevents its intrusion into the micropores of these ZIFs.

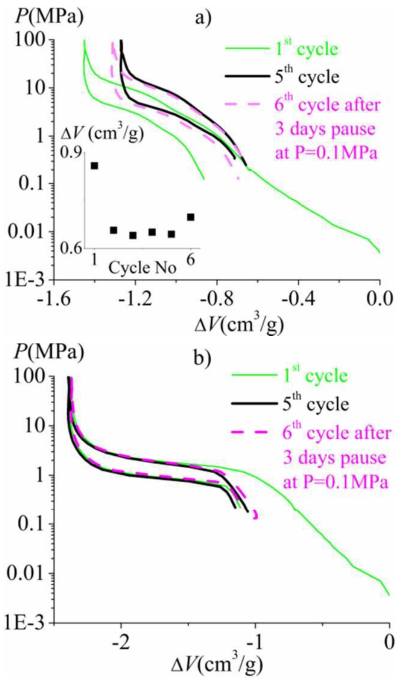

Figure. 2. Compression-decompression isotherms of a) {ZIF-67+mercury} and b) {ZIF-8+mercury} systems.

It can be seen from Figure 2a that at the pressure of c.a. 5 MPa ZIF-67 experiences pronounced volume variation associated with the flexibility of its framework. The volume variation due to such flexible effect decreases after the 1st compression-decompression cycle, but tends to recover at the 6th cycle after 3 days pause. This result complies well with intrusion-extrusion experiments at 275K (Fig. 1d) and suggests that the observed slow relaxation of energetic characteristics of {ZIF-67 + water} system is due to the relaxation of the flexible ZIF-67 framework. It also can be seen that for ZIF-67 framework the flexibility takes place in two steps. Most likely, this explains the two-step water extrusion of {ZIF-67 + water} system (Fig. 1).

In recent work it was experimentally shown that the threshold pressure at which reversible flexibility effect of MOF occurs depends on the pressurizing fluid [6]. This explains the fact that there is no observable flexibility effect at about 5 MPa before water intrusion (Fig. 1). From these experiments we see that 3 times lower pressure impact upon water intrusion (Fig.1b) has much more prominent effect on ZIF-67 compared to 100 MPa impact under non-intrusion conditions (Fig. 2a).

Such results are worth to compare with the pressure induced flexibility effect of ZIF-8 shown in Fig. 2b. This MOF exhibits a more pronounced flexibility effect (of about 1 cm^3·g^{-1}) at a much lower pressure of about 2 MPa with almost negligible decrease of the breathing effect inducing the volume variation at each successive cycle and fast recovery (framework relaxation) of about 30 min.

Table 1. Energetic characteristics of ZIFs based systems upon compression-decompression cycle.

	{ZIF-67 + water}	{ZIF-8 + water}	{ZIF-67 + mercury}	{ZIF-8 + mercury}
T, K	275	275	295	295
$□_{□□}$, J/g	6.6	8.8	2.5	1.9
$□_{□□□}$, J/g	4.1	5.7	1.0	0.9
H, %	38	35	60	53
$□_{□}$, MPa	18.8	23.0	10.0	1.8
$□_{□}$, MPa	11.6	17.3	4.0	0.8
$\Delta□$ cm^3/g	0.35	0.43	0.25	1.07

$□_{□□}$ and $□_{□□□}$ are stored and restored energy, H is stored-restored energy hysteresis, $□_{□}$ is threshold pressure upon compression, $□_{□}$ is threshold pressure upon decompression, $\Delta□$ is volume variation.

However, it is possible to detect some differences on *PV*-isotherms of the {ZIF-8 + water} system depending on the speed of compression-decompression cycle using the more sensitive to volume variations Transitiometer ST-7M (Fig. 2S): it can be seen that for all the investigated regimes the intrusion process is a one-step process associated with one-step plateau on the *PV*-isotherm due to forced intrusion of water molecules into the pores of ZIF-8. For extrusion it is a two-step process, which is well seen on the derivative plot in the inserts of Fig. 2S (two peaks of compressibility for extrusion, with only one peak for intrusion). It can be also seen that the two-step extrusion process shifts to one-step extrusion process as both temperature and compression-decompression speed increases. Considering experiments described above, it appears that the slow kinetic of the breathing of ZIF-8 structure is the reason for two-step extrusion and the threshold pressure of breathing effect might be temperature dependent.

The energetic characteristics of ZIF-67 and ZIF-8 obtained upon water intrusion-extrusion and the flexibility effect are listed together in Table 1: the {ZIF-8 + water} system has the best energetic indexes and is proven to be stable under high-pressure in the 275 – 330K temperature range [9].

Conclusions

In this paper we provide for the first time the stability test for ZIF-67 under high-pressure water intrusion cycles and show that stability of ZIF-67 in these conditions is highly temperature dependent. Such results stand in line with similar stability tests for ZIF-8 [9] and may provide another perspective for the testing of MOFs' stability, that is: 1) the impact of temperature and pressure should be investigated not only separately, but also concomitantly; 2) guest molecules entering pores of MOFs may strongly increase the impact of pressure and temperature on their stability.

We also for the first time document the pronounced breathing effect of ZIF-67 and ZIF-8 MOFs under compression-decompression cycles at rather low pressure, which can be used for mechanical energy storage following the approach proposed recently [5].

Finally, the effect of compression-decompression speed on the {ZIF-8 + water} system is shown to take place even in a rather narrow range, which means that such systems must be tested also at much higher operational frequencies to be used for practical applications.

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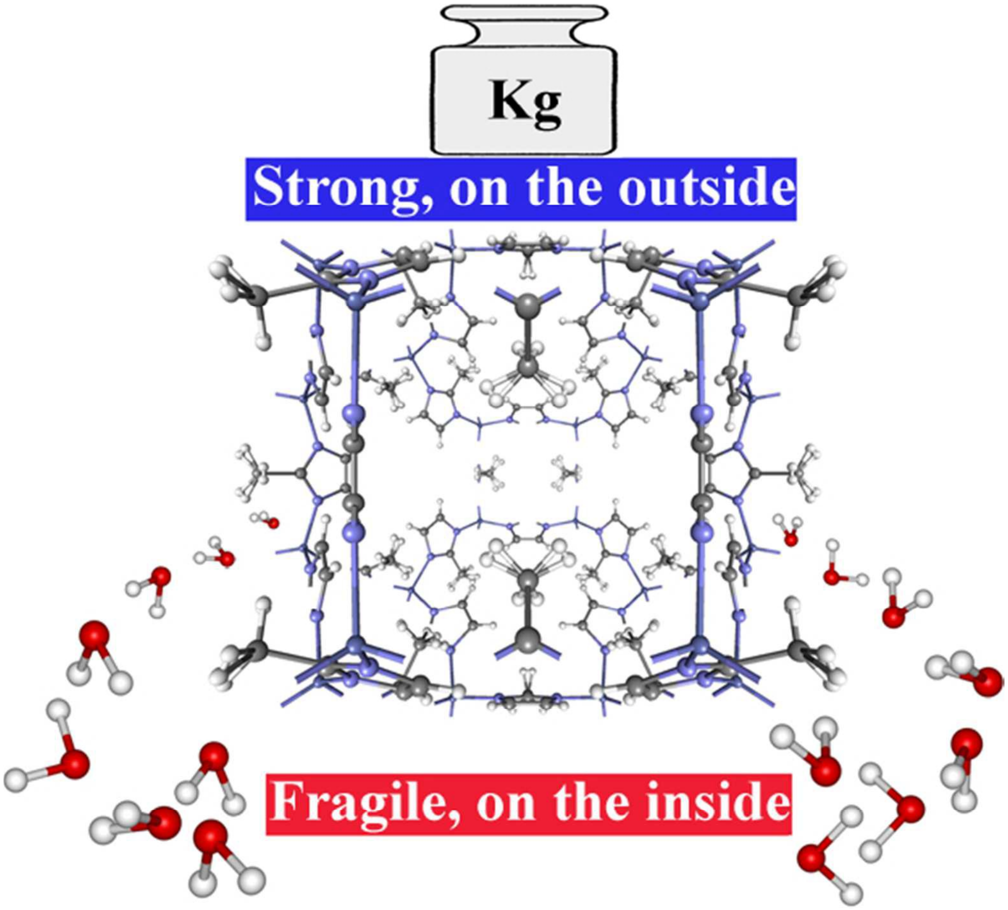

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