

Improving the CH₄ adsorption property and the CO₂/CH₄ separation of IRMOF-3 by functionalizing the organic linker

- Trang Moc Khung
- Pham Tran Nguyen Nguyen

University of Science, VUN-HCM

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ABSTRACT

Grand Canonical Monte Carlo (GCMC) simulation combining with the ideal adsorbed Solution Theory (IAST) are employed to study the effect of functionality on the CH₄ adsorption property and CO₂/CH₄ selectivity of modified irmoF-3 structures which include a diverse range of functional groups. The result shows that phenyl groups containing nitrogen (e.g. pyrazine, pyridine) and carboxyl group are able to increase the interaction energy between gas and mof, thereby increasing the gas adsorption capacity. In addition, transition metals can significantly enhance the CO₂/CH₄ selectivity.

Key words: MOFs, gas adsorption, CO₂/CH₄ selectivity, IAST, PSM

The straight-chain alkyl group and aniline groups just slightly improve the material property compared to other functional groups. We also note that materials with more than 50 percent of modification do not show a good performance at high pressure range (35–40 atm) due to its low porosity. We herein show that the functionalization of IRMOF-3 can remarkably improve the CH₄ uptake and CO₂/CH₄ separation; particularly, GCMC simulation is demonstrated as a beneficial tool to aid experimental chemists in designing new promising porous materials.

INTRODUCTION

The anthropogenic emission of CO₂ from industrial production processes and transportation has greatly affected the environment and developing economic issue. In addition, CH₄ is another strategic interesting gas that is negative greenhouse effect and is the main component of the natural gas. It is also considered as cleaner energy carrier than petroleum oil due to higher hydrogen to carbon ratio lead to lower the carbon emission. Indeed, the research for safe and capacity CH₄ and CO₂ storage systems has been a big challenge that has created tremendous studies with the goal to improve the existing related technologies. Through the physisorption-based processes involving porous solids offer an efficient storage/capacity alternative to ability

adsorption of porous metal-organic frameworks (MOFs) that they have attracted attention during the past decades in the field of gas adsorption/separation both experimentally and theoretically. Many MOFs were designed and synthesized with ultra-high porosity, including MIL-101, MOF-177, MOF-205, PCN-14, UCMC-2 which show high CO₂ or CH₄ uptakes. However the majority of these promising materials would require a high energy cost for regeneration and applications. In addition to obtain new MOFs, a number of techniques have been applied on well-defined MOFs such as changing the network topology, doping of organic ligands or metal ions into the framework. In particular, attaching different functional groups on the organic linking component by post-

synthetic modification method (PSM) [4], an effective way to improve the adsorptive capacity and storage gas of MOF, is high attractive to us.

Here, we focus on the study of functional groups on IRMOF-3-based materials for improving the selection of CO₂/CH₄ as well as enhancing the gas uptake by combining the Grand Canonical Monte Carlo (GCMC) simulation with the Ideal Adsorbed Solution Theory (IAST) [5]. According to the idea of PSM method, our proposed compounds were designed by changing the chemical composition of the linker into the framework materials but remaining crystal topologies. The result demonstrates that the PSM approach coupling with theory calculations is a promising way to improve the properties of materials.

METHODS

Grand-Canonical Monte Carlo (GCMC) simulations

The GCMC simulations were carried out using MUSIC software package [6]. The interaction between the adsorbent (MOF) with methane (CH₄) and carbon dioxide (CO₂) was described mainly by van der Waals forces. The electrostatic forces, in this case, do not play an important role. We used the Lennard-Jones model with the parameters obtained from the force field TraPPE (transferable force fields) for molecular gas (adsorbate) and dreiding force field [7] for the atoms in the MOF (adsorbent). The Lorentz-Berthelot rule was used to calculate the parameters of the interaction between gas molecules and the MOF. The Lennard-Jones interactions of distances greater than 12.8 Å are ignored. In the simulation, a supercell 2x2x2 (i.e. 8 unit cells) of MOF was kept rigid, the molecular gas was considered as a "spherical molecule". Each point of the isotherm was obtained by 15–20 million simulation steps. The authenticity of this methodology has been proved by reported literatures [8]. In the view of

adsorption theory, one needs to distinguish the nature of simulation with that of the experiment. While result calculated by GCMC simulation is the amount of gas molecules in the pore of adsorbent, namely the total amount N^{abs} , the current techniques of experiment are not able to characterize this absolute amount of adsorbed molecules. Fundamentally, these measurements just produce the difference in the amount of total adsorbed gas and the amount of bulk gas in the same condition of measurement, namely N^{ex} . The equation to converse between two quantities was given by equation (1) [9]. At low pressure (lower than 1 atm), the difference between these two values is negligible.

$$N^{ex} = N^{abs} - V_p \rho_g \quad (1)$$

Where N^{ex} , N^{abs} excess and absolute amount, respectively, V_p is the pore volume of the adsorbent and ρ_g is the fluid density in the bulk phase at the same temperature and pressure for adsorption, which is calculated by the Peng-Robinson equation of state [10].

Molecular Mechanics (MM)

Molecular mechanics are practical technique to study atomistic systems containing thousands of atoms per unit cell. Total potential energy of the system is determined for each set of positions of the atoms by using intermolecular/intramolecular potential function in the classical force field. It helps refining the repetitive geometry of a mechanical approach until some predetermined criterid of convergence are satisfied. Finally, the quality of geometrical optimization depends on the accuracy of force field. Among the diversity of force fields developed, the uff force field is probably the most versatile since its parameter is derived for most of the atoms in the periodic table. In addition, this force field can combine with the qeq method to study systems in which electrostatic interactions [11] are important. Moreover mm method possesses an advantage in

optimizing systems, such as MOF-205, PCN-14, MIL-101(Cr) [12] since the implement of high computational-cost calculations are not reasonably practicable. In this study, MOF structures are optimized with Dreiding force fields and UFF using GULP software [13].

Adsorption Enthalpy Calculation (ΔH_{ads})

The isosteric heat of adsorption [14] (Q_{st}) is based on the thermochemical parameters of the adsorption process. ΔH_{ads} can be calculated from gas adsorption isotherms simulated at two or more different temperatures by means of fitting of the virial equation. The zero-coverage isosteric heat corresponds to the interaction energy between the gas molecule and the strongest interaction site of the MOF. The virial equation (Equation 2) which consists of temperature-independent parameters a_i and b_i is used to fit the sorption data. Adsorption isotherms measured at 273 K and 298 K are used in this procedure by applying the statistical program origin 8.5 (microcal software inc., northampton, ma). δH_{ads} is then calculated by Equation 3.

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (2)$$

$$\Delta H_{ads} = -Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (3)$$

Where P is the pressure, N is the amount adsorbed CH_4 gas, T is the temperature, m and n represent the numbers of coefficients required to adequately describe the isotherms, R is universal gas constant.

Adsorption selectivity

Adsorption-based separation is a physisorptive operation governed by thermodynamic equilibrium process, which relies on the fact that guest molecules reversibly adsorb in nanopores at densities that far exceed the bulk density of the gas sources in equilibrium with the adsorbents [15].

It has been convinced in numerous published papers [16-19] that the IAST can be used to estimate quite accurately of the adsorption equilibrium of mixtures from pure component isotherm data. For a binary gas mixture adsorption (A, B components), the predicted adsorption selectivity ($S_{A/B}$) was calculated by:

$$S_{A/B} = \frac{x_A/x_B}{y_A/y_B} \quad (4)$$

Where x_A , x_B and y_A , y_B are the mole fractions of A and B in the adsorbed and bulk phases, respectively.

RESULTS AND DISCUSSION

MOF materials have been synthesized in previous literature [3, [4] by psm method, our MOF proposed models contain 50 % substituent groups (substituent converted to the linker with the yield of 50 %) due to the fact that too much attached substituent possibly lead to a decreasing in gas adsorption capacity [20]. All structures were carried out optimization and GCMC simulation on the CH_4 and CO_2 adsorption isotherms. To interpret the effects of the substituent group, we performed simulations for all of the new proposed MOFs such M3AMPh, M3AM5, M3URPh, M3AMPz, M3AMSal, M3AMPhN and M3CC. These materials are the products of the process of attaching the substituent benzoic anhydride (AMPh), hexanoic anhydride (AM5) and phenyl isocyanate (URPh), 2,3-pyrazine-dicarboxylate (AMPz), 3-hydroxyphthalic anhydride (AMSal), 2-pyridinecarboxy-aldehyde (AMPhN) and cyanuric chloride (CC) to IRMOF-3 linker, respectively. In addition, we also proposed doping of metal ions Pd^{2+} , Fe^{3+} , Cu^{2+} to the linkers of the material M3AMPhN, M3AMSal, M3AMPz, respectively, resulting new materials with corresponding names: M3AMPhNPd, M3AMSalFe and M3AMPzCu [21]. We also investigated CO_2/CH_4 selectivity by employing ideal adsorbed solution theory

IAST which was a widely used as a thermodynamic method for predicting the equilibrium adsorption of mixtures. The

volumetric uptake and isosteric heats of adsorption of MOFs are presented in Fig. 2, 3 and 4.

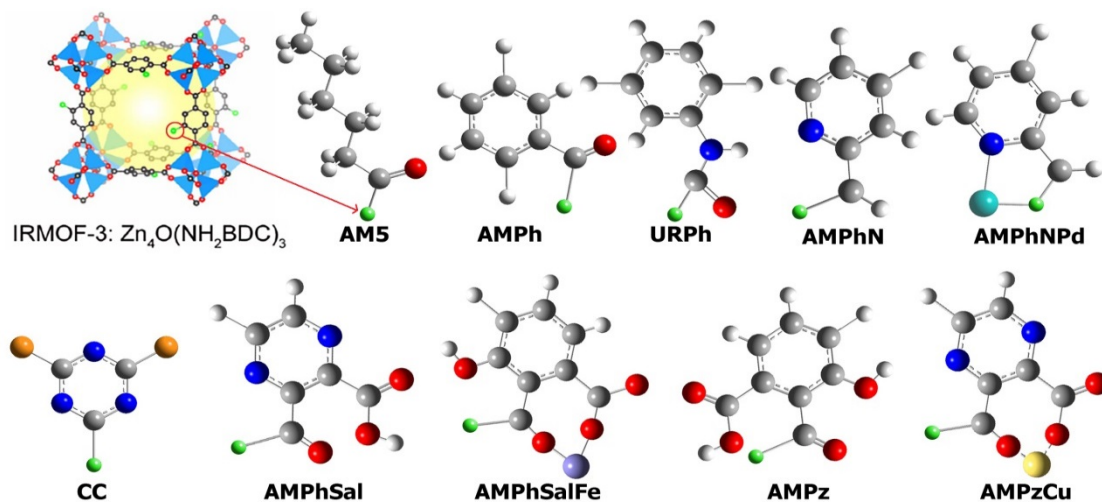


Fig.1. Model of IRMOF-3 structure and functional groups: the large spheres represent the void regions inside the cages (Zn polyhedral: blue for tetrahedral cage; C, gray; O, red; N, (green) blue, Cl, orange; Pd, cyan, Fe, purple; Cu, yellow). The extended organic linkers attach on IRMOF-3 are also presented.

Adsorption isotherms of methane (CH₄)

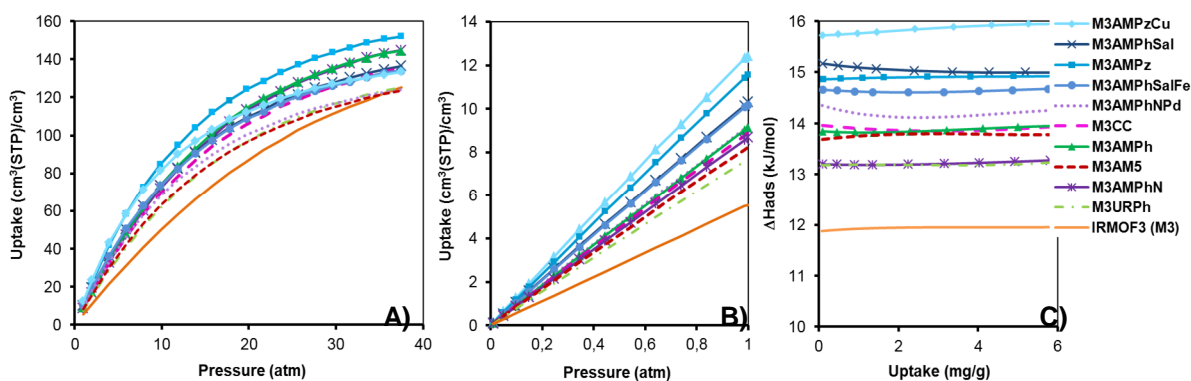
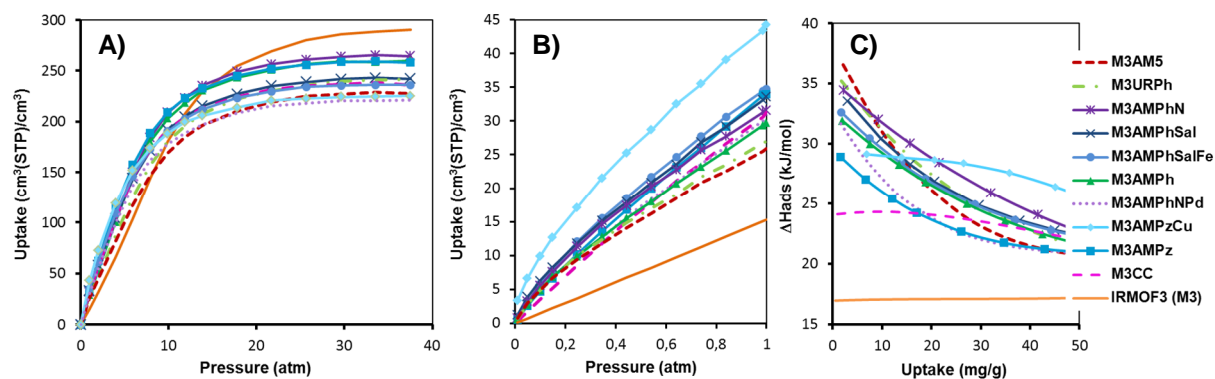


Fig 2. CH₄ isotherm at high pressure (A), low pressure (B) and isosteric heat of adsorption (C) at 298 K

The M3AMPz and M3AMPPhN (152 and 144 cc/cc) show higher volumetric uptakes of CH₄ than unmodified IRMOF-3 (125 cc/cc) and other MOFs at 298 K and 38 atm (high pressure), since they have containing-nitrogen phenyl group such as pyrazine and pyridine groups. These nitrogen atoms possess high affinity with gas, thereby improving isosteric heats of adsorption. In

contrast, M3AM5 and M3URPh (123 and 125 cc/cc) cannot improve the adsorption capacity of CH₄. Conversely, adding transition metal (Cu²⁺ like form open metal site) [22], created M3AMPzCu significantly enhances both volumetric uptake (12.42 cc/cc) and isosteric heat of adsorption of CH₄ (15.72 KJ/mol) at 298 K and 1 atm (low pressure).

Adsorption isotherms of carbon dioxide (CO₂)

 Fig. 3. CO₂ isotherm at high pressure (A), low pressure (B) and isosteric heat of adsorption (C) at 298 K

Similar to the result above, the M3AMPzCu has volumetric uptake of CO₂ (44.23 cc/cc) and the M3AM5 has isosteric heats of adsorption of CO₂ (38.31 KJ/mol) at 298 K and 1 atm (low pressure). They have significantly enhanced volumetric uptake and absorption heat of CO₂ than unmodified IRMOF-3 (15.28 cc/cc and

16.94 KJ/mol) as well as compared to other MOFs. However, the substituents attached too much (i.e., the percentage conversion of MOF is large) leads to a decreasing-in surface area and pore volume of the MOFs [23], resulting in reducing CO₂ adsorption capacity at 298 K and 38 atm (high pressure).

Table 1. Summary of porosity, CH₄ and CO₂ uptake (at 1 atm and 38 atm, 298 K), and enthalpy of adsorption for materials in this study

Material	ASA ^a (m ² /g)	V ^b _{pore} (cm ³ /g)	V ^c _{ch4} (cc/cc)	V ^d _{ch4} (cc/cc)	ΔH ^e _{adsch4} (kj/mol)	V ^c _{co2} (cc/cc)	V ^d _{co2} (cc/cc)	ΔH ^e _{adco2} (kj/mol)
IRMOF3 (M3)	3532	1.10	125.14	5.54	11.87	290.26	15.28	16.94
M3AMPZ	2542	0.90	151.99	11.56	14.86	258.02	34.01	28.54
M3AMSAL	2637	0.83	136.36	10.31	15.17	242.11	33.60	35.21
M3AMPHN	2703	1.05	144.77	8.67	13.21	264.33	31.55	35.24
M3AMPH	2943	0.97	144.39	9.12	13.85	259.70	29.73	32.62
M3CC	2442	0.92	135.07	8.89	13.97	235.93	31.25	24.05
M3AM5	2456	0.91	123.49	8.24	13.68	227.79	25.93	38.31
M3URPH	2805	0.93	125.13	7.69	13.18	241.66	26.96	36.16
M3AMPZCU	1727	0.65	133.33	12.42	15.72	225.10	44.23	32.76
M3AMSALFE	2338	0.78	133.89	10.17	14.66	236.04	34.72	33.34
M3AMPHNPD	2052	0.76	124.01	9.19	14.37	220.86	30.74	29.69

(a) Asa (accessible surface area)[23]

(b) Pore volume,

(c) Volumetric uptake at 38 atm,

(d) Volumetric uptake at 1 atm,

(e) Adsorption heat at zero coverage calculated from the virial equation.

adsorption selectivity (CO₂/CH₄)

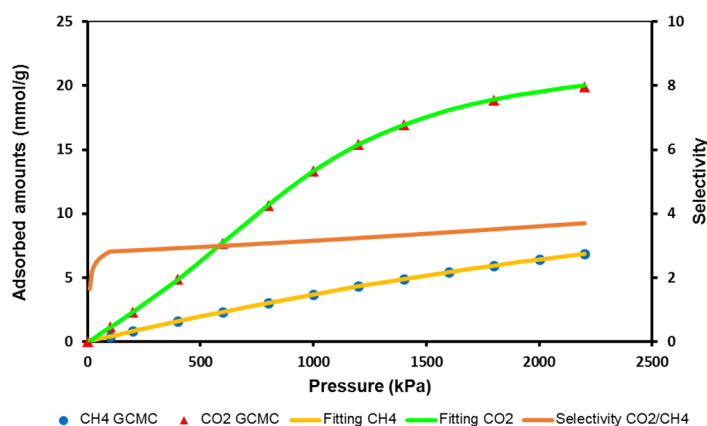


Fig. 4. The iast-predicted isotherms and selectivity's of equimolar mixture of CO₂ and CH₄ in IRMOF3 at 298 K

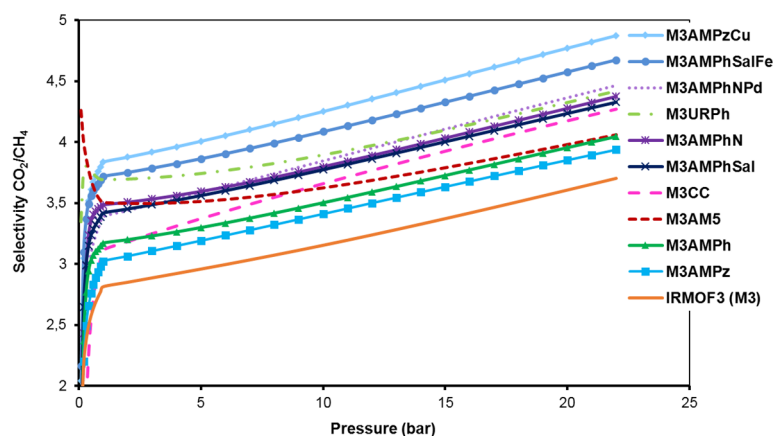


Fig. 5. Simulation results for separation of an equimolar mixture of CO₂/CH₄ in new MOFs at 298 K

In proportion to gas selectivity studies, the initial slopes for CO₂ and CH₄ adsorption uptakes indicate the noticeable affinity for CO₂/CH₄ of proposed structures at high pressure. We studied the selectivity adsorption by the ideal adsorbed solution theory (IAST), which calculates the system's gas selectivity capabilities of theoretical gas mixtures utilizing the pure component isotherms (Fig. 2, Fig. 3) and the results are shown in Fig. 5. It should be noted that even though IAST calculations are performed using GCMC isotherm, their selectivity results represent theoretical values that might deviate from practical applications. The selectivity for CO₂/CH₄ of new MOFs are quite significant at 22 bar for 50/50 mixture of CO₂ and CH₄. The

selectivity of MOFs that have attached metal ion such as Cu²⁺, Fe²⁺, Pd²⁺ and this value would increase with increasing pressure; while the M3AM5 increased at low pressure and decreased at high pressure. The validity of IAST calculations is dependent on the ideality of MOFs [25]. We confirm the results by calculating selectivity from the initial slopes of the isotherms (Fig. 4). The resulting selectivity for CO₂/CH₄ are in good agreement with the IAST value [26]. In summary, the transition metal (Cu²⁺, Fe²⁺, Pd²⁺) also contribute to enhance the CO₂/CH₄ selectivity.

CONCLUSION

In summary, we herein show that the functionalization of IRMOF-3 can remarkably

improve CH₄ uptake and CO₂/CH₄ separation. The substituent which have phenyl group containing nitrogen atoms inside such as pyrazine, pyridine groups shows better positive effect than the straight-chain alkane and aniline groups. This is explained by the increasing isosteric heats of adsorption. In addition, the transition metals (Cu²⁺, Fe²⁺, Pd²⁺) are able to enhance CO₂/CH₄ selectivity. Last but not least, the GCMC similar combining with the IAST is a powerful tool to investigate both the storage

capacities and isosteric heats adsorption of the gas also gas selectivity. Thus, it can be used to design new promising porous materials.

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Nghiên cứu cải thiện khả năng hấp phụ khí CH₄ và tách hỗn hợp khí CO₂/CH₄ của vật liệu IRMOF-3 bằng việc thay đổi nhóm thế trên linker

- Phạm Trần Nguyên Nguyên
- Trang Mộc Khung

Trường Đại học Khoa học Tự nhiên, ĐHQG-HCM

TÓM TẮT

Phương pháp mô phỏng Grand Canonical Monte Carlo (GCMC) kết hợp với lý thuyết IAST được sử dụng để nghiên cứu ảnh hưởng của nhóm thế lên khả năng hấp phụ khí CH₄ và độ chọn lọc của hỗn hợp khí CO₂/CH₄ của một số cấu trúc IRMOF-3 với các nhóm chức khác nhau. Kết quả cho thấy các nhóm phenyl chứa nitrogen trong vòng thí dụ như pyrazine, pyridin và nhóm carboxyl làm tăng khả năng tương tác giữa khí với vật liệu MOF, dẫn đến gia tăng lượng khí hấp phụ. Việc gắn những kim loại chuyển tiếp lên linker cũng làm gia tăng đáng kể độ chọn lọc CO₂/CH₄. Ngược lại, nhóm alkyl và nhóm aniline

Từ khóa: Vật liệu khung cơ kim (MOF), hấp phụ khí, độ chọn lọc khí, lý thuyết IAST, phương pháp biến đổi sau tổng hợp (Post-Synthetic Modification, PSM)

không cho thấy hiệu quả trong việc cải thiện tính chất hấp phụ của vật liệu. Ngoài ra, việc gắn quá nhiều nhóm thế sẽ làm giảm diện tích bề mặt và thể tích lỗ xốp, dẫn đến việc giảm lượng khí hấp phụ ở vùng áp suất cao (35-40 atm). Nghiên cứu đã chứng minh được sự thay đổi của các nhóm thế trên linker IRMOF-3 làm gia tăng đáng kể lượng hấp phụ khí CH₄ và độ chọn lọc CO₂/CH₄, qua đó cho thấy mô phỏng GCMC là công cụ hữu ích hỗ trợ các nhà hóa học thực nghiệm trong việc thiết kế tổng hợp vật liệu mới tiềm năng.

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