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Investigation of the Linker Swing Motion in the Zeolitic Imidazolate Framework ZIF-90

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ABSTRACT:

The linker swing motion in the zeolitic imidazolate framework ZIF-90 is investigated by density functional theory (DFT) calculation, molecular dynamics (MD) and grand-canonical Monte Carlo (GCMC) simulations. The relation between the terminal aldehyde group rotation and the linker swing motion is revealed. The extremely high activation energy of the linker swing motion in ZIF-90 can be attributed to the asymmetric geometry and electron distribution of aldehyde groups. The change in the gate structure resulting from the linker rotation is used to understand the guest adsorption in ZIF-90. This study shows that it is possible to tune the linker swing motion and then the properties of ZIF-90 by manipulating the terminal group rotation. The results highlight the importance of considering the internal freedom effects to correctly describe the linker

swing motion and the flexibility of metal-organic frameworks (MOFs).

Introduction

Metal-organic frameworks (MOFs) are an emerging class of nanoporous crystalline materials. One attractive character of MOFs is the structure flexibility, which confers specific properties on the materials for their application in gas separation, storage and purification.¹⁻² The structure flexibility of MOFs is considered as the main factor responsible for the sharp reduction of the molecular sieving ability and the high pressure selectivity.³⁻⁴ Therefore, the proper and effective application of MOFs could be improved by better understanding the framework flexibility.

The flexibility in MOFs materials was frequently described by the structural expansion/contraction (typically reaching $\sim 40\%$ variation) and by the corresponding changes in the unit cell and pore volume, referred-as the breathing phenomena.⁵⁻⁹ Major progress has been made by both experiment and theoretical effort to understand the whole mechanism of the large amplitude breathing of pores in MOFs.¹⁰⁻¹² However, this description applies for only a relatively small amount of MOFs; for most of them, the crystal structure results in a rather small volume variation. This is especially true for the exceptionally-stable zeolite imidazolate frameworks (ZIFs). For example, only 1.5% volume variation occurs in ZIF-8 in the high pressure experiment employing the hydrostatic medium of a methanol/ethanol mixture.¹³ Morris et al. revealed the rigidity of ZIF-8 using NMR and X-ray measurement.¹⁴ The flexibility in ZIFs exists and it has been proved to be of crucial importance for the understanding of the diffusion and adsorption of (even small) guest molecules.¹⁵⁻¹⁷

The flexibility in ZIFs is then more correctly described by two alternative parameters: the first is the lattice vibration, which from the point view of statistics, exists

in any material systems; the second is the organic linker swing motion. The lattice vibration was computationally proved to influence the migration of guests in ZIFs, such as ethane diffusion in ZIF-8.¹⁸ Experimental works by neutron spectroscopy revealed the vibrational states of ZIF-8.¹⁹ The linker swing motion has been found in carboxylate-based MOFs, such as MIL-53(Cr), MIL-47(V), UiO-66, MOF-5, etc.²⁰⁻²⁴ In ZIF-8, the swing motion of the 2-methylimidazolate (2-mIM) linkers was detected by 2H NMR method.²⁵ Coudert revealed the linker swing motion in ZIF-8 as continuous deformation upon adsorption.²⁶ A direct investigation of the linker swing motion in ZIF-8 was conducted by combining inelastic neutron scattering and high pressure.^{13,27} The authors found that the 2-mIM linker must be able to rotate freely in order to observe the linker swing motion.^{18,28} Kolokolov *et al.* measured the activation energy of the swing of 2-mIM linkers in guest-free ZIF-8, resulting in the very low value of ~ 0.36 Kcal/mol.²⁵ A correlation between computations and experimental data of the linker swing motion in ZIF-8 has been built.²⁹ It is reasonable to consider a fast but small-amplitude ($\pm 17^\circ$ at 295 K) swing motion of the 2-mIM linkers in ZIF-8.^{25, 30-32} The large-amplitude ($80^\circ \pm 10^\circ$) twist of the 2-mIM linker relative to the ZIF-8 window plane was recently shown experimentally by 2H NMR and dielectric spectroscopy.³³ This slow motion requires relatively high energy barrier (~ 12 Kcal/mol). Furthermore, the cooperative motion between the lattice vibration and the linker swing apparently is very important for guests propagation within the ZIF-8. The fast swing of the linkers in rigid ZIF-8 lattice (denoted as slow lattice vibration) can sharpen the molecular sieving capability.³³ The dominant role of the linker swing motion has been more and more emphasized in recent works on the ZIFs flexibility.

One interesting phenomena in MOFs resulting from the linker swing motion is the so-called gate-opening (or window-opening). For example, in ZIF-8 crystal, having a gate size of about 3.4 Å, studies have demonstrated the possible uptake of big guests, such as methane, having a kinetic diameter of ~ 3.8 Å, or branched *n*-alkanes (~ 4.3 Å), or aromatic rings like benzene or even p-xylene.³⁴⁻³⁷ This result proves the ability of linker swing motion and then gate-opening in ZIF-8.

Here we investigate the linker swing motion in ZIF-90 to gain insights into the functionalization of the linker. ZIF-90 owns the same topology (SOD) of the extensively studied ZIF-8, but a different terminal group in the position 2 of imidazolate linker, which based on an aldehyde group in ZIF-90 while it is based on a methyl group in ZIF-8. Our study shows that this small change strongly affects the linker swing motion and then the framework flexibility.

Computational Model and Methods

A periodic model of ZIF-90 was built from the XRD crystal structure.³⁸ For the periodical structure, the geometry optimization calculations were performed utilizing the CASTEP code³⁹ based on density functional theory (DFT).⁴⁰⁻⁴¹ The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm,⁴² with 600 eV cutoff energy and gamma point were employed. Generalized gradient approximation functional with Perdew–Burke–Ernzerhof parametrization (GGA-PBE)⁴³ using Vanderbilt's ultrasoft pseudopotential⁴⁴ and including dispersion corrections was chosen. Different exchange–correlation functions and k-point sets were tested (Tables S1-2) leading to very similar geometries. The ZIF-90 cluster models were built by carving out the fragment from the previously optimized

periodic structure. The dangling imidazolate nitrogen lone pairs in cluster models were terminated with Li ions to mimic dative ligand bonding to the missing Zn(II) cation (Figure S2).⁴⁵ The calculation details for the cluster structure can be found in Supporting Information.

The model used for the atomic simulation of ZIF-90 consists of $2 \times 2 \times 2$ unit cells with periodic boundary conditions. We performed grand-canonical Monte Carlo (GCMC) simulations to calculate the adsorption isobars using RASPA software.⁴⁶ Single-component isotherms were calculated at 298 K at a pressure ranging from 1×10^{-3} bar to 3×10^2 bar reaching the saturated vapor pressure of each adsorbate. The GCMC simulations were performed with 5×10^5 initializations followed by 5×10^5 Monte Carlo cycles, including the random attempts of displacing, regrowing, rotating, inserting, or removing molecules. Our GCMC simulations used the modified DREIDING force field which has been proved to accurately predict the adsorption of H_2 and CH_4 in ZIF-90.⁴⁷⁻⁴⁸ All interaction cutoff values were selected to be 16.0 Å.

Results and Discussion

The linker used for the synthesis of ZIF-90 results in asymmetrical aldehyde groups (-CHO); this is not the case in other sodalite (SOD) ZIFs such as ZIF-8, SALEM-2, ZIF-65, etc., which have symmetrical terminal groups^{13, 49-51} Structural investigations by XRD have shown that all SOD ZIFs display the same I-43m symmetry; this is because symmetrical terminal groups, such as the 3-fold methyl group in ZIF-8 and the 2-fold nitro group in ZIF-65, are compatible with space group I-43m symmetry. The redundant atoms on the position 2 of the imidazolate ring modify the structure of the ZIF-90 (Figure

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3 S1) and make it lose the I-43m symmetry. Only if the aldehyde group is vertical to the
4 imidazolate ring, the I-43m symmetry for ZIF-90 can be retrieved. Therefore, the
5 orientation of the terminal aldehyde group will affect the symmetry of ZIF-90.
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10 Besides these symmetry-related aspects, the orientation of the terminal aldehyde
11 group can tune the linker swing motion and then the gate structure in ZIF-90. Depending
12 on the orientation of the terminal aldehyde group three possible states of ZIF-90 can be
13 obtained as shown in Figure 1. In the left images in Figure 1, the aldehyde group is
14 parallel to the linker ring plane in ZIF-90 configuration. The group is then rotated by 90°
15 anticlockwise to form conformation A in which the -H terminals of the aldehyde group
16 are facing out (middle schemes in Figure 1). Respect to ZIF-90, the conformation A
17 results in an almost unchanged 6-ring gate but a narrower 4-ring gate. After the rotation,
18 the 6-ring gate is still consist of alternated -CH and aldehyde terminals. Further 180°
19 anticlockwise rotation of the aldehyde group results in the formation of the conformation
20 B structure in which the =O terminals of the aldehyde group are facing out (right part in
21 Figure 1). Respect to ZIF-90, both the 6-ring and 4-ring gate structures are changed in
22 conformation B. The linker swing motion can be traced by comparing the 6-ring gate
23 structure in conformation B with that in ZIF-90. In conformation B the three linkers
24 groups contributing to -CH terminals for 6-ring gate rotate outwards and then make it
25 possible to open the gate. The rotation of each of the three linkers contributing to
26 aldehyde terminals for 6-ring gate can sensibly narrow the gate opening. More precisely,
27 in conformation B, the 6-ring gate is dominated by three aldehyde terminals on three
28 alternated linker rings. Compared to the ZIF-90 and conformation A, the 4-ring gate in
29 conformation B is consisting of pure -CH terminals linkers and becomes larger owing to
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the linker swing motion.

Figure 1. The ZIF-90 gate structure transformation during the rotation of the terminal aldehyde group (-CHO). Blue, gray, blue gray, red and white denote N, C, Zn, O and H atoms, respectively.

Through the above analysis, we find intimate correlation between the linker swing motion and the terminal group rotation in ZIF-90. The structure of ZIF-90 conformation B proves that the rotation of aldehyde groups can induce the linker swing motion (Figure 1). In order to further understand this phenomenon, we have traced the energy evolution during the rotation of the aldehyde group in the ZIF-90 cluster model (Figure 2). According to this model, only one aldehyde group rotation is allowed. This is because except for the linker center and the connection between two ZnN_3 fragments, all other atoms positions were frozen to maintain the original geometry (Figure S2). Three main results can be derived from Figure 2. Firstly, the transition states correspond to the

vertical orientation of the aldehyde group; interestingly, both cluster models carved out from ZIF-90 conformation A and B periodical structures result in the same orientation of the aldehyde group in the transition states (Figure S3). This agreement will be helpful to calculate the energy barrier of the terminal group rotation. Secondly, the overall energy barrier of one aldehyde group rotation reaches 14.1 Kcal/mol. This value is quite large compared to the quasi-free methyl rotation in ZIF-8.⁵² Finally, the linker swing motion can reach a maximum value of 12°, which is close to the swing amplitude value of 17° in ZIF-8 at room temperature.⁸ However, this swing amplitude value seems to be much lower than that in the periodical model (right part in Figure 1). Considering the swing motion of all linkers in the periodical model, it may indicate that the interaction between linkers can contribute to the linker swing amplitude in ZIF-90.

Figure 2. Energy vs. rotation of the aldehyde group in ZIF-90. All H atoms, except one H on the rotating aldehyde group, are omitted for clarity.

In order to study the effect of the adjacent linkers' contributions to the swing

amplitude, we performed the energy scan for the aldehyde group rotation in ZIF-90 conformation A and B cluster models (Figure S3). The maximum swing angle in ZIF-90 conformation A is only 13° , while it reaches 92° in ZIF-90 conformation B. This is due to the different orientation of the adjacent linkers: in ZIF-90 conformation B, the upper two linkers are closed while the lower ones are opened (Figure S3). The linker swing motion can be understood from the electron density distribution (Figure 3). The =O terminal and -H terminal in aldehyde group are respectively electron-acceptor (negatively charged) and electron-donor (positively charged) sites. The -CH terminal in imidazolate ring is positively charged. In ZIF-90, the horizontal orientation of the aldehyde group can keep the upper two adjacent linkers opened owing to the steric effect (left in Figure 3). Once the aldehyde group rotates to the vertical orientation, the steric effect is weakened and the electronic effect becomes dominant. In ZIF-90 conformation A (middle in Figure 3), the negative =O terminal points down and attracts the lower two adjacent linkers (positive -CH terminal) to form a closed state as the original orientation. Meanwhile, the repulsive interaction between the positive -H terminal of aldehyde group and -CH terminal of imidazolate ring makes the upper two linkers to open. In ZIF-90 conformation B (right in Figure 3), as the negative =O terminal points up it attracts strongly the upper two adjacent linkers (positive -CH terminal); this can affect the orientation of other nearby linkers. As a result, the two upper linkers close and the lowers open. The central linker swings widely owing to the extrusion from the upper two closed linkers.

Figure 3. Electron density distribution of ZIF-90, conformation A and B.

Figure 4. Energy barrier for the rotation of one aldehyde group in ZIF-90 using the cluster model.

The energy for driving a large swing amplitude in ZIF-90 cluster model can reach up to 93.7 Kcal/mol (Figure 4). In this figure, the two transition states come from the highest energy structures in ZIF-90 conformation A and B cluster models. In the cluster model, the high energy barrier is attributed to the large swing amplitude and the number of involved linkers (seven in this model). When more linkers are involved in the swing motion, the driving energy from ZIF-90 to conformation A (conformation B) increases considerably. We computed the driving energy considering the swing motion of all

linkers in the periodic model (Figure 5): the required transformation energy results particularly large, reaching up to 585.4 Kcal/mol. Owing to this large value, the structure transformation between ZIF-90 and conformation A (conformation B) is actually difficult to occur under conventional conditions.

Figure 5. Energy barrier for the transformation from ZIF-90 to conformation A and B.

In previous experiments, ZIF-8 was usually considered as a candidate for investigating the linker swing motion. Kolokolov *et al.* found by means of ^2H NMR that the linkers of ZIF-8 exhibit two-site flips with amplitude of 17° with a very low activation barrier (0.36 Kcal/mol).²⁵ Also, the methyl group on the position 2 of the imidazolate ring was found to rotate quasi-freely.⁵² No relation was established between the linker swing and the terminal methyl rotation in ZIF-8. However, based on our calculations, ZIF-90 behaves that the terminal group rotation can directly induce the

linker swing motion. This difference is ascribed to (1) the asymmetric geometry of the aldehyde group and (2) to the high energy barrier (14.1 Kcal/mol) of the aldehyde rotation in ZIF-90. Thus, the internal relation between the terminal rotation and the linker swing in ZIF-90 is easily ascertained. Meanwhile, the swing motion in ZIF-90 is non-isolated: during the rotation of the aldehyde group, the asymmetric distributed negative charge on the aldehyde (Figure 3) can attract and repulse the adjacent linkers so that the high-amplitude swing motion spreads around the whole crystal structure. This phenomenon is rare in other ZIFs characterized by a symmetrical distributed charge on the terminal group. Furthermore, the structure transformation from ZIF-90 to conformation A (conformation B) is very difficult to occur, based on the computed large activation energy (585.4 Kcal/mol). However, this transformation is still possible to be realized with other ZIFs: a previous experiment has shown that the high-pressure phase of ZIF-8 can be obtained under the methanol/ethanol mixture solvent pressure of 1.47 GPa.¹³ Considering the low activation barrier of the single linker swing, the driving pressure for the ZIF-8 phase change is quite large. The higher activation barrier of the single linker swing in ZIF-90 will undoubtedly require much higher pressure to drive the transformation between ZIF-90 and conformation A (conformation B). This point actually can increase the ZIF-90 structure stability to some extent.

In addition, we computed the energy profile for the swing motion itself employing the lowest energy structure of ZIF-90 cluster (Figure 6). We found that the 35° swing angle of one linker in ZIF-90 requires an energy of ~6 Kcal/mol. While, the computed energy needed for the similar amplitude of one imidazolate linker swing motion in ZIF-8 is ~4 Kcal/mol.²⁶ The comparison of the linker swing motion in ZIF-90 and ZIF-8 has to

be further performed using the swing frequency, owing to the continuous swinging process and the dependence of energy value on the swing angle. The computed frequency of the linker swing in ZIF-90 cluster model is $\nu_{\text{swing}} = 67, 71$ and 79 cm^{-1} , which can be compared to the $\nu_{\text{swing}} = 60(\pm 10) \text{ cm}^{-1}$ in ZIF-8.²⁶ Among them, the frequency of 67 cm^{-1} can bring large swing amplitude in ZIF-90 (Linker Swing at frequency of 67 cm^{-1} .avi). In SALEM-2 (with SOD topology and unsubstituted imidazolate linker), the required energy for swing motion with the same amplitude is a mere 0.8 Kcal/mol .²⁶ It indicates that the functionalization of the linker can change its motion in ZIFs. This stabilization of ZIF-90 (compared to ZIF-8 and SALEM-2) can be attributed to the strong dispersive interactions between the terminal aldehyde groups and the neighboring windows, which restricts the linker swing motion. The “swing effects” in ZIF-90 are much more severe than in ZIF-8 and SALEM-2. The energy vs. swing angle is quadratic (Figure 6) and the energy barrier for one linker swing motion in ZIF-90 can be crossed over by the thermal vibration. Thus, the nature of the swing motion in ZIF-90 is still a soft vibration mode.

Figure 6. The system energy as a function of the dihedral angle C–N–Zn–N in ZIF-90 cluster model.

The linker swing motion and the following structure transformation in ZIF-90 can affect the adsorption of guest molecules. Although the ZIF-90 conformation A and B are high energy structures, the high guest pressure or the specified external field may stabilize them, according to the experiences in ZIF-8.^{13,33} Based on our model we predict the adsorption isotherms of H₂ and CH₄ in ZIF-90, conformation A and B (Figure 7). The adsorption of guest molecules in ZIF-90 conformation B is obviously the weakest, especially at high loading pressure values. This is ascribed to the decrease of the solvent accessible volume (SAV) in ZIF-90 conformation B (Table 1).

Table 1. The solvent accessible volume of ZIF-90 in three states. The CASTEP optimized frameworks were used in the computation.

	ZIF-90	Conformation A	Conformation B
Solvent accessible volume (SAV)	48.94%	46.70%	38.92%
SAV: Helium pore volume			

This computation was performed by using the poreblazer_v3.0.2 code.⁵³

Figure 7. GCMC-simulated single-component isotherms of H_2 and CH_4 (298 K) adsorption in ZIF-90, conformation A and B.

Conclusions

In conclusion, we found that the aldehyde terminal group rotation can drive the linker swing motion in ZIF-90. The energy barrier for single group rotation can reach up to 14.1 Kcal/mol. The asymmetric electron distribution on aldehyde group, attracting and

repulsing the adjacent linkers during the rotation, is found to be the main cause for the enhanced linker swing motion. Since the ZIF-90 structure transformation involves all the linkers to synergistically swing, it requires an extremely high activation energy (585.4 Kcal/mol). This type of structure transformation in guest-free ZIF-90 can be achieved by manipulating the orientation of the aldehyde group. We found that the 4-ring gate is closed in ZIF-90 conformation A (vertical orientation of aldehyde group with outer –H terminal in Figure 1) and the 6-ring gate is opened in ZIF-90 conformation B (vertical orientation of aldehyde group with outer =O terminal in Figure 1). Respect to ZIF-90, the adsorption of guest molecules was lower in both ZIF-90 conformation A and B, due to the reduction of the solvent accessible volume. Our study show the ability of ZIF-90 to precisely tuning the linker swing motion (gate structure) by the aldehyde group rotation in guest-free ZIF-90. The relation between the linker motion and other internal freedom in other MOF structures will also be investigated in future studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: The calculated energy values and unit cell parameters. The ZIF-90 cluster model. The optimized structures (CIF format) and input files for representation calculations. Linker Swing at frequency of 67 cm⁻¹.avi: Video of the ZIF-90 linker swing motion at the frequency of 67 cm⁻¹.

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Notes

The authors declare no competing financial interest.

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