โครงการ

การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ การดูดซับและการแพร่ของ H_2 , N_2 และ H_2 / N_2 ในวัสดุโครงข่ายโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์-67 โดยการคำนวณทางคอมพิวเตอร์ขั้นสูง

Adsorption and diffusion of H_2 , N_2 and H_2 / N_2 in Zeolitic Imidazolate Framework-67 by advanced computational calculations

ชื่อนิสิต นางสาวชนัญชิดา กันศิริ

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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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By

Miss Chanunchida Kunsiri

A Report Submitted is a Partial Fulfillment of the Requirements
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ชื่อโครงการ การดูดซับและการแพร่ของ H_2 , N_2 และ H_2 / N_2 ในวัสดุโครงข่ายโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์-67 โดยการคำนวณทางคอมพิวเตอร์ขั้นสูง

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บทคัดย่อ

ZIF-67 (Zeolite Imidazolate Frameworks-67) เป็นวัสดุชนิดเลีนยแบบซีโอไลต์ที่มีโครงข่ายรูพรุนชนิดหนึ่งซึ่งใช้เป็นตัวเร่งปฏิกิริยาเคมี, วัสดุกักเก็บแก๊ส และใช้ในกระบวนการแยกแก๊ส ZIF-67ประกอบด้วยโลหะโคบอลต์ (Co) เชื่อมต่อกับสารอินทรีย์เมทิลอิมิดาโซลเลท (MeIM) งานวิจัยนี้ใช้เทคนิคการจำลองแบบกิบบส์อองซอมเบิลมอนติคาร์โล และการจำลองแบบทางพลวัติ ศึกษาพฤติกรรมการดูดซับและการแพร่ของแก๊สเดี่ยว H_2 และ N_2 และแก๊สผสม H_2/N_2 ที่ 3 อุณหภูมิ ผลไอโซเทอร์มการดูดซับ ที่ได้จากการจำลองนี้แสดงให้เห็นว่า ZIF-67 สามารถดูดซับ N_2 ได้มากกว่า H_2 และปริมาณการดูดซับจะลดลงเมื่ออุณหภูมิเพิ่มขึ้น และชุดพารามิเตอร์ของโคบอลต์ที่แตกต่างกันไม่ส่งผลต่อการดูดซับอย่างมีนัยสำคัญ จากค่าการคำนวณฟังก์ชันการกระจายเชิงรัศมี ตำแหน่งดูดซับที่ชอบของแก๊ส H_2 และ N_2 อยู่ที่บริเวณส่วนเชื่อมต่ออินทรีย์ ซึ่ง N_2 เกาะยึดได้ดีกว่า H_2 เพื่อศึกษาพฤติกรรมเชิงพลวัติของโมเลกุลแก๊สในวัสดุนี้ ซึ่งได้มีการคำนวณค่าสัมประสิทธิ์การแพร่ในตัวเองของแก๊ส พบว่าค่าสัมประสิทธิ์การแพร่ในตัวเองของ N_2 น้อยกว่าค่าสัมประสิทธิ์การแพร่ในตัวเองของ H_2 นั่นหมายความว่า N_2 เคลื่อนที่ได้ช้ากว่า H_2 ทำให้สรุปได้ว่า ZIF-67 มีความเหมาะสมในการคัดแยกแก๊ส H_2 จาก N_2

คำสำคัญ: วัสดุโลหะอินทรีย์ชนิดเลียนแบบซีโอไลต์-67, การดูดซับ, การแพร่, การคำนวณด้วยคอมพิวเตอร์ขั้นสูง

Project Title Adsorption and diffusion of H_2 , N_2 and H_2 / N_2 in Zeolitic Imidazolate Framework-67 by advanced computational calculations
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Abstract

ZIF-67 (Zeolitic Imidazolate Framework-67) is a class of porous materials which have applications as catalysis, gas storage and gas separation. ZIF-67 consists of Cobalt (Co) connected to Methylimidazolate (MeIM). In this work, Gibbs Ensemble Monte Carlo (GEMC) simulations and Molecular Dynamics (MD) simulations were carried out to study adsorption behavior, structural and dynamics properties of Hydrogen (H_2) and Nitrogen (N_2) in ZIF-67 at three temperatures. The adsorption isotherms results indicate that ZIF-67 can adsorb N_2 in higher amount than H_2. The amount adsorbed decreases with the increase in temperatures. The different sets of Co force field parameters do not significantly affect the gas adsorption, except at lower temperatures. From the Radial Distribution Functions (RDFs), the preferential adsorption site for H_2 and N_2 is around the organic linker zone. N_2 binds stronger than H_2. In order to observe the dynamics behavior of gases, the self-diffusion (D_s) was calculated. It was found that D_s of N_2 is the lower than D_s of H_2. That means N_2 moves slower than H_2. Finally, it can be concluded that ZIF-67 is well suited to separate H_2 from N_2.

Keywords: Zeolitic Imidazolate Framework-67, Adsorption, Diffusion, Computational Calculations

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I would like to gratefully and sincerely thank my advisor, Professor Dr. Supot Hannongbua and my co-advisor, Assistant Professor Dr. Tatiya Chokbunpiam for not only teaching, giving a useful guidance but also encouraging me during the time of my project. I would also like to thank Priv.-Doz. Dr. rer. nat. habil. Siegfried Fritzsche and Assistant Professor Dr. Tawun Remsungnen for giving several suggestions and helping me improve my project.

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Chapter 1

Introduction

1.1 Background of this study

Currently, the world's energy demand rises. Hydrogen (H_2) is used as alternative energy for a limited volume and no pollution after using. Energy from H_2 is considered to be energy efficient, clean and environmentally friendly. At the same time, Nitrogen (N_2) is another type of gas that plays an important role in the petrochemical industry which increase the yield and efficiency of the oil. For this reason, porous materials that have been researched and developed to separate and store gas are Zeolites and Metal Organic Frameworks (MOFs) [1].

In recent years, Zeolite Imidazolate Frameworks (ZIF) have been discovered as metal-organic materials. This is a compound with similar properties to zeolite in terms of stability and similar to the organic metal network material in terms of the ability to modify a variety of structural easily. It also has several outstanding properties, such as strong structure, flexibility, high surface area and can resist heat. This material is used in the industry as a catalyst, gas storage container and in the gas separation process [2], [3], [4].

In 2012, Quen *et al.* [5] have synthesized ZIF-67 for the first time in aqueous solutions at room temperature. They found that ZIF-67 were highly stable up to 350°C. In 2017, Verpoort *et al.* [6] reported that the ZIF-67 was developed from ZIF-8. It consists of Cobalt (Co) connected to Methylimidazolate (MeIM) set to strong crystalline structure, high temperature stability and higher specificity for gas storage than ZIF-8. In addition, Economou *et al.* [7] confirmed that ZIF-67 separated gas better than ZIF-8 for propylene/propane.

This work is interested to studying the behavior of H_2 and N_2 and H_2/ N_2 gas mixture in ZIF-67. This method can provide information on molecular structure and interaction which is difficult to test experimentally. It also reduces the cost of the experiment. In addition, the knowledge gained will be beneficial for the design and development of ZIF to be effective and suitable for further industrial applications.

1.2 Objectives of this study

To study the adsorption behavior of H_2, N_2 and H_2 / N_2 gas mixture in the ZIF-67 using Gibbs Ensemble Monte Carlo (GEMC) simulations and Molecular Dynamics (MD) simulations and to study the structural and dynamic properties.

1.3 Benefits of this study

To understand gas storage of H_2, N_2 and gas separation of H_2 / N_2 mixture in the Zeolitic Imidazolate Framework-67.

1.4 Zeolitic Imidazolate Framework-67 (ZIF-67)

ZIF-67 is comprised of Co^{2+} metal ions and 2-methylimidazole. Its structure is applied from ZIF-8 structure by replacing Zn metal atom with Co^{2+} as shown in Fig.1.

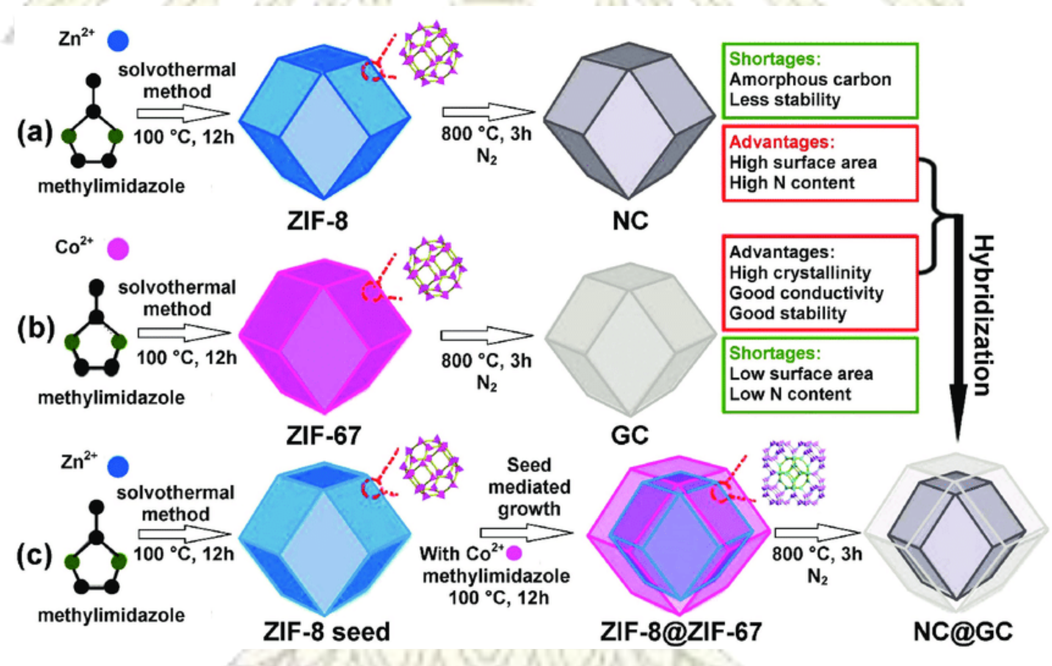


Figure1 Synthesis scheme for the preparation of ZIF-8 and ZIF-67 [8]

1.5 Molecular mechanics and Force field parameters

The potential energy of the system in molecular dynamics was described by the force field parameters. The total energy depended on bonded potential and nonbonded potential in Eq.1 [9]

$$\mathrm{E_{total}} = \mathrm{E_{bonded}} + \mathrm{E_{nonbonded}} \qquad \text{(Eq.1)}$$

The bonded potential was described by bond stretching, angle bending and dihedral angle torsion following Eq.2, while the nonbonded potential was described by the Van Der Waals potential and Coulomb potential following Eq.3.

$$\mathrm{E_{bonded}} = \Sigma_{\mathrm{bonds}}\, K_b(\mathrm{r}\text{-}\mathrm{r_0})^2 + \Sigma_{\mathrm{angles}}\, K_\theta\,(\theta\text{-}\ \theta_{\,0})^2 + \Sigma_{\mathrm{dihedrals}}\, K_\emptyset\,[1 + \cos(n\emptyset\text{-}\emptyset_0)] \qquad \text{(Eq.2)}$$

WhereK_b,K_θ, $K_\emptyset$ are the force constants of the bond stretching, angle bending and dihedral angle constant. While r_0, θ_0, $\emptyset_0$are the equilibrium bond distance, equilibrium angle and equilibrium dihedral angle.

$$\mathrm{E_{nonbonded}} = \mathrm{E_{Van\ Der\ Waals}} + \mathrm{E_{coulomb}} = \Sigma\frac{\mathrm{q_i q_j}}{4\pi\varepsilon_0 \mathrm{r_{ij}}} + \Sigma\, 4\varepsilon_{\mathrm{ij}}\left[\left(\frac{\sigma_{\mathrm{ij}}}{\mathrm{r_{ij}}}\right)^{12} - \left(\frac{\sigma_{\mathrm{ij}}}{\mathrm{r_{ij}}}\right)^{6}\right] \qquad \text{(Eq.3)}$$

$\mathrm{q_i}$, $\mathrm{q_j}$ are the atomic charges of atom i and j, ε_0 is the effective dielectric constant and r_{ij} is the distance between atom i and j, $\varepsilon_{\mathrm{ij}}$ is the potential well depth and σ_{ij} is the distance between atom i and j at the zero potential energy.

The Van Der Waals interaction between two atoms arises from a balance between repulsive and attractive forces. The van der Waals interaction is most often modeled using the Lennard-Jones potential which expresses the interaction energy using the atom-type dependent constants.

The Coulomb potential represented the electrostatic interaction between a pair of atoms.

The Lennard-Jones potential for diatomic parameters used the Lorentz-Berthelot combining rules following Eq.4 and Eq.5.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad \text{(Eq.4)}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad \text{(Eq.5)}$$

1.6 Gibbs Ensemble Monte Carlo (GEMC) simulations

Gibbs Ensemble Monte Carlo (GEMC) simulations were performed using homemade software called Gibbon which was already used in [10,12]. This system consisted of two simulations boxes. One box contains bulk gas and another one contains the framework with guest molecules. The particles move within each simulations boxes. Furthermore, the particles can be swapped between the two boxes and they keep the total number of particles fixed**.** The chemical potential is equal in both boxes when the system is in equilibrium. The pressure of the system can be chosen by adjustment of the box sizes and the total particles.

1.7 Molecular Dynamics (MD) simulations

Molecular dynamics (MD) simulations is the computational calculation which computes the forces acting on each atom using molecular mechanics and force field parameters. In addition, MD updates position and velocity of each atom using Newton's laws of motion following Eq.6 and Eq.7 [13].

$$F_i = m_i a_i \qquad \text{(Eq.6)}$$

$$F_i = m_i \frac{d^2 r_i t}{dt^2} \qquad \text{(Eq.7)}$$

Where F_i is the force on particle i, m_i is the mass of particle i, a_i is the acceleration on particle i, r_i is the radius of particle I and t is the time.

Thermodynamics properties of the system can be described by various ensembles [14].

1.7.1 Microcanonical ensemble

The number of particles (N), volume (V) and total energy (E) are fixed. The system cannot exchange the particles or energy with environment.

1.7.2 Canonical ensemble

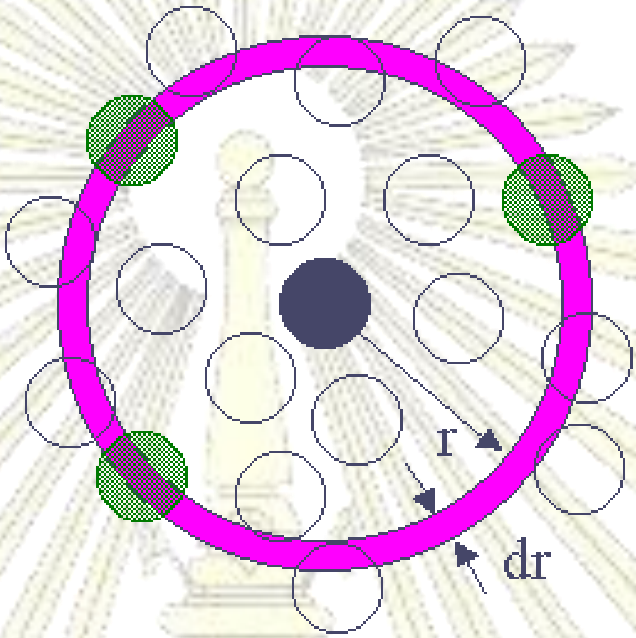
The number of particles (N), volume (V) and temperature (T) are fixed. The system can exchange energy with environment.

1.7.3 Grand Canonical ensemble

The number of chemical potential (μ), volume (V) and temperature (T) are fixed. The system can exchange the particles and energy with environment.

1.8 Radial Distribution Functions (RDFs)

The radial distribution functions, g(*r*) is a tool to describe the structure of a system. It measures the probability to find a particle in the distance (r) away from another particle as shown in Fig.2



1.9 Self-Diffusion coefficient (D_s)

The diffusion of the molecules describes the dynamic behavior of guest molecules. Molecular dynamics simulations are used to predict the self-diffusion coefficient by using the Einstein relation [13].

Einstein related the self-diffusion coefficient to the mean square displacement of a particle as a function of observation time.

$$< [\vec{r}(t) - \vec{r}(0)]^2 > = 6D_s t \qquad \text{(Eq.8)}$$

Where r is the distance at the time *t* and D is diffusion coefficient.

1.10 Adsorption, diffusion and membranes selectivities

The effectivity of separation processes can be expressed by the selectivities. They are defined by the following formulas

$$\alpha_{ij}^{adsorption} = {\left[N_i/N_j\right]_{adsorbed}}/{\left[N_i/N_j\right]_{gas}} \quad \text{(Eq.9)}$$

$$\alpha_{ij}^{diffusion} = D_j^{diffusion}/D_i^{diffusion} \quad \text{(Eq.10)}$$

$$\alpha_{ij}^{membrane} = \alpha_{ij}^{adsorption} \times \alpha_{ij}^{diffusion} \quad \text{(Eq.11)}$$

In these formulas N_i and N_j denote the total particle numbers of kind i and j in the gas phase and in the adsorbed phase, respectively. Their ratio is also the ratio of the concentrations. D_i and D_j are the self-diffusion coefficients of kind i and j. The membrane selectivity is formed as the product of the adsorption selectivity and the diffusion selectivity [14].

Chapter 2

Calculation details

2.1 Simulations

The generated crystal structure of ZIF-67 consists of 64 unit cells (4 x 4 x 4) and 8 unit cells (2 x 2 x 2) using for GEMC and MD simulations, respectively. There are seven atom types Co, N, C1, C2, C3, H1 and H2 in the ZIF-67 structure. All positions can be seen in Figure.3

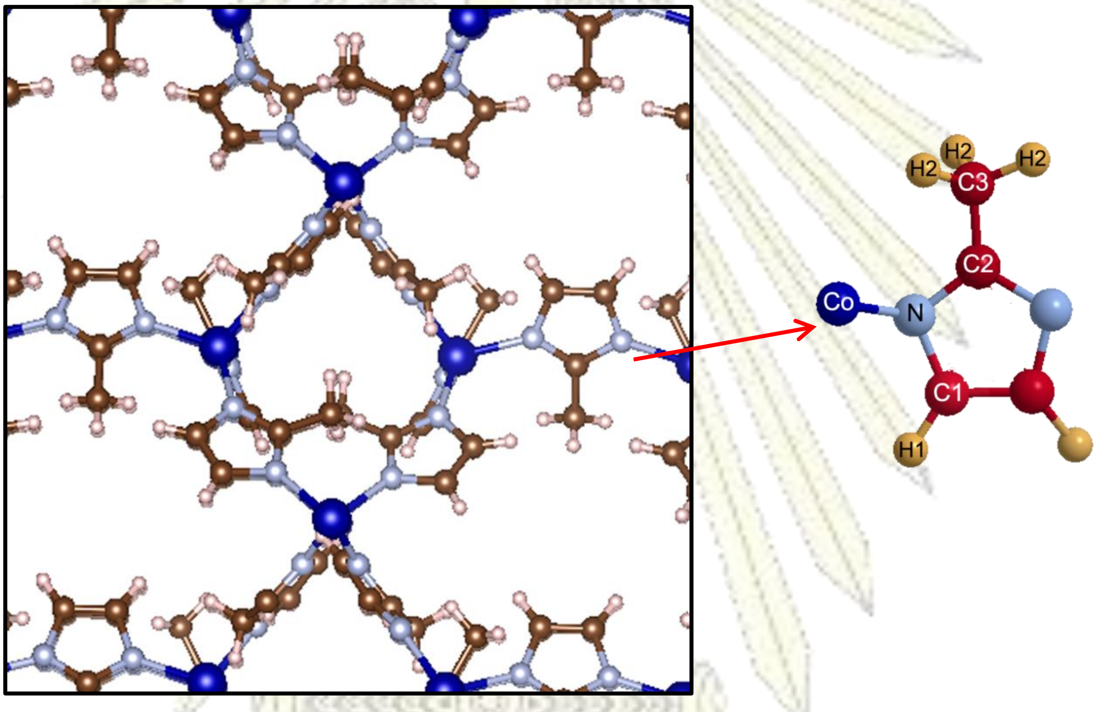


Figure 3 The structure of ZIF-67

2.1.1 Force Fields

The force field parameters describe the potential energy of the systems that means bonded and nonbonded interactions. The nonbonded can be described by Coulombic and Lennard-Jones potentials (LJ)

The force field parameters of each atom type in ZIF-67 were taken from AMBER [15] whereas the parameters of Co were taken from two sources AMBER [15] and Li, P. *et. al.* [16] as shown in Table1.

Table 1 The Lennard-Jones potential parameters of ZIF-67 [15]

Atom type	ε in kcal/mol	σ in Å
Co	1.196	2.499
	0.0286 [16]	2.185 [16]
N	0.1700	2.650
C1	0.0860	3.400
C2	0.0860	3.400
H1	0.0150	2.511
C3	0.1094	3.400
H2	0.0157	2.650

The partial charge of atoms in ZIF-67 was taken from Krokidas, P. *et. al.* [17]. The total sum of charges is not equal zero so we adjust charge of some atoms to make the sum to be zero as shown in Table2.

Table 2 Partial charge of each atom types in ZIF-67

Atom type	**Partial charge (q) [17]**	**Adjust partial charge(q)**
Co	1.3497	1.3500
N	-0.6956	-0.6956
C1	-0.0581	-0.0581
C2	0.7846	0.7846
H1	0.0910	0.0910
C3	-0.3094	-0.3094
H2	0.0584	0.0584

The structures of H_2 and N_2 were modeled as united atom. The parameters of H_2 including charge were taken from Hertag, L *et. al.* [3]. While the parameters of N_2 were taken from TraPPE, Potoff *et. al.* [18] with bond length of 1.097 Å.

Table 3 The Lennard-Jones potential parameters of H_2 and N_2

	σ (A^{o})	**ϵ (kcal/mol)**	**q**
H_2	3.314	0.00147	0
N of N_2	3.310	0.2993	-0.482
X of N_2 (ghost atom)	0	0	0.964
N of N_2	3.310	0.2993	-0.482

2.1.2 Gibbs Ensemble Monte Carlo (GEMC) simulations details

GEMC simulations were used to study adsorption behavior of gas molecules in ZIF. [16] In this work, we applied Gibbs Ensemble Monte Carlo (GEMC) simulations using the so called Gibbon software which was used in many works. This system consisted of 2 simulations boxes. The first box and second box contained the guest molecules and the material and guest molecules, respectively. The molecules can be swapped between 2 boxes and temperatures are equal for each. The pressure can be chosen by adjustment of the size of the boxes and the total number of particles. When the system is in equilibrium, the energy of each box is equal to each other. After equilibrium was reached, the pressures were calculated by the Peng-Robinson equation. Adsorption isotherms of Hydrogen and Nitrogen in ZIF-67 were compared to investigate adsorption behavior and the most suitable Co force fields for the system.

2.1.3 Molecular Dynamics (MD) simulations details

MD simulations were used to calculate structure and dynamics properties using DL_POLY software. The Lorentz-Berthelot mixing rules were used for LJ cross parameters. In this work, we simulated in canonical ensemble (NVT) in which the number of particles in the system (N), volume (V) and temperature are fixed for rigid framework. The simulations were carried out at 3 temperatures (233K, 263K and 303K). The cutoff was chosen to be 12 Å for rigid framework. The self-diffusion coefficient and radial distribution function are discussed in the results part.

Table 4 The number of particles for each system in MD simulations

Co parameter	**Temperature**	**Number of H_2 particles**	**Number of N_2 particles**
1	233	67	67
	263	37	37
	303	20	20
2	233	53	53
	263	29	29
	303	16	16

Chapter 3

Results and Discussion

3.1 Gibbon Ensemble Monte Carlo (GEMC)

The adsorption experiments have been done at 233K, 263K and 303K. GEMC simulations were performed for test parameters. The force field parameters of ZIF-67 were taken from AMBER and Li, P. *et. al.* The Co (1) refers to Co parameters taken from AMBER while Co (2) refers to Co parameters taken from Li, P. *et. al.* The parameters of H_2 and N_2 were taken from Hertag, L *et. al.* and TraPPE, Potoff *et. al.*, respectively. These parameters have been used in MD simulations. The results from GEMC will show the effect of temperature and different Co force field parameters.

3.1.1 Adsorption Isotherm

3.1.1.1 Single gases

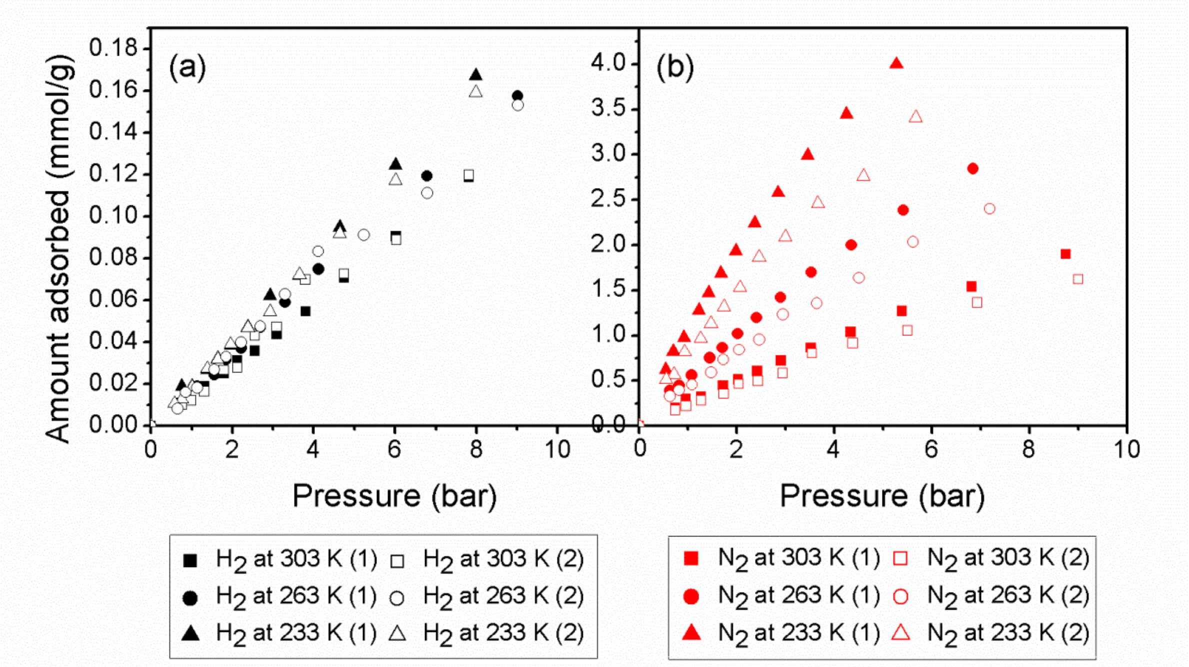


Figure 4 Adsorption isotherms for single gas (a) H_2 and (b) N_2 at 233K, 263K and 303K in ZIF-67

The results of H_2 and N_2 adsorption isotherms show that force field parameters of H_2 and N_2 can produce the adsorption isotherms. N_2 has the greater amount adsorbed than H_2.

The temperature effects to adsorption of gases. The amount adsorbed decreases with the increase of temperatures. For the effect of Co force field parameters in H_2, the amounts adsorbed are not much large. On the other hand, the amounts adsorbed of N_2 in Co (1) are slightly higher.

3.1.1.2 Mixtures H_2/N_2

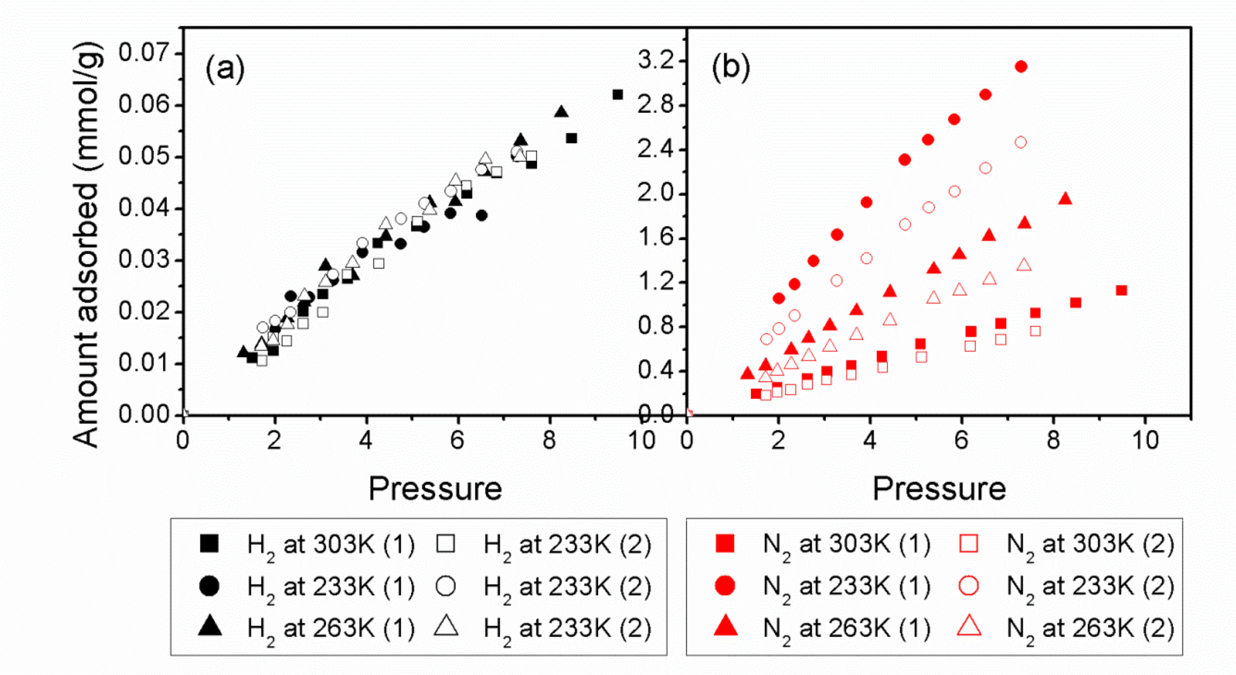


Figure 5 Adsorption isotherms for mixtures (a) H_2 and (b) at 233K, 263K and 303K in ZIF-67

From the mixture adsorption isotherms confirms that N_2 adsorbed more than H_2 in ZIF-67. The maximum amount adsorbed for H_2 is 0.0621 mmol/g at 303K while the maximum amount adsorbed for N_2 is 3.1508 mmol/g at 233K. In addition, the temperature and different parameters trend are the same with single gas.

The different parameters trend is the same with single gases that Co (1) and Co (2) do not affect H_2 too large but Co (1) affect N_2 to can be adsorbed slightly more than Co (2).

3.1.2 Adsorption Selectivity

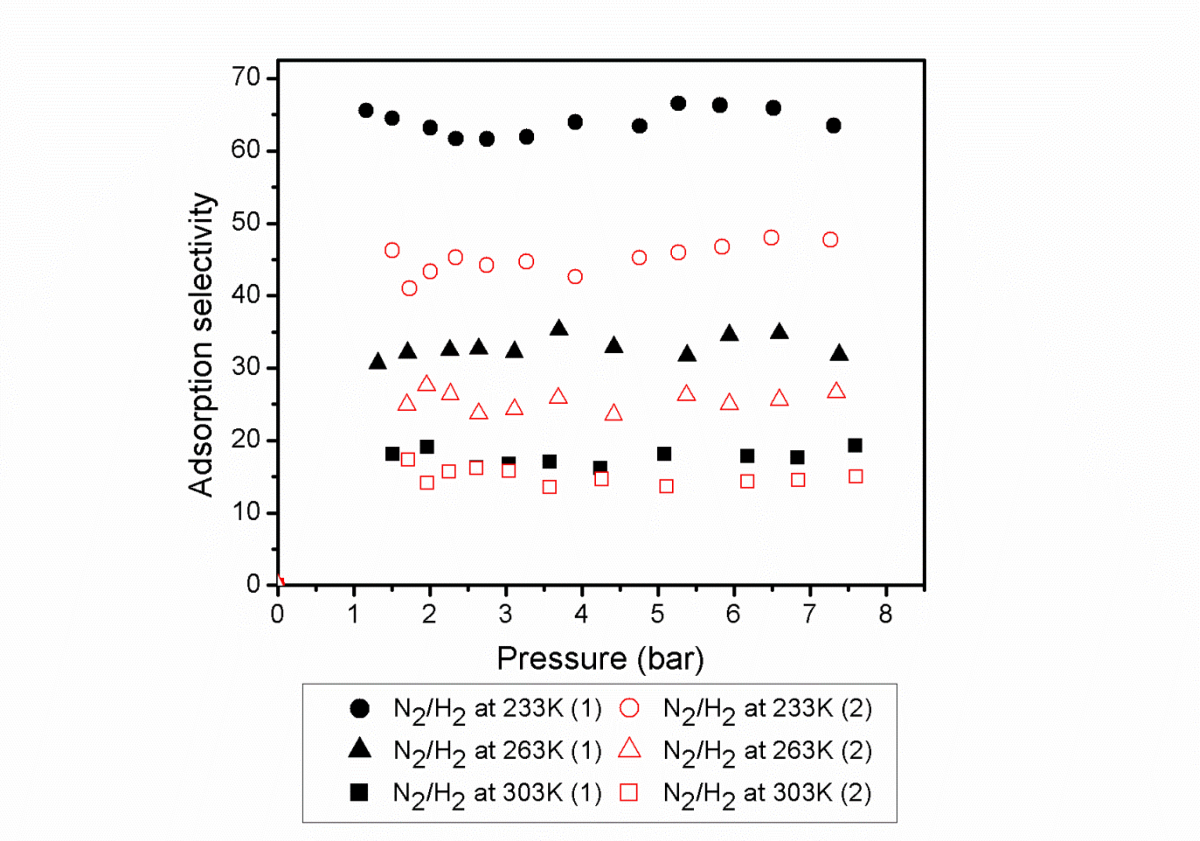


Figure 6 Adsorption selectivity for mixtures N_2/H_2 at 233K, 263K and 303 K in ZIF-67

We calculated the N_2/H_2 adsorption selectivity and present to the results in Fig.6. The selectivity varies between 10 and 65, indicating that at all the pressures studied N_2 is preferentially adsorbed in ZIF-67 compared to H_2. We found that the adsorption selectivity decreases with increasing temperature.

The equilibrium pressures are around 7 bar but rather different. We have taken the particle numbers for MD simulations from the results of the GEMC simulations at around 7 bar. As H_2 can be adsorbed very few amounts so we have chosen the equal particle numbers to N_2. These particles numbers are: (Co1) 67 H_2 and N_2 at 233K, 37 H_2 and N_2 at 263K, 20 H_2 and N_2 at 303K (Co2) 53 H_2 and N_2 at 233K, 29 H_2 and N_2 at 263K, 16 H_2 and N_2 at 303K, respectively.

3.2 Molecular Dynamics (MD) Simulations

3.2.1 Radial Distribution Functions (RDFs)

The Radial Distribution Functions (RDFs) of guest molecules was analyzed to locate the adsorption sites of guest molecules.

3.2.1.1 Single gases (H_2 and N_2)

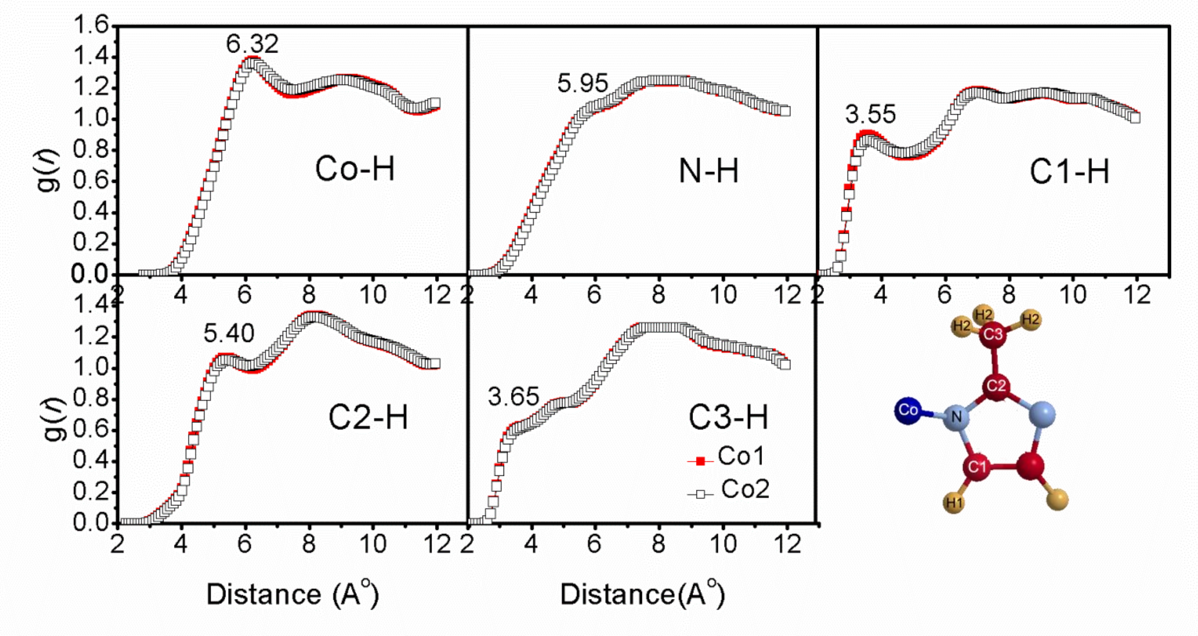


Figure 7 Radial Distribution Functions (RDFs) between Hydrogen of H_2 and 5 atom types (Co, N, C1, C2, C3) of ZIF-67 at 233K

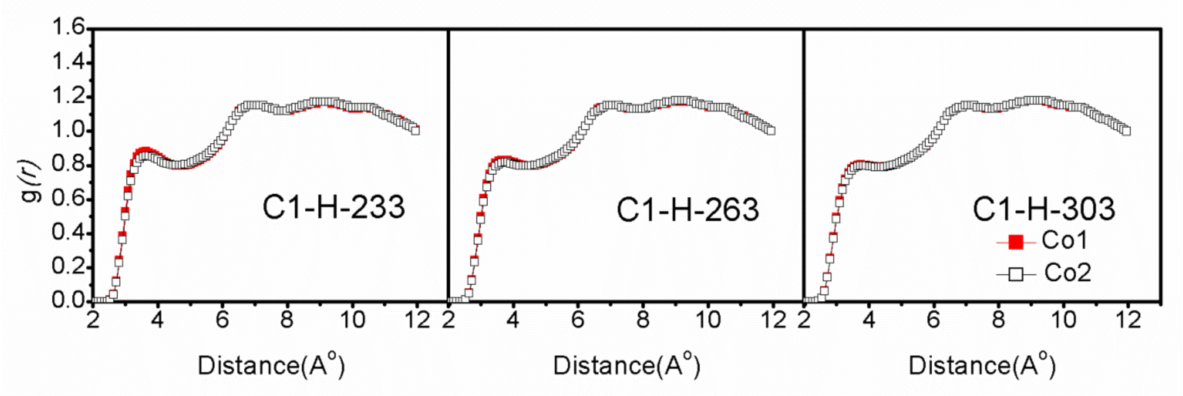


Figure 8 Radial Distribution Functions (RDFs) between adsorption site (C1) and Hydrogen of H_2 at 233K, 263K and 303K

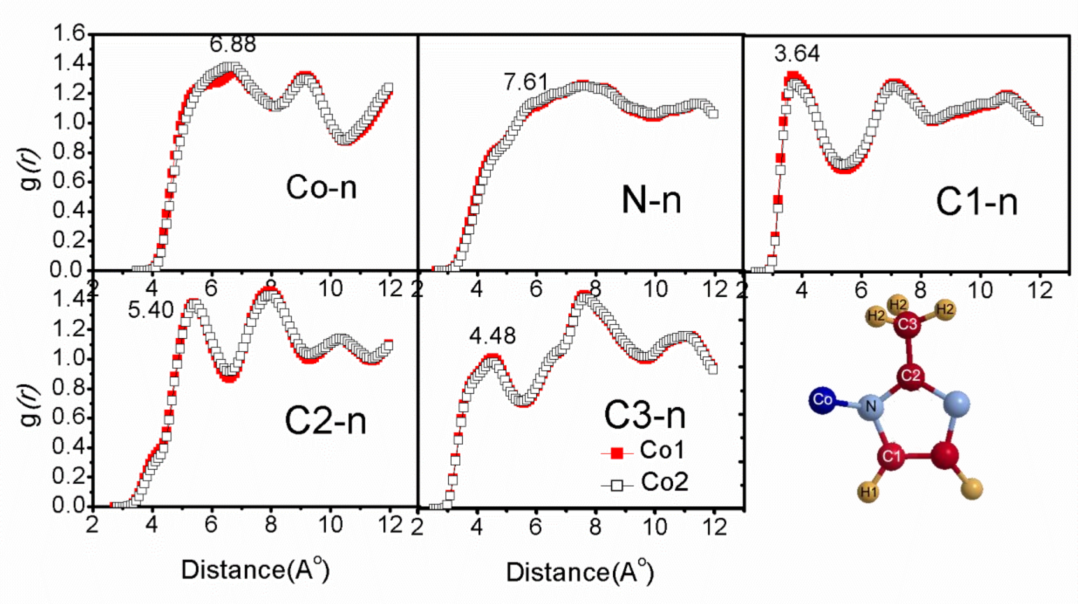


Figure 9 Radial Distribution Functions (RDFs) between Nitrogen of N_2 and 5 atom types (Co, N, C1, C2, C3) of ZIF-67 at 233K

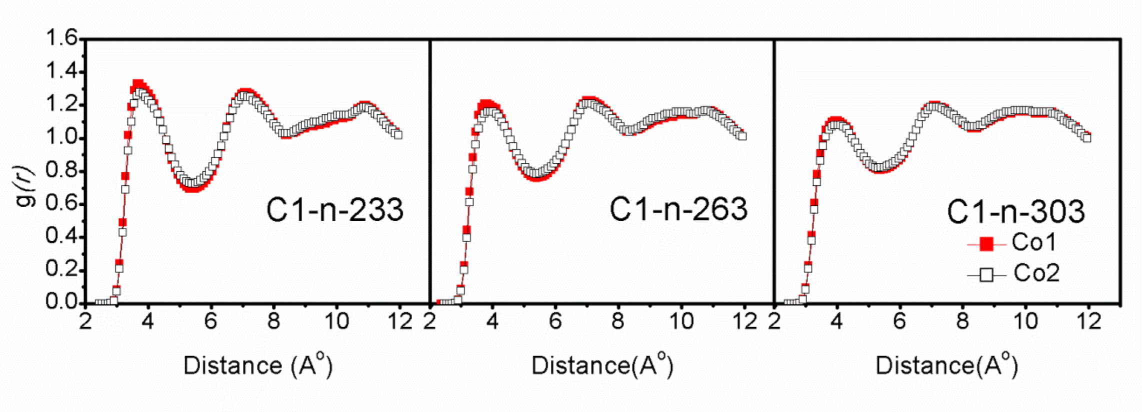


Figure 10 Radial Distribution Functions (RDFs) between adsorption site (C1) and Nitrogen of N_2 at 233K, 263K and 303K

RDFs of all atom types in ZIF-67 (Co, N, C1, C2, and C3) at 233K were plotted as shown in Fig. 7 and Fig.9. The result shows that C1 was the adsorption site of both (H_2 and N_2) which was the shortest distance of all atom types. In addition, the peak between N_2 and C1 was higher than H_2 and C1. That means N_2 shows the stronger contact peaks with C1.

For the effect of different Co force fields parameter, RDFs was not much large. The temperatures did not affect RDFs of H_2 as shown in Fig.8. While Fig. 10 shows a bit effect of temperature on the adsorption sites of N_2. At the 233K, the adsorption sites had the strong peak more than other temperatures.

3.2.1.2 Mixtures H_2/N_2

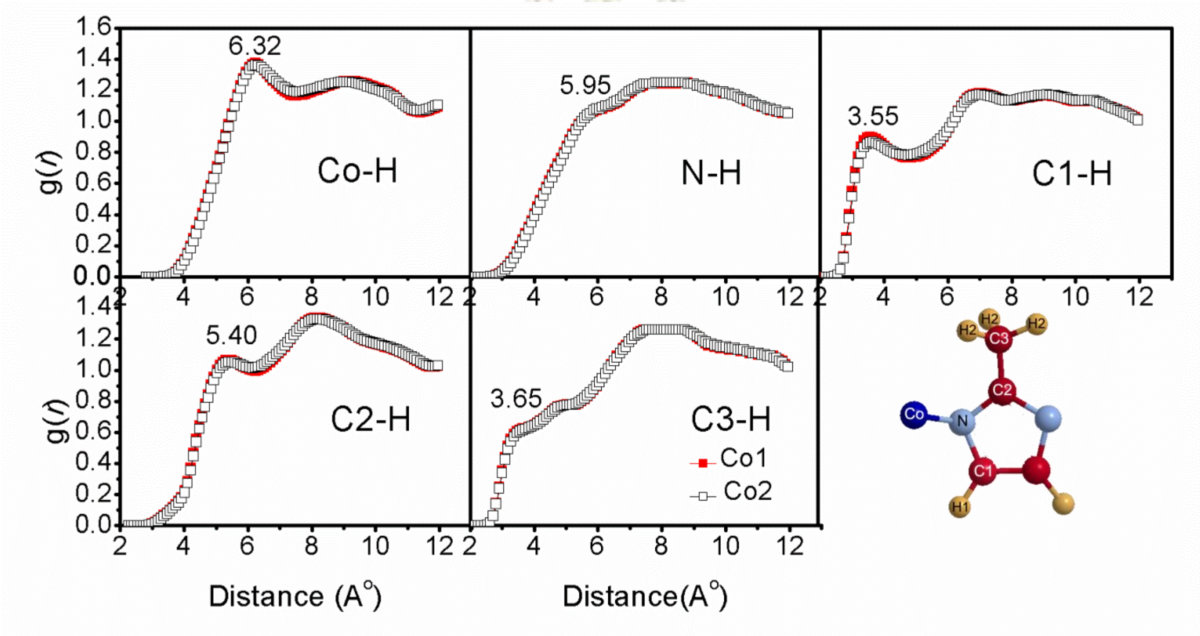


Figure 11 Radial Distribution Functions (RDFs) between Hydrogen of H_2 in mixtures H_2/N_2 and 5 atom types (Co, N, C1, C2, C3) of ZIF-67 at 233K

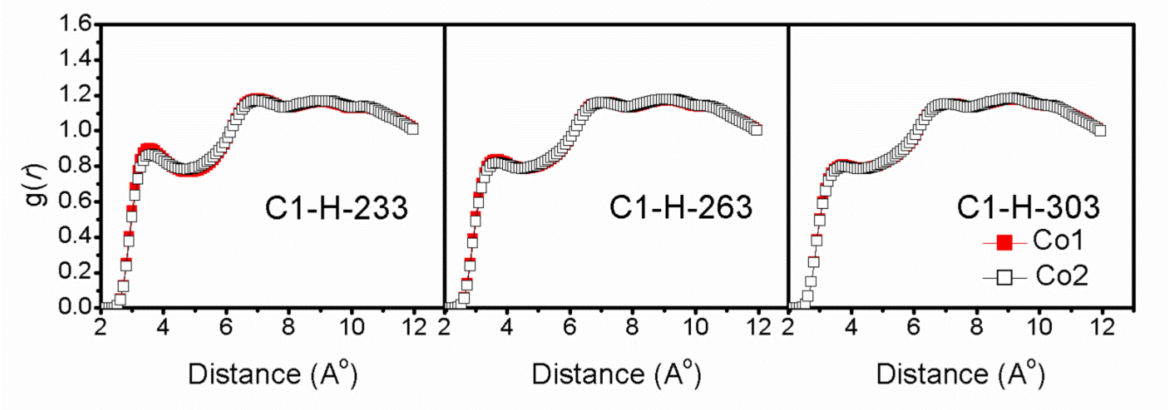


Figure 12 Radial Distribution Functions (RDFs) between adsorption site (C1) and Hydrogen of H_2 in mixtures H_2/N_2 in ZIF-67 at 233K, 263K and 303K

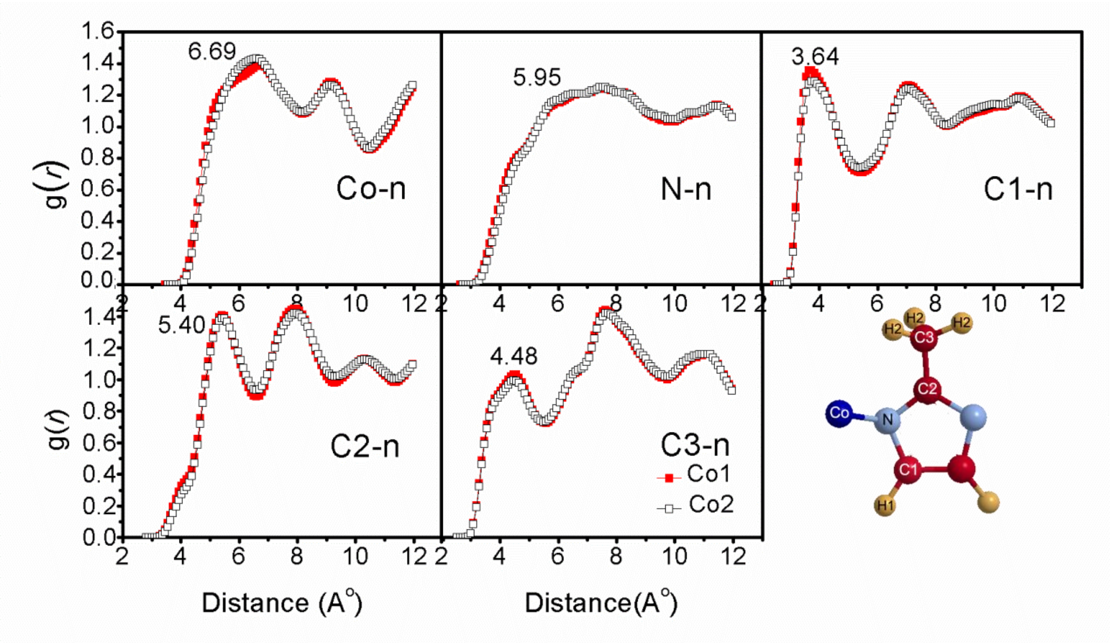


Figure 13 Radial Distribution Functions (RDFs) between Nitrogen of N_2 in mixtures H_2/N_2 and 5 atom types (Co, N, C1, C2, C3) of ZIF-67 at 233K

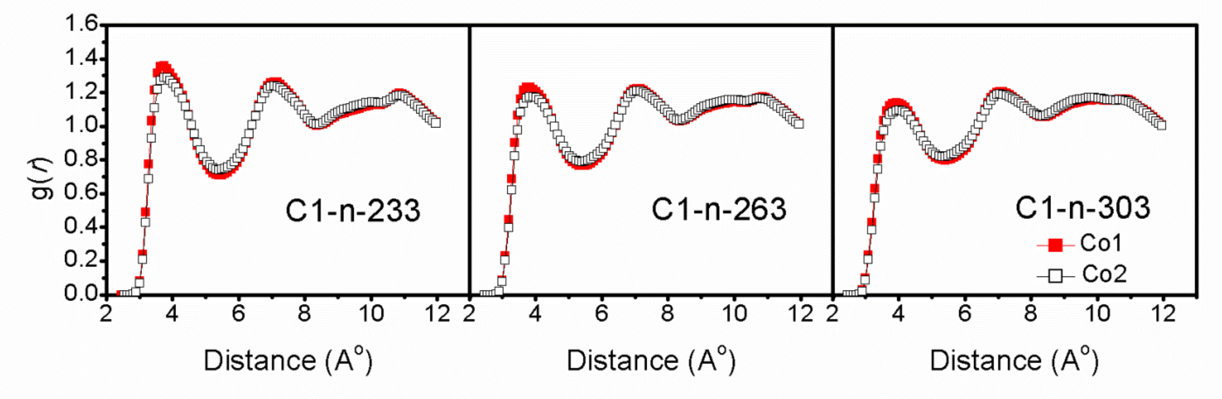


Figure 14 Radial Distribution Functions (RDFs) between adsorption site (C1) and Nitrogen of N_2 in mixtures H_2/N_2 in ZIF-67 at 233K, 263K and 303K

RDFs of all atom types in ZIF-67 (Co, N, C1, C2, and C3) at 233K were plotted as shown in Fig.11 and Fig.13. The result shows that C1 was the adsorption site of N_2 of mixtures which produced dominant peaks more than other atom types. For the effect of temperatures and different Co force fields parameter, RDFs were not much different.

The RDFs results showed the same trends of single gases and mixtures. C1 was the preferential adsorption site for both. In addition, the peak between N_2 and C1 was higher than H_2 and C1. That means N_2 shows stronger contact peaks with C1 than H_2. The RDFs were related to the adsorption isotherms which ZIF-67 can adsorb N_2 more than H_2.

3.2.2 Self-diffusion

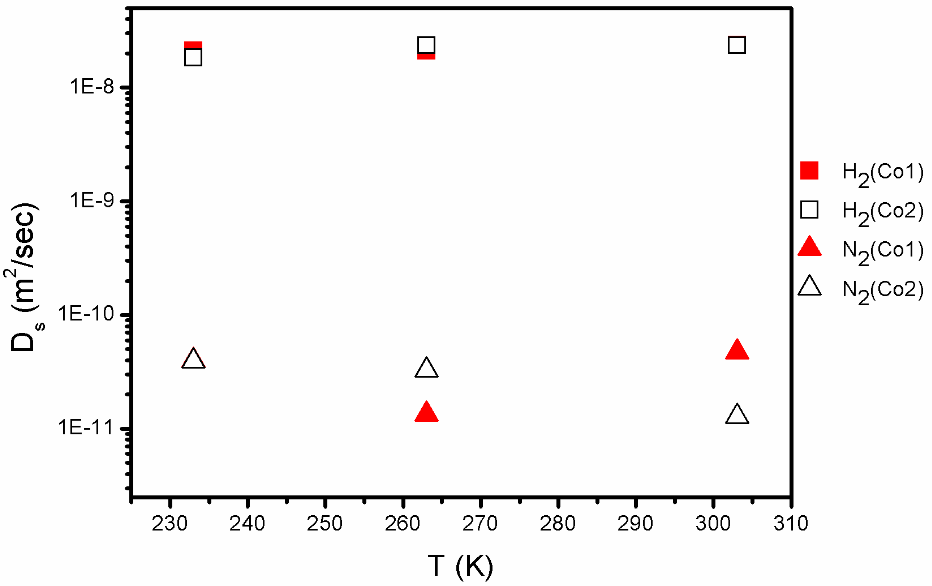


Figure 15 Temperature dependence of the self-diffusion coefficient with ln(Ds) versus T for single gases (H_2 and N_2)

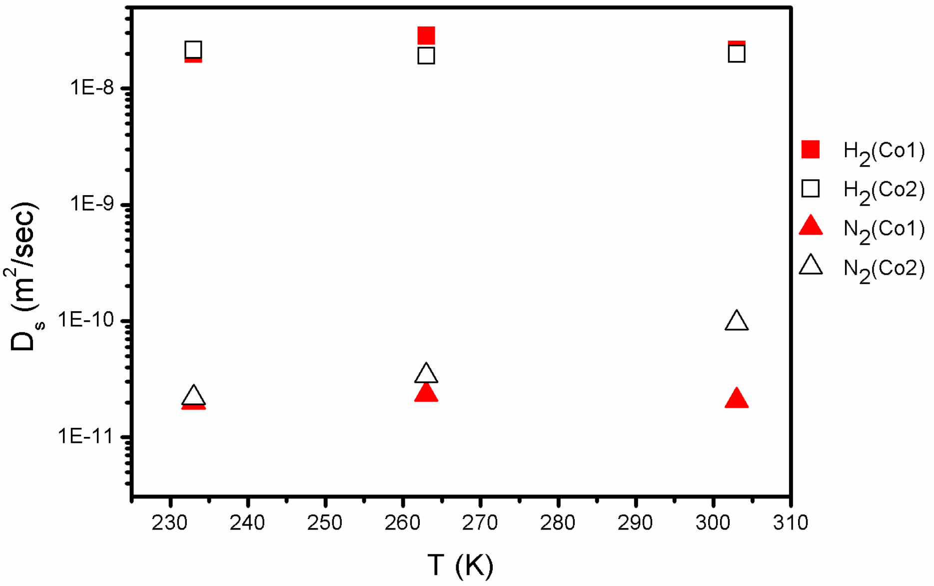


Figure 16 Temperature dependence of the self-diffusion coefficient with ln(Ds) versus T for mixtures H_2/N_2

The self-diffusion coefficient (D_s) was calculated by the slope of MSD plot. The D_s of H_2 was higher than the D_s of N_2 both singles gases and mixtures. The results agreed with the theory of diffusion. That is the lower mass can move faster so H_2 move faster than N_2.

For single gases, the highest D_s of H_2 is 2.39 x 10^{-8} m^2/sec at 303K and the highest D_s of N_2 is 4.74 x 10^{-11} m^2/sec at 303K. On the site of mixtures, the highest D_s of H_2 is 2.86 x 10^{-8} m^2/sec at 263K where the highest D_s of N_2 is 9.68 x 10^{-11} m^2/sec at 303K. This results show the higher temperature can move faster that is in line with kinetic energy.

From the D_s results show the related results of D_s, RDFs and adsorption isotherms. That was N_2 can be adsorbed more than H_2 in ZIF-67. So it shows the stronger contact with the shaper peak in RDFs and it shows the slower motion with the higher D_s than H_2.

3.2.3 Adsorption, diffusion and membrane selectivity

The adsorption, diffusion and membrane selectivity were calculated using the Eq.9 , 10 and 11 as shown on page 17.

Table 5 The adsorption selectivity, diffusion selectivity and membrane selectivity of the N_2/H_2 mixture in ZIF-67 using Co (1)

T (K)	Pressure (bar)	Adsorption selectivity ($\alpha_{ij}^{adsorption}$)	Diffusion selectivity ($\alpha_{ij}^{diffusion}$)	Membrane selectivity ($\alpha_{ij}^{membrane}$)
233	7.2907	63.46	0.001000	0.06346
263	7.3604	31.842	0.000822	0.02616
303	7.5982	19.299	0.000967	0.01867

Table 6 The adsorption selectivity, diffusion selectivity and membrane selectivity of the N_2/H_2 mixture in ZIF-67 using Co (2)

T (K)	Pressure (bar)	Adsorption selectivity ($\alpha_{ij}^{adsorption}$)	Diffusion selectivity ($\alpha_{ij}^{diffusion}$)	Membrane selectivity ($\alpha_{ij}^{membrane}$)
233	7.2662	47.722	0.001014	0.04838
263	7.3467	26.606	0.001776	0.04725
303	7.6036	14.967	0.004864	0.07280

The results of Table 7 and 8 show the same trends for two Co parameter sources. The separation at lower temperature is more effective. The adsorption selectivity is somewhat larger than the membrane selectivity. So we can predict that ZIF-67 is well suited to separate H_2 from N_2.

Chapter 4

Conclusions

Adsorption and diffusion of single gases (H_2 and N_2) and H_2/ N_2 mixtures in rigid ZIF-67 was examined by Gibbs Ensemble Monte Carlo (GEMC) simulations and Molecular Dynamics (MD) simulations at three temperatures. Our adsorption isotherms results indicate that ZIF-67 can adsorb N_2 in higher amount than H_2. The amount adsorbed decreases with the increase in temperatures. The different Co force field parameters do not affect significantly the gas absorption, except at lower temperatures. The selectivity decreases with increasing temperature. From the Radial Distribution Functions (RDFs), the shortest distance between the gas molecule and ZIF-67 was found at C1 position of ZIF-67 around 3.55 Å. It can be summarized that C1 was the preferential adsorption site. In addition, the RDFs peak between N_2 and C1 were higher than H_2 and C1. This suggests that N_2 shows stronger contact peaks with C1 than H_2. In order to observe the dynamics behavior of gases, the self-diffusion (D_s) was calculated. It was found that N_2 had the lower D_s than H_2. That means N_2 moves slower than H_2. Finally, it can be concluded that ZIF-67 is well suited to separate H_2 from N_2, especially at lower temperature.

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Appendix

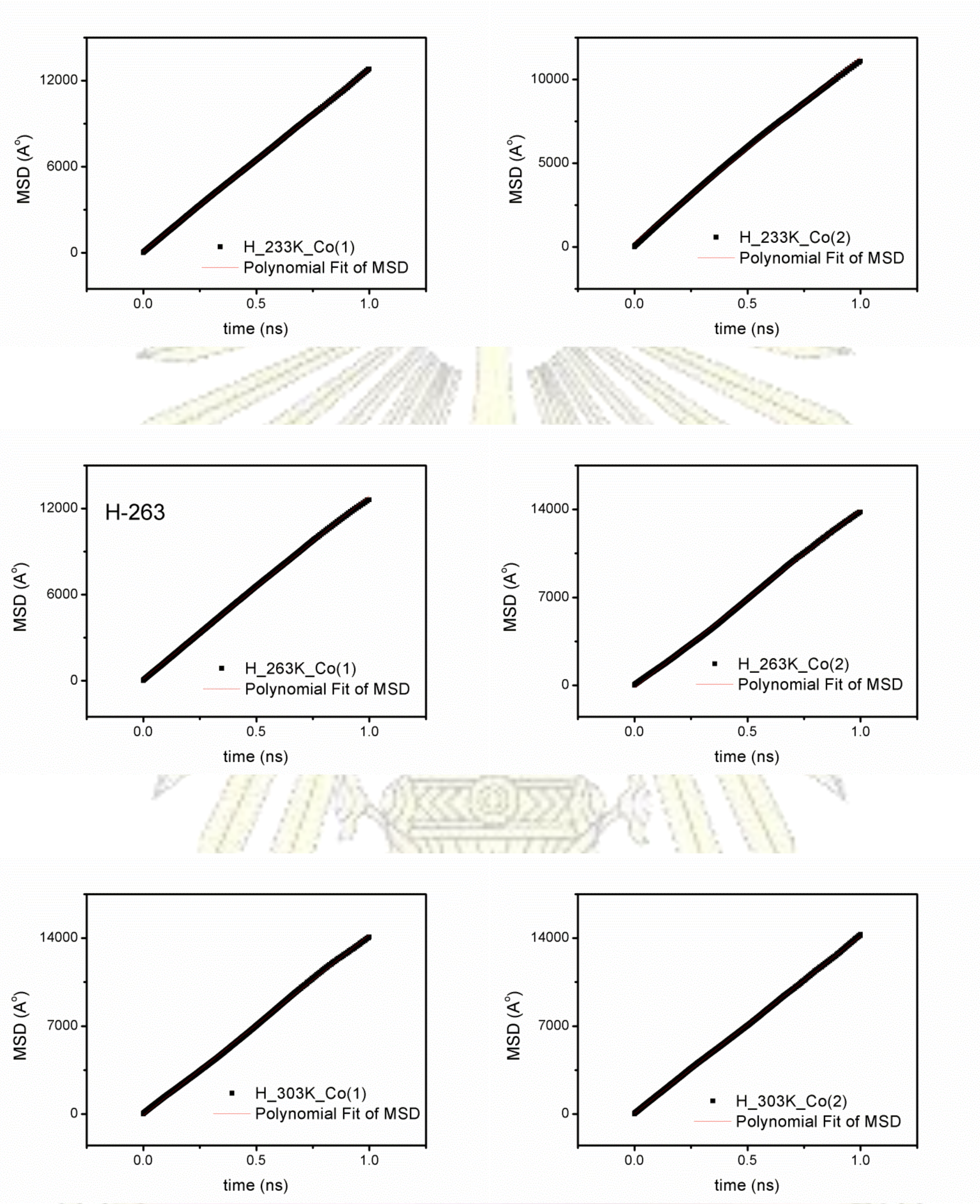

Figure 17 The mean square displacement (MSD) of Hydrogen (H_2) in ZIF-67 at three temperatures using two Co parameter sources from NVT ensemble

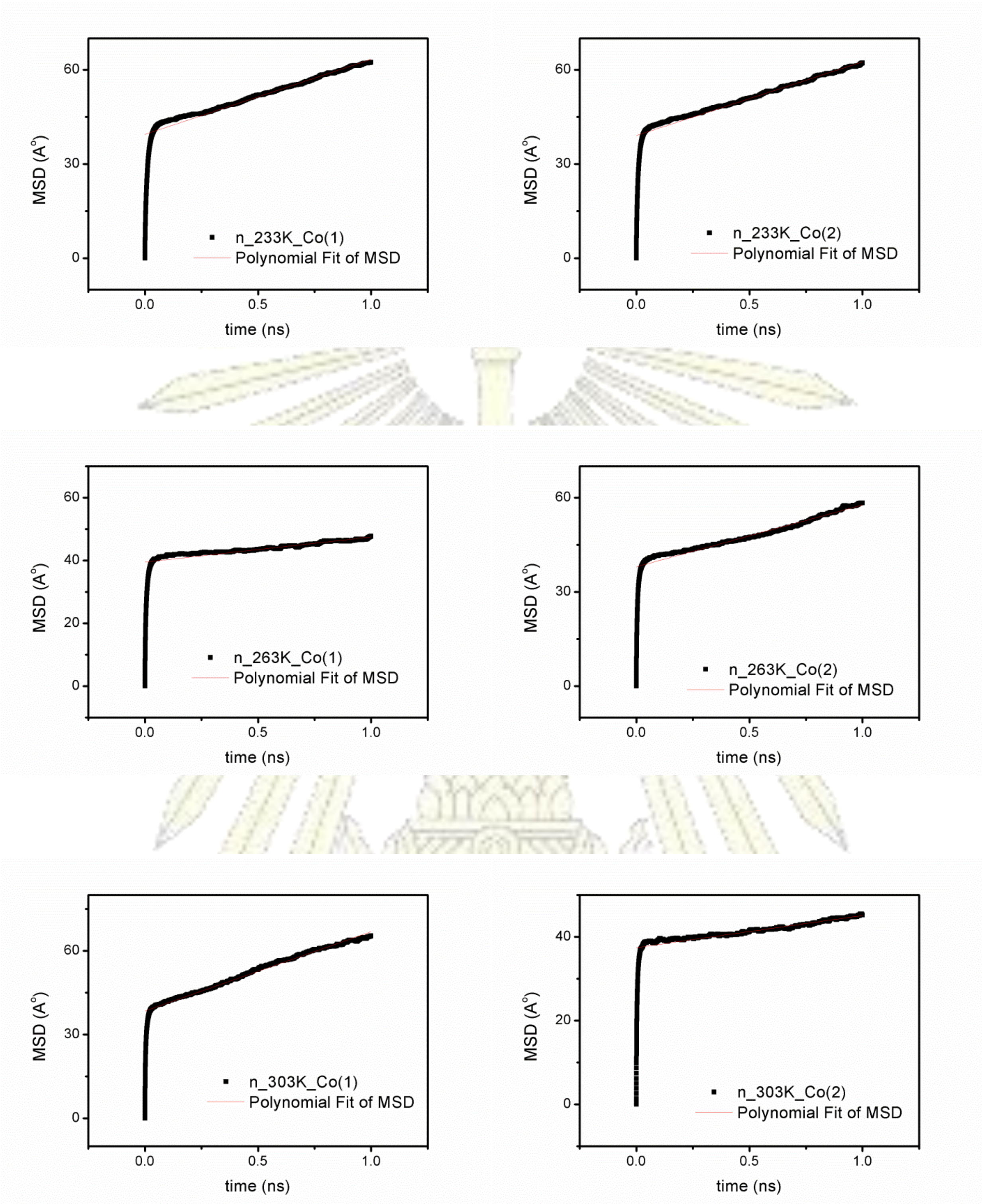

Figure 18 The mean square displacement (MSD) of Nitrogen (N_2) in ZIF-67 at three temperatures using two Co parameter sources from NVT ensemble

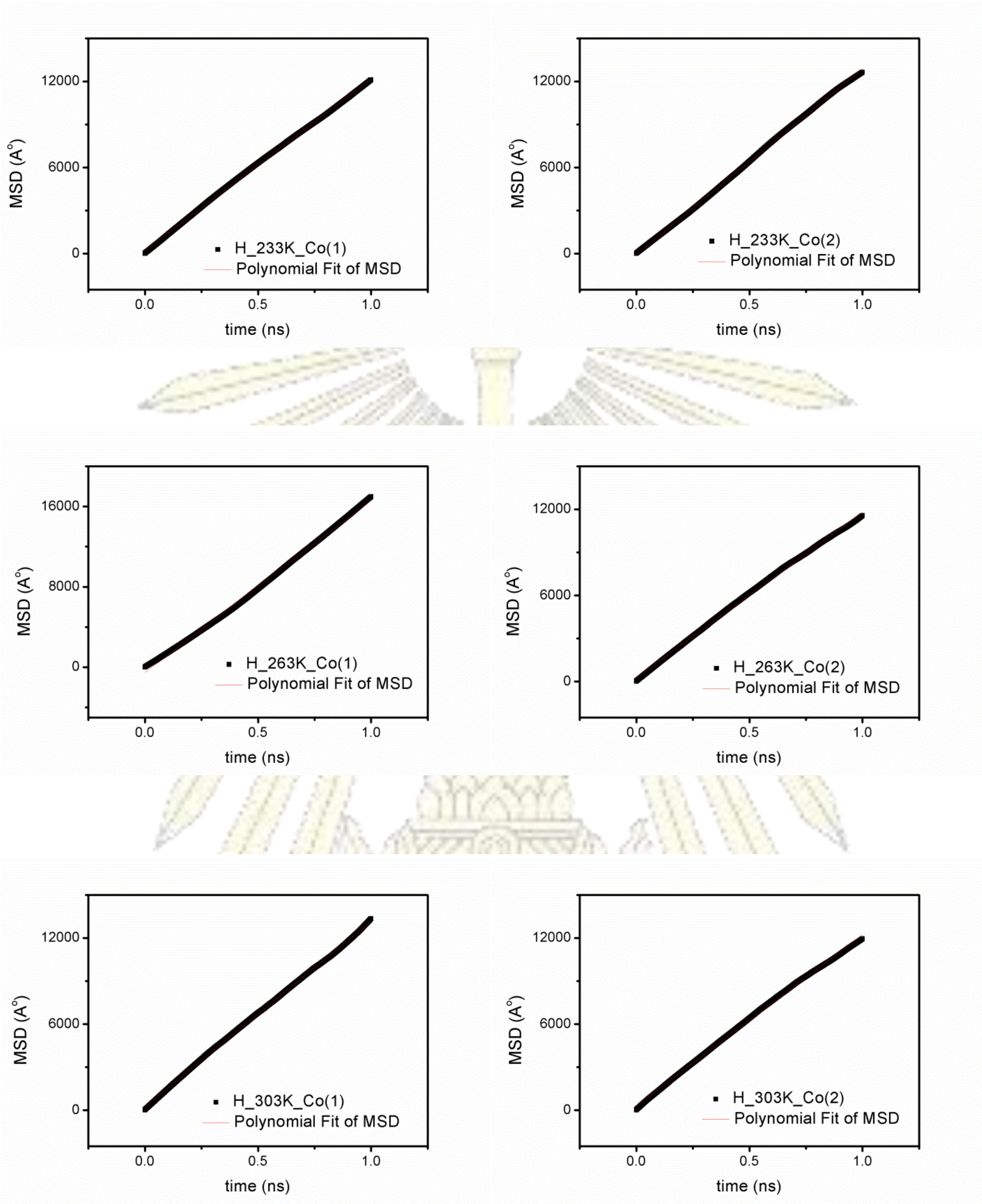

Figure 19 The mean square displacement (MSD) of Hydrogen (H_2) in mixtures in ZIF-67 at three temperatures using two Co parameter sources from NVT ensemble

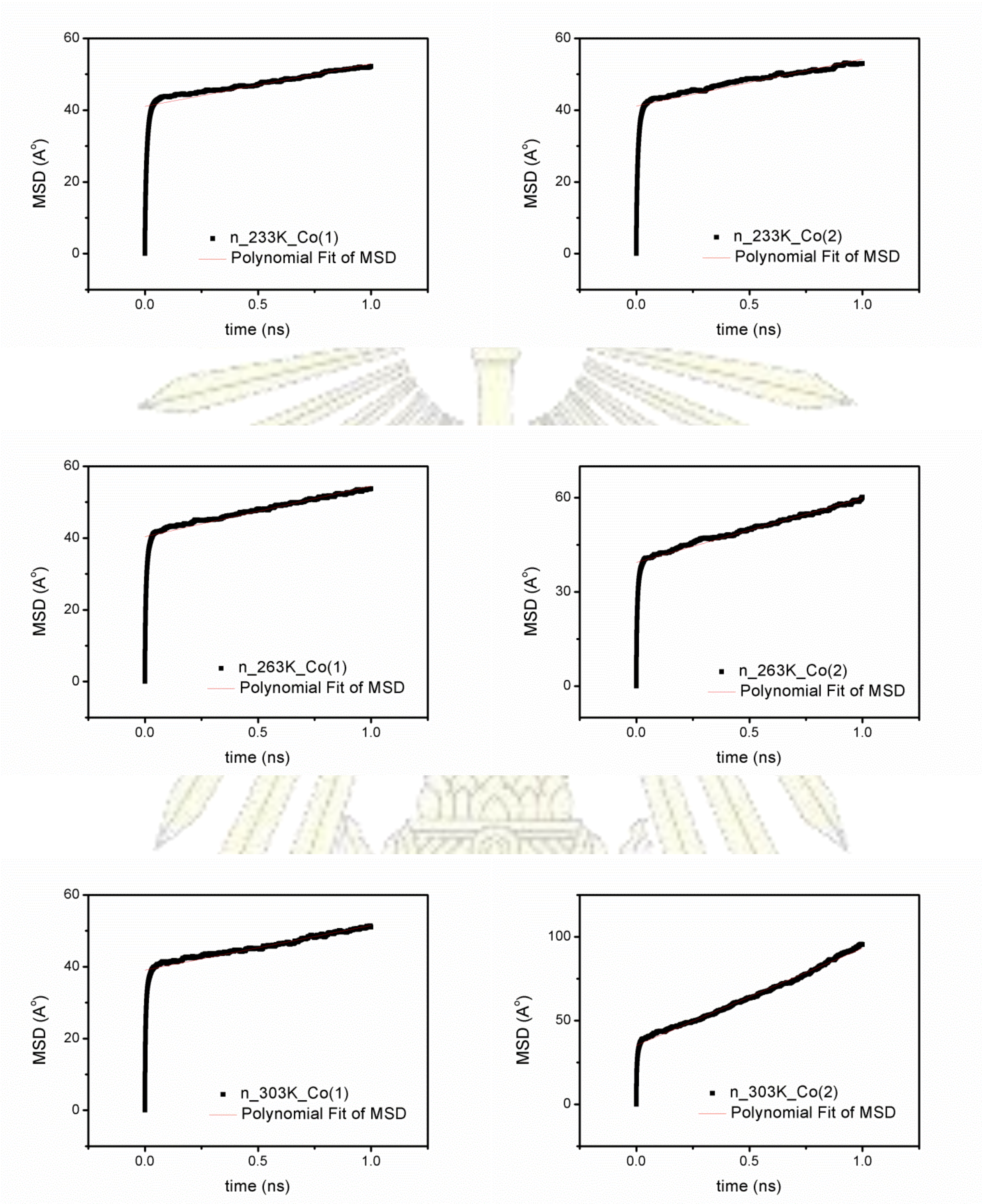

Figure 20 The mean square displacement (MSD) of Nitrogen (N_2) in mixtures in ZIF-67 at three temperatures using two Co parameter sources from NVT ensemble

Table 7 The self-diffusion coefficient (D_s) of single gases (H_2 and N_2) in ZIF-67 at three temperatures

T(K)	Co parameter	Pressure(bar)	D_s of H_2 (m^2/sec)	D_s of N_2 (m^2/sec)
233	1	7.2907	2.12 x 10^{-8}	3.99 x 10^{-11}
	2	7.2662	1.84 x 10^{-8}	3.92 x 10^{-11}
263	1	7.3604	2.12 x 10^{-8}	1.34 x 10^{-11}
	2	7.3467	2.36 x 10^{-8}	3.28 x 10^{-11}
303	1	7.5982	2.39 x 10^{-8}	4.74 x 10^{-11}
	2	7.6036	2.36 x 10^{-8}	1.28 x 10^{-11}

Table 8 The self-diffusion coefficient (D_s) of mixtures in ZIF-67 at three temperatures

T(K)	Co parameter	Pressure(bar)	D_s of H_2	D_s of N_2 (m^2/sec)
233	1	7.2907	1.99 x 10^{-8}	1.99 x 10^{-11}
	2	7.2662	2.16 x 10^{-8}	2.19 x 10^{-11}
263	1	7.3604	2.86 x 10^{-8}	2.35 x 10^{-11}
	2	7.3467	1.92 x 10^{-8}	3.41 x 10^{-11}
303	1	7.5982	2.15 x 10^{-8}	2.08 x 10^{-11}
	2	7.6036	1.99 x 10^{-8}	9.68 x 10^{-11}

Curriculum Vitae

Miss Chanunchida Kunsiri was born on December 3rd, 1995 in Suphanburi, Thailand. In 2013, she graduated from Mathematics-Science program from Kannasootsuksalai School, Suphanburi, Thailand. In 2014, she was admitted to a Bachelor's degree program: major in Chemistry, Faculty of Science and minor in Faculty of Communication Arts, Chulalongkorn University. She would complete the program in 2018. Her address is 77 Moo 13, Tambon Hnong-ong, Amphoe U-Thong, Suphanburi 72160.