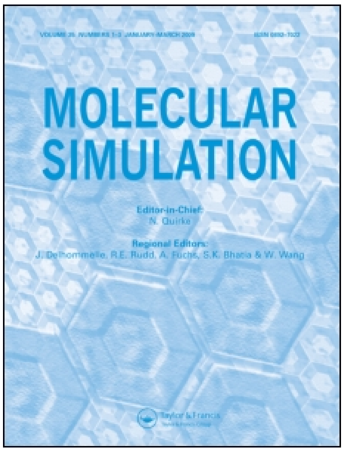
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Adsorption of methane in heterometallic metal-organic frameworks with anions: a molecular simulation study

Dahuan Liu[a]; Qingyuan Yang[a]; Chongli Zhong[a]
[a] Laboratory of Computational Chemistry, Department of Chemical Engineering, Beijing University of Chemical Technology, Beijing, People's Republic of China

To cite this Article Liu, Dahuan , Yang, Qingyuan and Zhong, Chongli(2009) 'Adsorption of methane in heterometallic metal-organic frameworks with anions: a molecular simulation study', Molecular Simulation, 35: 3, 213 — 219

To link to this Article: DOI: 10.1080/08927020802412644

URL: http://dx.doi.org/10.1080/08927020802412644

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation
Vol. 35, No. 3, March 2009, 213–219

Adsorption of methane in heterometallic metal-organic frameworks with anions: a molecular simulation study

Dahuan Liu, Qingyuan Yang* and Chongli Zhong

Laboratory of Computational Chemistry, Department of Chemical Engineering, Beijing University of Chemical Technology, Beijing, People's Republic of China

(*Received 17 June 2008; final version received 16 August 2008*)

In this work, grand canonical Monte Carlo (GCMC) simulation was performed to study the adsorption of methane in novel heterometallic metal-organic frameworks (MOFs). The results show that the anions play a significant role in the methane adsorption behaviour in heterometallic MOFs, and are the preferential adsorption sites at low pressure. However, this kind of priority is not pronounced at high pressure. Methane was adsorbed closer to the linking units containing Ag atoms than to the bridging structures containing Fe atoms. Based on the simulations, this work indicates that an appropriate selection of anions at a given pressure may control the methane adsorption sites in heterometallic MOFs, which is useful for understanding the function of these novel porous materials in practical applications.

Keywords: adsorption; anion; heterometallic metal-organic framework; methane; simulation

1. Introduction

Metal-organic frameworks (MOFs) have received widespread interest due to the extraordinary combination of high internal surface area and chemical tunability [1,2]. These kinds of porous materials are found to be particularly useful in gas storage [3–5], separation [6,7] and heterogeneous catalysis [8–10]. The present studies have indicated that the continuing challenges in the field of MOFs are the topology prediction of a MOF based on the structure of precursors [2,11], as well as the introduction of complex functionality [1,12]. Recently, a novel class of MOFs, heterometallic MOFs, has been synthesised using 'metalloligands' as building blocks in lieu of simple organic ligands [1]. This attractive strategy can give rise to extended materials with a variety of predictable structures and rich physical properties [13,14]. Considering the potential applications of heterometallic MOFs as catalysts or functional materials, it is important to understand gas adsorption behaviour in the pores of these MOFs. However, to date, heterometallic MOFs have been received much less attention compared to the monometallic ones, especially in their applications [15]. In our previous work [16–18], molecular simulation has been performed for gas adsorptions in monometallic MOFs, and in the present work, it was extended to heterometallic MOFs. Considering that methane is one of the key molecules in petrochemical industries, and it is in connection with energy problems strategically, we chose methane as a probe molecule in this work to explore the gas adsorption behaviour in heterometallic MOFs.

2. Models and computational method

2.1 Structures of the heterometallic MOFs studied

In the present study, six heterometallic MOFs, MOF-Fe/$AgBF_4$-1, MOF-Fe/$AgPF_6$-1, MOF-Fe/$AgSbF_6$-1, MOF-Co/$AgBF_4$-1, MOF-Co/$AgPF_6$-1 and MOF-Co/$AgSbF_6$-1, synthesised by Cohen et al. [13,14] were adopted as representatives of heterometallic MOFs. The crystal structures of these MOFs were built from their X-ray diffraction data [13,14] using Materials Visualizer [19] (Figure 1). As shown in Figure 1, for these materials, 'metalloligands' containing Ag were used as the building block in lieu of simple organic ligands, introducing another kind of metal in addition to the core metal Fe in tris(dipyrrinato) complexes as the bridging structure. Details of the structural properties for these heterometallic MOFs are summarised in Table 1. The accessible surface area (S_{acc}) and total free volume (V_{free}) of each MOF material were estimated using the 'Atoms Volume & Surfaces' calculation within the Materials Studio® package. Because of the high dependency on adsorbate size, the former was calculated by a probe molecule with the diameter equal to the kinetic diameter of CH_4 (3.73 Å), while a probe size of 0.0 Å was applied to determine the total free volume not occupied by the framework atoms.

2.2 Force fields

In this work, CH_4 molecule was represented as a spherical Lennard-Jones (LJ) interaction site, for which the potential parameters were taken from the TraPPE force field

---

*Corresponding author. Email: qyyang@mail.buct.edu.cn

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020802412644
http://www.informaworld.com

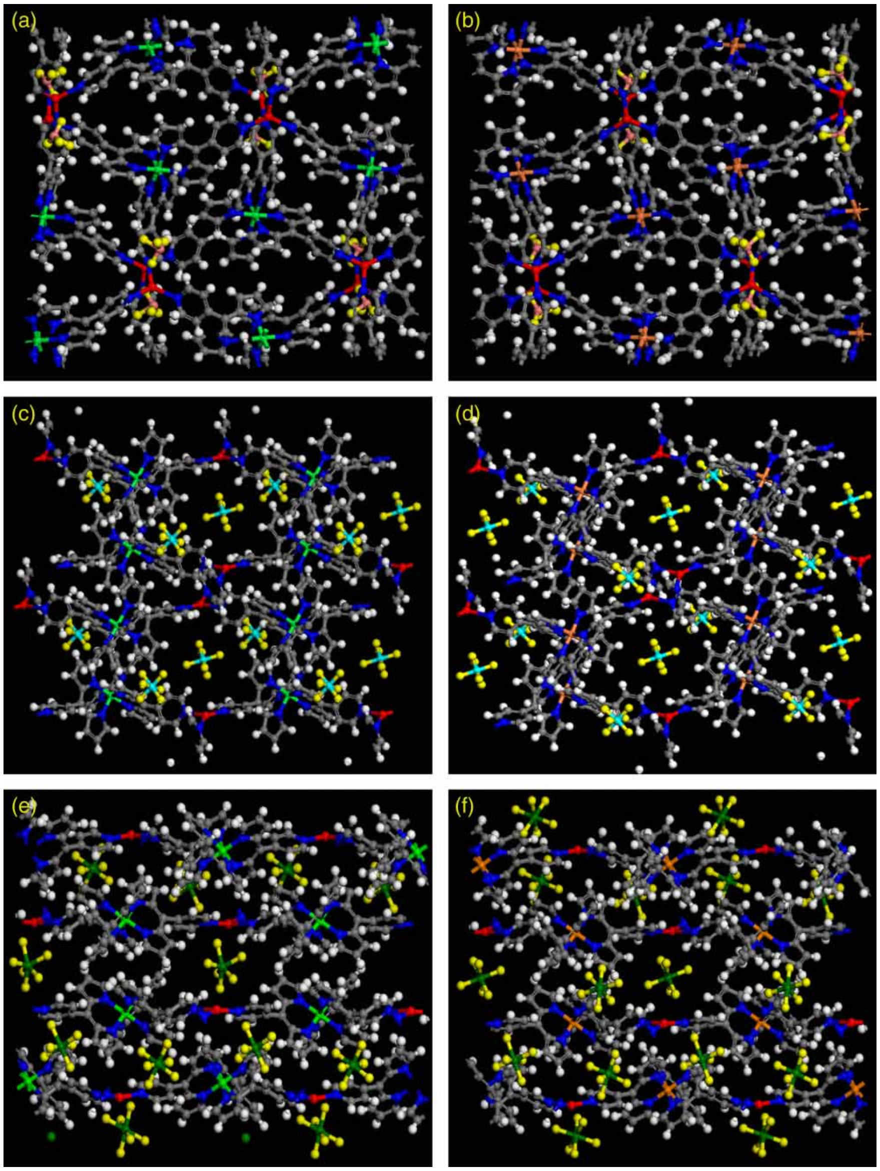


Figure 1. Crystal structures of heterometallic MOFs used in the simulation: (a) MOF-Fe/$AgBF_4$-1, (b) MOF-Co/$AgBF_4$-1, (c) MOF-Fe/$AgPF_6$-1, (d) MOF-Co/$AgPF_6$-1, (e) MOF-Fe/$AgSbF_6$-1, (f) MOF-Co/$AgSbF_6$-1 (Fe, light green; Ag, red; Co, orange; B, pink; P, cyan; F, yellow; Sb, dark green; N, blue; C, grey; H, white).

Table 1. Properties of the heterometallic MOF materials studied in this work.

Materials	Unit cell[a] (Å)	ρ_{crsy}[a] (g/cm^3)	S_{acc}[b] (m^2/g)	V_{free}[b] (cm^3/g)
MOF-Fe/$AgBF_4$-1	$a = 26.959$, $b = 12.309$, $c = 33.493$	1.089	636.9	0.472
MOF-Co/$AgBF_4$-1	$a = 33.410$, $b = 26.932$, $c = 12.365$	1.044	774.2	0.473
MOF-Fe/$AgPF_6$-1	$a = 13.089$, $b = 16.265$, $c = 16.105$	1.139	591.2	0.412
MOF-Co/$AgPF_6$-1	$a = 13.120$, $b = 16.111$, $c = 16.134$	1.144	611.6	0.417
MOF-Fe/$AgSbF_6$-1	$a = 15.874$, $b = 24.606$, $c = 16.377$	1.100	683.0	0.365
MOF-Co/$AgSbF_6$-1	$a = 15.7911$, $b = 25.454$, $c = 16.378$	1.112	603.0	0.373

[a] Obtained from the XRD crystal data [13,14].
[b] Calculated with the Materials Studio package [19].

Table 2. LJ potential parameters for CH_4 and the MOFs used in this work.

	LJ parameters	
Atoms	σ (Å)	ε/k_B (K)
CH_4	3.73	148.0
MOF-Fe	2.59	6.54
MOF-Ag	2.80	18.12
MOF-Co	2.56	7.05
MOF-C	3.43	52.84
MOF-N	3.26	34.72
MOF-B	3.64	90.58
MOF-P	3.69	153.50
MOF-Sb	3.94	225.90
MOF-F	3.00	25.16
MOF-H	2.57	22.14

developed by Martin and Siepmann [20], as listed in Table 2. This force field has been successfully used to simulate the adsorption of CH_4 in MOFs [18,21,22]. For the heterometallic MOFs studied here, an atomistic representation was used to model all of them. The site–site LJ potential was also used to calculate the interactions between the adsorbate molecules and the atoms in adsorbents. The potential parameters were taken from the universal force field (UFF) of Rappé et al. [23] (Table 2), which has been successfully employed to depict the adsorption [24,25], diffusion [26,27] and separation [28,29] of several light gases and their mixtures in MOFs. The TraPPE force field for methane in combination with the UFF for the atoms in frameworks has been proved to be able to obtain the simulation results that are in good agreement with the experiment [21], and this kind of force field is successfully used to study the adsorption and diffusion of methane within MOFs [27,29]. In our simulations, all the LJ cross-interaction parameters were determined by the Lorentz–Berthelot mixing rules.

2.3 *Grand canonical Monte Carlo (GCMC) simulation*

In this work, conventional GCMC simulation was performed to calculate the adsorption of CH_4 in all heterometallic MOFs at 298 K. Details of this method can be found elsewhere [30]. The chemical potentials needed in the GCMC simulations were calculated from isobaric–isothermal (NPT) ensemble Monte Carlo simulations of bulk gas using the test-particle insertion method. Based on the simulated chemical potentials at various pressures, the relationships between pressures and chemical potentials were established to convert pressures to chemical potentials, and vice versa. The simulation box contained 3 ($1 \times 3 \times 1$), 3 ($1 \times 1 \times 3$), 12 ($3 \times 2 \times 2$), 12($3 \times 2 \times 2$), 8 ($2 \times 2 \times 2$) and 8 ($2 \times 2 \times 2$) unit cells for the six heterometallic MOFs (MOF-Fe/$AgBF_4$-1, MOF-Co/$AgBF_4$-1, MOF-Fe/$AgPF_6$-1, MOF-Co/$AgPF_6$-1, MOF-Fe/$AgSbF_6$-1 and MOF-Co/$AgSbF_6$-1), respectively. The simulations with larger boxes showed that no finite-size effects existed using the above boxes. Similar to previous works [16–18,26–29], all the MOFs were treated as rigid with atoms frozen at their crystallographic positions during simulations. In addition, as an initial study, the positions of the anions BF_4^-, PF_6^- and SbF_6^- in the crystal structures of MOFs were also kept fixed. Periodic boundary conditions were applied in all three dimensions. A cut-off radius was set to 12.8 Å for the LJ interactions. As done in our previous work [16,17], to increase the computational efficiency, the potential energies between the adsorbate and the adsorbent were initially tabulated on a series of three-dimensional grid points with a grid spacing of 0.15 Å. During the simulations, the potential energy at any position in the adsorbent was determined by interpolation [31]. Interpolation with such grid spacing has been proven to be able to greatly increase the computational efficiency over the direct pairwise summation of the adsorbate–adsorbent interaction and the accuracy of the potential energy was preserved less than 0.4% [32]. For each state point, GCMC simulation consisted of 1.0×10^7 steps to guarantee the equilibration, followed by 1.0×10^7 steps to sample the desired thermodynamic properties.

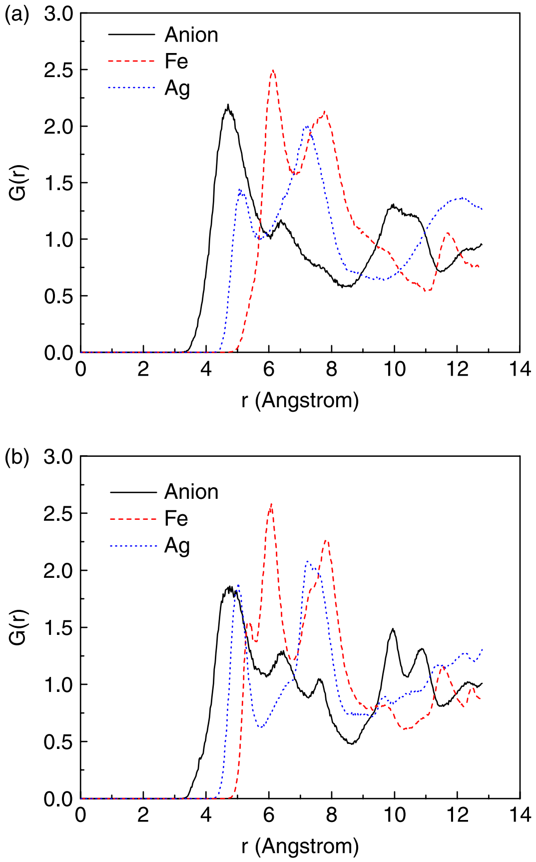


Figure 2. Radial distribution functions between the adsorbate molecules and the different atoms in MOF-Fe/$AgBF_4$-1 at two pressures: (a) $P = 0.1$ MPa, and (b) $P = 3.0$ MPa.

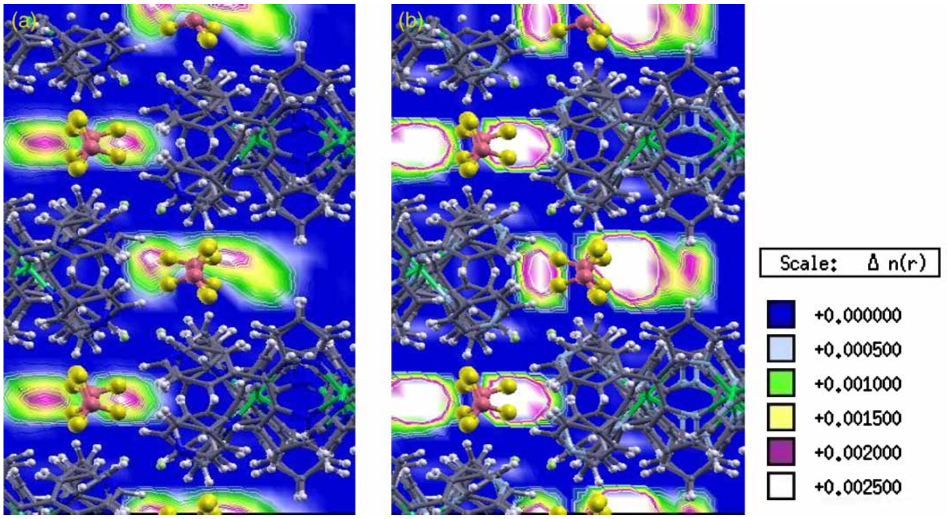


Figure 3. Probability distribution plots of COM probability density in planes through the anion area in MOF-Fe/$AgBF_4$-1 (anions, large balls; not anions, small balls): (a) $P = 0.1$ MPa, and (b) $P = 3.0$ MPa.

3. Results and discussion

3.1 *Preferential adsorption sites in heterometallic MOFs*

To investigate the adsorption sites in heterometallic MOFs, GCMC simulations were performed for CH_4 adsorption at 298 K in the six MOFs. As the first step, we take MOF-Fe/$AgBF_4$-1 as an example, and the radial distribution functions $G(r)$ of the adsorbate molecules from the different kinds of atoms were calculated. Considering that the metal sites are very important to the practical applications of MOFs, especially in catalysis [10], and the studies on monometallic MOFs have indicated that the metal-oxide cluster is primarily responsible for the adsorption of gas molecules [33], only the radial distribution functions of CH_4 from the metal atoms (Ag and Fe) as well as the anions were listed in Figure 2. As can be seen from Figure 2(a), at $P = 0.1$ MPa, CH_4 molecules are adsorbed closer to the anions than to the Ag and Fe atoms by comparing the positions of the first peak of $G(r)$, which is mainly due to the stronger interaction strength with the anions. The other peaks of $G(r)$ including the first peak of Fe may be caused by the effect of the accumulation of CH_4 around the other atoms, since the positions are far from the core atoms. With the increase in pressure, CH_4 molecules are still accumulated closer to the anions, while the density is not larger than those around the Fe and Ag atoms as shown in Figure 2(b). It can be attributed to the fact that at high pressure, the pore volume began to play an important role in the adsorption instead of interaction, and more and more adsorbate molecules were adsorbed in the pore area and not around the anions. The similar situations were found in other heterometallic MOFs considered in this work. This indicates that the anions are the preferential adsorption sites especially at low pressure, but the priority becomes less evident at high pressure. From Figure 2, it can be found that the metal atoms play a secondary role for CH_4 adsorption. It is worth noting that CH_4 gathered closer to the Ag atoms than to the Fe atoms, and the density around the Ag atoms changed more than that around the Fe atoms with increasing pressure. This may be because that the Ag atoms serve to link the ‘metalloligands’, which allow for a stronger interaction strength with CH_4, leading to more opportunities to contact the adsorbate when compared to the Fe atoms, which are buried in the cores of the metalloligands. By studying the $G(r)$ in the other heterometallic MOFs, it may be concluded that the linking unit containing the Ag atoms play more important roles in the CH_4 adsorption than the bridging unit containing the Fe atoms.

In order to exhibit the adsorption sites inside the heterometallic MOFs more intuitively and credibly, centre of mass (COM) probability distributions of CH_4 at different pressures were calculated on the basis of all of the configurations recorded during the Monte Carlo simulations, and the results are shown in Figure 3. Obviously, at low pressure, CH_4 molecules are mainly adsorbed around the anions, with a slight accumulation in other regions in the pores; while at high pressure, the situation is a little different with more and more CH_4 molecules beginning to distribute in the area not around the anions. This confirms that the anion plays an important role in offering the preferential site to the CH_4 adsorption in heterometallic MOFs, especially at low pressure.

3.2 *The effect of the anions on the adsorption sites*

To understand the effect of the anions on the CH_4 adsorption sites, we examine the adsorption behaviours of CH_4 in three heterometallic MOFs with the different

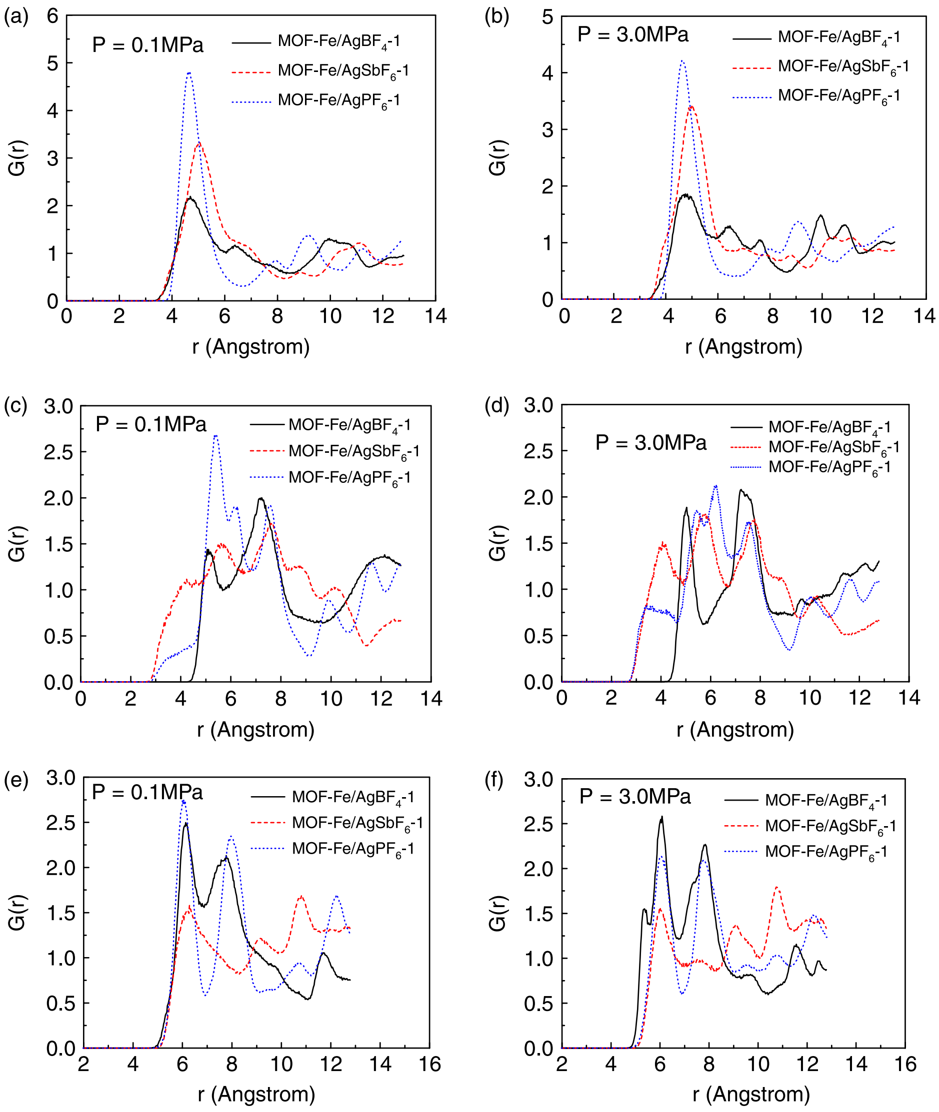


Figure 4. Radial distribution functions between the adsorbate molecules and atoms in heterometallic MOFs with different anions: (a, b) anions, (c, d) Ag atoms, and (e, f) Fe atoms.

anions and the same metal atoms (MOF-Fe/AgBF$_4$-1, MOF-Fe/AgPF$_6$-1 and MOF-Fe/AgSbF$_6$-1). A comparison among the radial distribution functions of the adsorbate in materials with different anions was made by taking anions and metal atoms as representative atoms, and the results are listed in Figure 4. It was observed that CH$_4$ molecules were accumulated at nearly similar distance around the anions. With the increase in pressure, the main accumulation distances of CH$_4$ were not changed too much as shown in Figure 4(a),(b). This indicates that CH$_4$ has already been located around the anions at low pressure, and the increase in pressure does not influence the adsorption distances of the adsorbate in this area greatly. On the other hand, different anions induced the CH$_4$ molecules mainly gathered around the Ag atoms at different distances (Figure 4(c),(d)), since the Ag atoms are located in the linking unit in the heterometallic MOFs and have more occasions to contact the adsorbate. In the heterometallic MOFs with PF_6^- and SbF_6^-, the adsorption distances of the adsorbate from the Ag atoms are similar, and are both shorter than that in materials with BF_4^-, which may be related to the different adsorption amounts in different materials. With the increase in pressure, more and more CH$_4$ were accumulated closer to the Ag atoms, which is consistent with the finding in Figure 3 that high pressure leads to the distribution of CH$_4$ molecules in the pore area and not around the anions. As far as the third adsorption sites are concerned, CH$_4$ molecules are adsorbed at nearly the same distance from the Fe atoms in the heterometallic MOFs with different anions (Figure 4(e),(f)), because they are all located in the cores of tris(dipyrrinato) coordination complexes and are farther

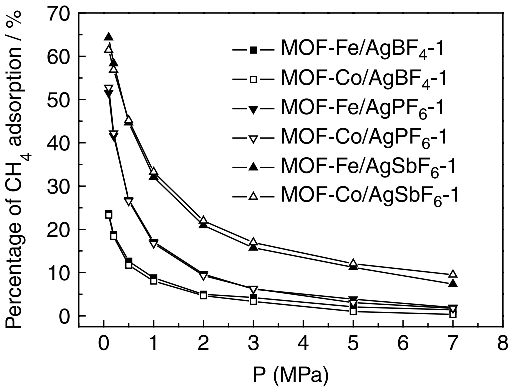


Figure 5. Percentage contributions of the interactions of CH_4 with anions to its adsorption, as a function of bulk pressure.

from the adsorbate than the other kinds of adsorption sites. It is worth noting that with the increase in pressure, there is little change in the accumulation of CH_4 around the Fe atoms, except for the materials with BF_4^-, where CH_4 molecules are gathered closer to the Fe atoms at high pressure. Combining with the values in Table 1, the reason may be that the heterometallic MOFs with BF_4^- have the largest free volume, improving the CH_4 accumulations in the pores at high pressure. Since the free volume is related to the topology of heterometallic MOFs, which can be controlled by the anions [14], the anions have a significant effect on the CH_4 adsorption in this class of materials. In addition, the radial distribution functions of the adsorbate in heterometallic MOFs with the different core metal atoms (Fe and Co) and the same anions were also examined, and it was found that there are no evident differences.

3.3 The effect of the anions on the CH_4 adsorption

According to the above results, it is useful to further study the effect of the anions on the CH_4 adsorption. To do this, GCMC simulations were further performed for the six heterometallic MOFs by switching off the interactions between the CH_4 molecules and the anions. In order to study the role of the interactions of anions quantitatively, the contributions of the anions in terms of percentage of the CH_4 adsorption are calculated by considering the change in adsorption amounts, as shown in Figure 5. Depending on the chemical composition of the framework and the anions, the contribution of the anions can be as large as 65% at low pressures, and the contribution becomes less evident with increasing pressures; this indicates that the CH_4 adsorption of heterometallic MOFs at low pressure can be attributed largely to the interactions of the anions. However, although the presence of the anions provides the preferential adsorption sites, they reduce the free volume as well as increase the weight per unit volume of the material. Therefore, at high pressure, the contribution of the presence of the anions may be negative, which has been observed in other porous materials such as zeolites [34–37]. Furthermore, Figure 5 also shows that the contributions of the same type of anions on the CH_4 adsorption are similar in heterometallic MOFs with the different core metal atoms.

4. Conclusion

In conclusion, CH_4 adsorption in novel heterometallic MOFs was investigated using GCMC simulations in this work. The results showed that CH_4 molecules tended to accumulate around the anions at low pressure. At high pressure, however, the preferential adsorption around anions is not pronounced. CH_4 molecules were gathered closer to the linking units containing the Ag atoms than to the bridging structures containing the Fe atoms. In addition, this work shows that the anions play an important role in the CH_4 adsorption of heterometallic MOFs, while the effect of the core metal atoms (Fe and Co) was generally found to be negligible. Therefore, an appropriate selection of anions at a given pressure can lead to the control of the adsorbate adsorption sites in heterometallic MOFs, which may be useful for the practical applications of these novel porous materials, such as in the field of catalyst. Based on the results obtained in this work, it would be interesting to further investigate the other applications of these novel heterometallic MOFs, including gas separations.

Acknowledgements

The financial supports of the National Natural Science Foundation of China (nos. 20725622 and 20706002) are greatly appreciated.

References

[1] S. Kitagawa, R. Kitaura, and S. Noro, *Functional porous coordination polymers*, Angew. Chem. Int. Ed. 43 (2004), pp. 2334–2375.

[2] G. Férey, *Hybrid porous solids: past, present, future*, Chem. Soc. Rev. 37 (2008), pp. 191–214.

[3] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O.M. Yaghi, *Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage*, Science 295 (2002), pp. 469–472.

[4] A.G. Wong-Foy, A.J. Matzger, and O.M. Yaghi, *Exceptional H_2 saturation uptake in microporous metal-organic frameworks*, J. Am. Chem. Soc. 128 (2006), pp. 3494–3495.

[5] S.S. Kaye, A. Dailly, O.M. Yaghi, and J.R. Long, *Impact of preparation and handling on the hydrogen storage properties of Zn_4O(1,4-benzenedicarboxylate)$_3$ (MOF-5)*, J. Am. Chem. Soc. 129 (2007), pp. 14176–14177.

[6] D. Bradshaw, T.J. Prior, E.J. Cussen, J.B. Claridge, and M.J. Rosseinsky, *Permanent microporosity and enantioselective sorption in a chiral open framework*, J. Am. Chem. Soc. 126 (2004), pp. 6106–6114.

[7] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R.V. Belosludov, T.C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, and Y. Mita, *Highly controlled acetylene accommodation in a metal-organic microporous material*, Nature 436 (2005), pp. 238–241.

[8] D.N. Dybtsev, A.L. Nuzhdin, H. Chun, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, and K. Kim, *A homochiral metal-organic material with permanent porosity, enantioselective sorption properties, and catalytic activity*, Angew. Chem. Int. Ed. 45 (2006), pp. 916–920.

[9] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, and S. Kitagawa, *Three-dimensional porous coordination polymer functionalized with amide groups based on tridentate ligand: Selective sorption and catalysis*, J. Am. Chem. Soc. 129 (2007), pp. 2607–2614.

[10] S. Horike, M. Dincă, K. Tamaki, and J.R. Long, *Size-selective Lewis acid catalysis in a microporous metal-organic framework with exposed* Mn^{2+} *coordination sites*, J. Am. Chem. Soc. 130 (2008), pp. 5854–5855.

[11] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, and O.M. Yaghi, *Reticular chemistry: occurrence and taxonomy of nets and grammar for the design of frameworks*, Acc. Chem. Res. 38 (2005), pp. 176–182.

[12] J.T. Hupp and K.R. Poeppelmeier, *Better living through nanopore chemistry*, Science 309 (2005), pp. 2008–2009.

[13] S.R. Halper and S.M. Cohen, *Heterometallic metal-organic frameworks based on tris(dipyrrinato) coordination complexes*, Inorg. Chem. 44 (2005), pp. 486–488.

[14] S.R. Halper, L. Do, J.R. Stork, and S.M. Cohen, *Topological control in heterometallic metal-organic frameworks by anion templating and metalloligand design*, J. Am. Chem. Soc. 128 (2006), pp. 15255–15268.

[15] Y. Wang, P. Cheng, J. Chen, D.-Z. Liao, and S.-P. Yan, *A heterometallic porous material for hydrogen adsorption*, Inorg. Chem. 46 (2007), pp. 4530–4534.

[16] Q. Yang and C. Zhong, *Molecular simulation of adsorption and diffusion of hydrogen in metal-organic frameworks*, J. Phys. Chem. B 109 (2005), pp. 11862–11864.

[17] Q. Yang and C. Zhong, *Understanding hydrogen adsorption in metal-organic frameworks with open metal sites: A computational study*, J. Phys. Chem. B 110 (2006), pp. 655–658.

[18] Q. Yang and C. Zhong, *Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks*, J. Phys. Chem. B 110 (2006), pp. 17776–17783.

[19] Accelrys, Inc., *Materials Studio, 3.0 V*, Accelrys Inc., San Diego, CA, 2003.

[20] M.G. Martin and J.I. Siepmann, *Transferable potentials for phase equilibria. 1. united-atom description of* n-*alkanes*, J. Phys. Chem. B 102 (1998), pp. 2569–2577.

[21] T. Düren, L. Sarkisov, O.M. Yaghi, and R.Q. Snurr, *Design of new materials for methane storage*, Langmuir 20 (2004), pp. 2683–2689.

[22] S. Wang, *Comparative molecular simulation study of methane adsorption in metal-organic frameworks*, Energ. Fuel. 21 (2007), pp. 953–956.

[23] A.K. Rappé, C.J. Casewit, K.S. Colwell, W.A. Goddard, III, and W.M. Skiff, *UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations*, J. Am. Chem. Soc. 114 (1992), pp. 10024–10035.

[24] G. Garberoglio, A.I. Skoulidas, and J.K. Johnson, *Adsorption of gases in metal organic materials: comparison of simulations and experiments*, J. Phys. Chem. B 109 (2005), pp. 13094–13103.

[25] V. Krungleviciute, K. Lask, L. Heroux, A.D. Migone, J.-Y. Lee, J. Li, and A. Skoulidas, *Argon adsorption on* $Cu_3(\text{Benzene-1,3,5-tricarboxylate})_2(H_2O)_3$ *metal-organic framework*, Langmuir 23 (2007), pp. 3106–3109.

[26] A.I. Skoulidas and D.S. Sholl, *Self-diffusion and transport diffusion of light gases in metal-organic framework materials assessed using molecular dynamics simulations*, J. Phys. Chem. B 109 (2005), pp. 15760–15768.

[27] Y.H. Jhon, M. Cho, H.R. Jeon, I. Park, R. Chang, J.L.C. Rowsell, and J. Kim, *Simulations of methane adsorption and diffusion within alkoxy-functionalized IRMOFs exhibiting severely disordered crystal structures*, J. Phys. Chem. C 111 (2007), pp. 16618–16625.

[28] S. Keskin and D.S. Sholl, *Screening metal-organic framework materials for membrane-based methane/carbon dioxide separations*, J. Phys. Chem. C 111 (2007), pp. 14055–14059.

[29] B. Liu, Q. Yang, C. Xue, C. Zhong, B. Chen, and B. Smit, *Enhanced adsorption selectivity of hydrogen/methane mixtures in metal-organic frameworks with interpenetration: A molecular simulation study*, J. Phys. Chem. C 112 (2008), pp. 9854–9860.

[30] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, San Diego, CA, 2002.

[31] Q. Yang and C. Zhong, *Electrostatic-field-induced enhancement of gas mixture separation in metal-organic frameworks: a computational study*, ChemPhysChem. 7 (2006), pp. 1417–1421.

[32] B. Smit and J.I. Siepmann, *Computer simulations of the energetics and siting of* n-*alkanes in zeolites*, J. Phys. Chem. 98 (1994), pp. 8442–8452.

[33] T. Yildirim and M.R. Hartman, *Direct observation of hydrogen adsorption sites and nanocage formation in metal-organic frameworks*, Phys. Rev. Lett. 95 (2005), pp. 215504-1-4.

[34] A.B. Pinar, L. Gomez-Hortiguela, and J. Perez-Pariente, *Cooperative structure directing role of the cage-forming tetramethylammonium cation and the bulkier benzylmethylpyrrolidinium in the synthesis of zeolite ferrierite*, Chem. Mater. 19 (2007), pp. 5617–5626.

[35] Y. Lee, H.H. Lee, D.R. Lee, T.J. Shin, J.-Y. Choi, and C.-C. Kao, *Cation-dependent compression behavior in low-silica zeolite-X*, J. Am. Chem. Soc. 129 (2007), pp. 4888–4889.

[36] M. Alvaro, J.F. Cabeza, D. Fabuel, H. Garcia, E. Guijarro, and J.L. Martinez de Juan, *Electrical conductivity of zeolite films: Influence of charge balancing cations and crystal structure*, Chem. Mater. 18 (2006), pp. 26–33.

[37] S. Calero, D. Dubbeldam, R. Krishna, B. Smit, T.J.H. Vlugt, J.F.M. Denayer, J.A. Martens, and T.L.M. Maesen, *Understanding the role of sodium during adsorption: A force field for alkanes in sodium-exchanged faujasites*, J. Am. Chem. Soc. 126 (2004), pp. 11377–11386.