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Probing Methane Adsorption in MIL Metal-Organic Frameworks using Molecular Dynamics Simulations

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ABSTRACT

In this study, we investigated the adsorption properties of three metal-organic frameworks (MOFs): MIL-101(Cr), MIL-100(Fe), and MIL-100(Al), for high-pressure methane storage in Adsorbed Natural Gas (ANG) applications. Utilizing the Materials Studio software and Monte Carlo simulations, we conducted molecular dynamics simulations under a constant pressure of 35 atm and a temperature of 300 K. The results revealed distinct methane adsorption capacities for each MOF, with values of 0.008 g, 0.089 g, and 0.035 g of methane per gram of adsorbent for MIL-101(Cr), MIL-100(Fe), and MIL-100(Al), respectively. To validate our findings, we compared the calculated adsorption capacity of MIL-101(Cr) with experimental data, resulting in a close match with the reported value of 0.036 g of methane per gram of absorbent. The simulations also unveiled insights into the adsorption patterns, demonstrating that methane molecules selectively interacted with different regions of the frameworks based on their orientation. Our study suggests that MOFs hold promise as suitable adsorbents for natural gas storage in ANG technologies. Among the three studied MOFs, MIL-100(Al) emerged as the most efficient option, presenting potential for future industrial-scale implementation, subject to economic and production considerations. These results further emphasize the significance of nanomaterials, particularly MOFs, in advancing ANG development and highlight the importance of validation with experimental data to ensure accuracy and reliability.

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1. Introduction

Natural gas is a mixture that contains 70-90% methane by volume. Due to factors such as high-octane number, clean combustion, reduced engine maintenance costs, and low pollution levels, it has been able to establish itself as a fuel in the world. The increasing threat of global warming due to the emission of harmful greenhouse gases has prompted interest in clean energy research. Methane (CH_4) has the ability to replace hydrocarbon-based fuels such as oil due to its maximum H to C ratio. Natural gas transportation is generally done in its liquid form. Conventionally, there are three different methods for storing natural gas, which are (1) compressed natural gas (CNG), (2) liquefied natural gas (LNG), and (3) adsorbed natural gas (ANG). The traditional method of storing and maintaining natural gas in vehicles involves using heavy steel tanks under pressure of about 220 atmospheres, which, in addition to being bulky, also has safety issues (Rasoulzadeh et al.,2008; Miana et al.,2010; Mokhatab et al.,2015; Wang,2022).

There are many MOFs (Metal-Organic Frameworks) that have been studied for ANG (Adsorbed Natural Gas) storage, and new materials are always being developed and tested. Some of the important factors when evaluating MOFs for ANG storage include: Methane adsorption capacity: This is the amount of methane that a MOF can adsorb at a specific temperature and pressure. The higher the adsorption capacity, the more methane a MOF can store. Selectivity: This refers to a MOF's ability to preferentially adsorb methane over other gases, such as carbon dioxide or nitrogen. A MOF with high selectivity for methane is desirable for ANG storage because it minimizes the number of other gases adsorbed and maximizes the amount of methane stored. Stability: MOFs must be stable under ANG storage conditions, which may involve high pressures and temperatures. They must also be resistant to degradation over time. Reproducibility: MOFs must be able to effectively release the adsorbed methane and be easily regenerated for reuse. Cost and availability: MOFs must be economically feasible and readily available in large quantities. Pore size and structure: The pore size and structure of MOFs can affect their methane adsorption capacity and selectivity. MOFs with larger pores may have a higher methane adsorption capacity but may also have lower selectivity for methane relative to other gases. Kinetics: The rate at which methane can be adsorbed and desorbed by MOFs is an important consideration for ANG storage, especially during filling and emptying cycles. Compatibility with other materials: MOFs must be compatible with other materials used in ANG storage systems such as tanks, pipelines, and valves. This can affect the overall performance and efficiency of the system. Scalability: MOFs must be scalable for commercial production and integration into ANG storage systems. Safety: MOFs must be safe for handling and use and should not pose risks such as explosion or other hazards. Ultimately, the best MOF for ANG storage depends on various factors such as the specific application and operational conditions. Researchers continue to study and develop new MOFs and optimize existing ones to improve their performance for ANG storage (Davarpanah and Mirshekari,2019; Dang et al.,2020; Wu et al.,2021; Cai et al.,2023; Mergenthal et al.,2023; Wu et al.,2023; Zhang et al.,2023a; Zhang et al.,2023b).

In addition to these factors, it should be noted that MOFs are just one of several materials under investigation for ANG storage. Other materials include activated carbons, porous polymers, and zeolites. The optimal materials for ANG storage depend on various factors, and research continues to identify the most effective and efficient materials for this application (Tagliabue et al.,2009; Alhasan et al.,2016; He et al.,2019; Mahmoud et al.,2019; Bhattacharjee et al.,2020; Reza et al.,2020; Pérez-Botella et al.,2022).

Kinetics is an important factor in evaluating the suitability of adsorbents for ANG storage, as

the rate of methane adsorption and desorption by adsorbents can affect the overall efficiency of the storage system. The kinetics of gas adsorption and desorption depends on factors such as temperature, pressure, and the properties of the gas and adsorbents (Bhattacharjee et al.,2020; Nikravesh et al.,2023).

In ANG storage systems, kinetics can affect the filling and emptying time of the storage tanks. An adsorbent with slow kinetics may require longer filling and emptying times, which can increase the overall time and energy required for filling and emptying the tank. On the other hand, an adsorbent with fast kinetics may provide faster filling and emptying times, which can improve the overall efficiency of the storage system. Several studies have investigated the kinetics of methane adsorption and desorption by MOFs. One approach involves using gravimetric methods to measure the amount of gas absorbed or desorbed as a function of time. Another method involves using pressure measurement techniques to monitor pressure changes during gas adsorption or desorption (Ceglarska-Stefańska and Zarębska,2002; Busch et al.,2004; Gao et al.,2020; Ursueguia et al.,2020).

There are multiple factors that can influence the gas absorption and desorption kinetics by MOFs, including:

Temperature: Higher temperatures generally lead to faster kinetics, but they may also reduce the methane adsorption capacity of MOFs. Pressure: Higher pressures can increase the methane adsorption capacity of MOFs and also lead to faster kinetics. However, it may also require more energy for filling and discharging the storage vessel. Pore size and structure: The size and structure of MOF pores can influence gas adsorption and desorption kinetics. MOFs with larger pores may exhibit faster kinetics, but they might have lower selectivity for methane. MOF properties: MOF properties, such as surface area, pore volume, and surface chemistry, can also affect gas adsorption and desorption kinetics.

Several methods have been used to study gas adsorption and desorption kinetics by MOFs, including gravimetric techniques, pressure measurement techniques, and spectroscopic methods. These studies can provide valuable insights into the factors influencing gas adsorption and desorption kinetics and can assist researchers in optimizing MOFs for ANG storage applications. Overall, gas adsorption and desorption kinetics are crucial considerations when evaluating MOFs for ANG storage, and optimizing this kinetics can improve the efficiency of ANG storage systems (Ceglarska-Stefańska and Zarębska,2002; Busch et al.,2004; Teo et al.,2017; Gao et al.,2020; Ursueguia et al.,2020)

Until now, various porous materials, such as silica gel, activated carbon, carbon nanotubes, zeolites, and covalent-organic and metal-organic frameworks (MOFs), have been experimentally investigated for ANG (Adsorbed Natural Gas) applications. The classical method for surface adsorption studies involves the synthesis or acquisition of raw materials, designing and implementing the adsorption process, and finally conducting device experiments for characterization and measurement of the adsorption capacity. Considering the costs of raw materials and the required facilities, especially in high-pressure processes, the importance of computational and simulation methods has become more pronounced. One common approach is molecular dynamics simulation, a numerical method used to solve Newton's equations of motion for individual particles in a system. Due to the advantages of metal-organic frameworks for methane storage, research in this area has recently increased. Among the most important metal-organic frameworks used in these studies is the MIL family, known for its high porosity, suitable pore size, and favorable intermolecular interactions, resulting in significant methane adsorption capacity. For instance, Kayal et al. (2016) obtained an approximate methane adsorption of 0.25-0.5 kg of methane per kilogram of adsorbent at 600

kilopascals using Monte Carlo simulations, which was in line with experimental findings. Zhang et al. (2019) calculated methane adsorption to be around 125 molecules per large hexagonal pore and about 50 molecules per small pentagonal pore of MOFs, using different computational methods (Bimbo et al.,2021) reported an average methane enthalpy of adsorption of 13.5 kJ/mol for the specific framework. In a study conducted by Zhao et al. (2020) the isosteric heat of methane adsorption on this framework was found to be 22.94 kJ/mol (Furukawa and Yaghi,2009; Zhu and Zhao,2014; Bimbo et al.,2021; Moradi et al.,2021; Moradi et al.,2022)

In this study, methane adsorption on metal-organic frameworks MIL-101(Cr), MIL-100(Fe), and MIL-100(Al) was simulated using the DS BIOVIA Materials Studio 2017 software.

2. Methods And Materials

In this study, three different metal-organic frameworks (MOFs) were chosen for methane adsorption simulations: MIL-101(Cr), MIL-100(Fe), and MIL-100(Al). MOFs are a class of highly porous materials with a high surface area, making them promising candidates for gas storage and separation applications. MIL-101(Cr) was characterized with a surface area of 2600 m^2/g, which makes it particularly attractive for gas storage purposes.

2.1.Crystal Structure Optimization:

Before performing the simulations, the crystal structure of each MOF was optimized for use in the molecular dynamics simulation software. This optimization involved considering the atomic ratios, bond types, hydrogen atoms in the structure, and framework energies using the Compass force field and the atom-based summation method. The Compass force field is a widely used force field for organic and inorganic materials, and the atom-based summation method is utilized to efficiently compute interactions between atoms in the system.

The equations used in computational chemistry for geometry optimization with a force field involve calculating the potential energy of the system and the forces acting on each atom. One common form of the potential energy equation used in molecular mechanics force fields is the following:

$$Etotal=\sum bondskr(r-req)2+\sum angleskθ(θ-θeq)2+\sum torsions2Vn(1+cos(nϕ-γ))+\sum non\text{-}bonded(r12A-r6B)+\sum electrostatic4πϵ0rijqiqj \quad \text{(eq-1)}$$

Where:

E_{total} is the total potential energy of the system.

K_r and r_{eq} are the force constant and equilibrium bond length for each bond.

k_θ and θ_{eq} are the force constant and equilibrium angle for each angle.

Vn, n, and γ are parameters describing torsional rotations.

A and B are parameters for the Lennard-Jones potential describing van der Waals interactions.

q_i and q_j are the charges on atoms i and j, and r_{ij} is the distance between them, for electrostatic interactions. (Sun,1998)

2.2.Methane Molecule Optimization

In order to represent the methane molecule accurately in the simulation, it was drawn and optimized using the graphical tool provided by the DS BIOVIA Materials Studio 2017 software. This optimization ensures that the geometry and bond lengths of the methane molecule are at their most stable configuration, which is essential for reliable simulations. Equations for methane optmizations are same as (eq-1).

2.3.Simulation Setup:

The simulations were carried out using the adsorption and molecular dynamics modules of the software. The Universal force field, which is a general-purpose force field suitable for organic and inorganic systems, was employed to model the interactions between methane molecules and the MOFs. The Ewald summation method

was used to handle the long-range electrostatic interactions between charged species in the system, providing accurate energy calculations.

2.4. Sorption and Forcite Modules:

The Sorption module was used to perform adsorption simulations, where methane molecules were introduced into the MOF structures to investigate their adsorption behavior at different temperatures and pressures. The forcite module was utilized for molecular dynamics simulations, which allowed the investigation of the dynamic behavior of methane molecules within the MOFs over time.

The equations used in forcite for molecular dynamics simulations involve calculating forces and energies associated with bonded and non-bonded interactions. Here's an overview of the equations:

Bended interactions:

$$\textit{Bond stretching: } E_{\text{bond}} = \frac{1}{2} k_{bond} (r - \text{req})^2 \quad \text{(eq-2)}$$

$$\textit{Angle bending: } E_{angle} = \frac{1}{2} K_{angle} (\theta - \theta eq)^2 \quad \text{(eq-3)}$$

Here, k_{bond} and K_{angle} are force constants, r is the bond length, r_{eq} is the equilibrium bond length, θ is the bond angle, and θ_{eq} is the equilibrium bond angle.

For dihedral or torsional terms, Forcite typically uses a Fourier expansion:

$$E_{dihedral} = \sum_{n=1}^{N} Vn[1 + cos(n\phi - \gamma)] \quad \text{(eq-4)}$$

Here, Vn are the Fourier coefficients and γ represents the phase angle.

In Forcite simulations, typically, Lennard-Jones (van der Waals) and Coulomb (electrostatic) interactions are considered as non-bonded interactions. However, in this case, we assume the absence of charged molecules and ions, rendering Coulomb interactions negligible.

$$E_{LJ} = \sum_{i<j} 4\,\epsilon_{ij} \left[\left(\frac{rij}{\sigma ij} \right)^{12} - \left(\frac{rij}{\sigma ij} \right)^{6} \right] \quad \text{(eq-5)}$$

Here, ϵ_{ij} is the depth of the potential well, σ_{ij} is the finite distance at which the inter-particle potential is zero, q_i and q_j are the charges, and r_{ij} is the distance between particles i and j (Shankar et al.,2022).

2.5. Experimental Parameters:

In molecular dynamics simulations, a molecular system is described with various parameters, including the volume and temperature. These parameters are crucial for understanding the behavior of gases in porous materials. The volume of the simulation cell influences the amount of gas that can be adsorbed, and the temperature affects the kinetic energy and motion of the molecules. Volume of each was obtained from crystallography open database and assumption for temperature was 298 K.

2.6. Force Field Analysis:

After conducting the simulations, the Force Field Analysis tool was used to calculate and plot the concentration profile and adsorption capacity of methane within the MOFs. This analysis provided insights into the distribution and uptake of methane molecules at different temperatures and pressures (Zhao et al.,2020; Frenkel and Smit,2023).

3. Results and Discussion

In this study, surface adsorption of methane on the MIL-101(Cr) MOF was simulated under a constant pressure of 35 atmospheres and a temperature of 300 K, using a total of 140,000-time steps, each lasting 1 femtosecond. The reason for choosing this temperature and pressure is to replicate the conditions used in Kayal et al.'s research to ensure accurate simulation with the optimized force field.

In Kayal's research, the methane adsorption capacity for these conditions in the MIL-101(Cr) MOF was reported (He et al.,2019).

By using simulations with different force fields, the optimal force field can be determined. The adsorption levels at different time intervals are shown in (Figure 2). As observed, shortly after starting, the system reaches equilibrium and adsorbs 1435 methane molecules per cell. With simple multiplication and division calculations and having information about the density, temperature, pressure, and crystal size used in the simulation, this value is calculated as 0.035 kg of methane per kilogram of MOF.

According to Kayal et al.'s research (2016), this value was experimentally determined and reported as 0.036 kg of methane per kilogram of MOF. The difference between the simulation and experimental values (about 5.5%) can be attributed to various factors, such as experimental errors, truncation errors in numerical calculations, limited time intervals in the simulation, and the choice of force field (He et al.,2019; Frenkel and Smit,2023).

Other adsorption values obtained through similar calculations are listed in (Table 1).

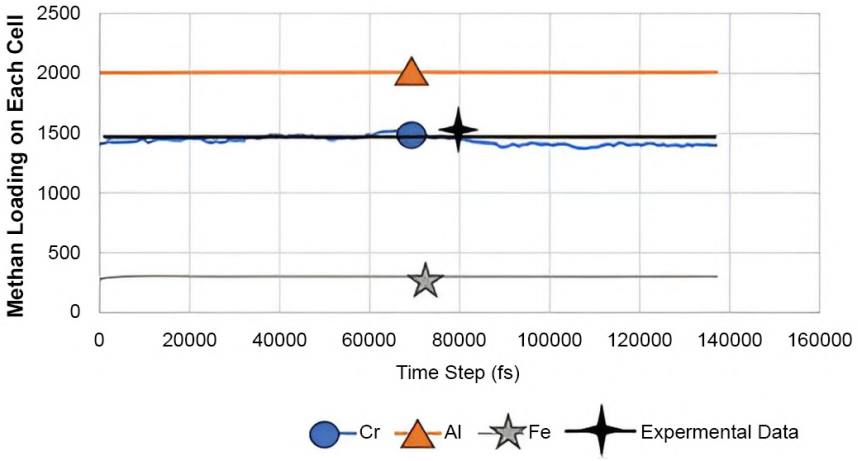

Figure 1. Methane loading on each simulation cell for different MOFs during Time

Table 1. Result of Simulation on Different MOFs

MOF	Adsorbed molecule per cell	Mass of each cell (amu)	Loading (g/g)
MIL-100(Fe)	303	236156	0.008
MIL-100(Al)	2007	14039	0.089
MIL-101(Cr)	1461	264256	0.035

(Figure 2) illustrates the adsorption fields in the MIL-101(Cr) MOF. The blue points indicate stronger adsorption fields, and the color intensity represents the strength of the adsorption field. These figures demonstrate that methane adsorption and storage occur throughout the MOF, including in both pentagonal and hexagonal cavities, as well as near the linker and cluster connection points or the center of empty cavities.

In the methane molecule, partial positive charges reside on the hydrogen atoms, while partial negative charges are present on the carbon atom. The orientation of methane molecules trapped in the framework varies depending on their location. Methane is adsorbed from its carbon part near the hydrogen and chromium atoms in the framework, and it is adsorbed from its hydrogen part near the oxygen atoms. Considering that methane

contains more hydrogen atoms, it is logical to have stronger adsorption fields (highlighted regions in Figure 2) around the oxygen atoms.

Finally, (Figure 3) represents the adsorption profile at different distances from the framework. The left side of the simulation cell is set as the center coordinates, and the cell width is divided into 10 equal parts. The concentrations are given as averages in the z-direction relative to the lowest concentration. Therefore, the concentration reaches its maximum value in the middle of the framework, indicating the convergence of equations towards equilibrium. By using larger time steps in the simulation, more accurate and close-to-real results can be achieved.

It's important to note that relative concentration refers to the ratio of the absorbed gas concentration within the framework to the concentration of the gas not absorbed in the surrounding vicinity of the framework. The variance in adsorption across different frameworks within the MOF family can be attributed to the interaction between methane and metal clusters, as well as differences in cavity dimensions. To clarify, relative concentration signifies the quantity of gas absorbed within the framework compared to the amount of gas present in the surrounding area outside the framework.Overall, these simulations provide valuable insights into the adsorption behavior of methane in the MIL-101(Cr) MOF and help us understand the interaction between methane molecules and the MOF structure.

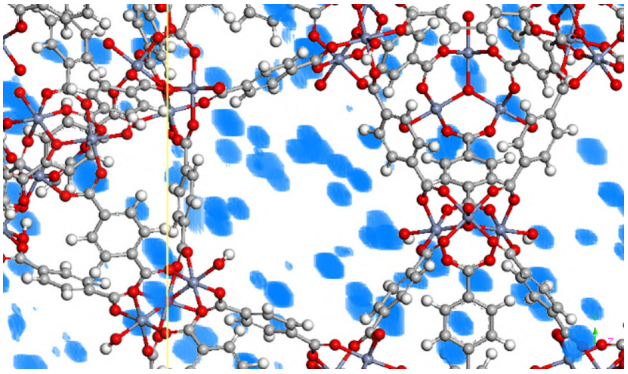

Figure 2. Adsorption field in MOF. The intensity of colors indicates the strength of the fields

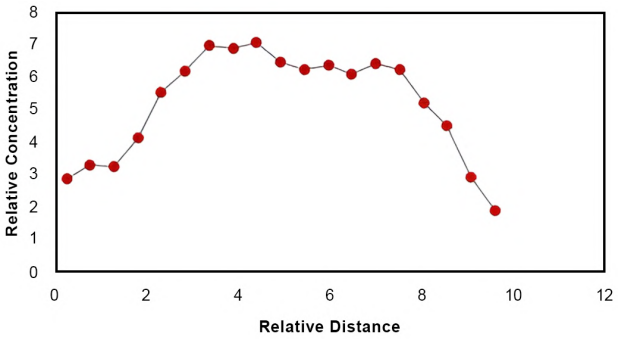

Figure 3. The concentration profile of methane adsorption for MIL-101(Cr) at the end of the simulation time

4. Conclusions

The three metal-organic frameworks (MOFs) and methane structures were placed together in the Materials Studio software, and intermolecular interactions were calculated for each of them at a pressure of 35 atmospheres and a temperature of 300 K using the Universal force field. According to the simulation results, adsorption amounts of 0.008 g, 0.089 g, and 0.035 g of methane per gram of absorbent were obtained for the clusters with iron, aluminum, and chromium cores, respectively. To verify the obtained values, another research that experimentally calculated the adsorption amount on the chromium core framework under the same conditions and found 0.036 g of methane per gram of absorbent was used. Considering the acceptable range of adsorption amounts for various practical adsorbents in ANG technology, such as activated carbon and zeolites, it can be said that the studied MOFs are suitable frameworks for gas adsorption and storage. Among these frameworks, MIL-100(Al) proves to be the best option, and if its industrial-scale production is feasible, it can be used as an adsorbent in ANG. It is worth noting that this research and similar studies indicate the technical efficiency of metal-organic frameworks. However, the hindrance to their practical application lies in economic and mass production considerations, which can be addressed with the growth of relevant technologies. In conclusion, metal-organic

frameworks have shown promise as efficient adsorbents for natural gas storage in ANG applications. The development of these frameworks may be limited by economic and production factors, but with advancing technologies, their practical application can be improved.

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بررسی جذب متان در چارچوب‌های فلزی-آلی MIL با استفاده از شبیه‌سازی دینامیک مولکولی

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چکیـــــــده

در این مطالعه، خواص جذب سه چارچوب فلز-آلی MIL-100 (Al) و MIL-100 (Fe)، MIL-101 (Cr) - برای ذخیره‌سازی متان با فشار بالا در گاز طبیعی جذب شده بررسی شد. با استفاده از نرم‌افزار Materials Studio و شبیه‌سازی مونت‌کارلو، شبیه‌سازی دینامیک مولکولی تحت‌فشار ثابت ۳۵ اتمسفر و دمای ۳۰۰ کلوین انجام شد. میزان جذب به ترتیب ۰/۰۰۸، ۰/۰۸۹ و ۰/۰۳۵ گرم متان در هر گرم جاذب برای MIL-100 (Al) و MIL-100 (Fe)، MIL-101 (Cr) گزارش شد. برای تأیید یافته‌ها، ظرفیت جذب محاسبه‌شده MIL-101 (Cr) با داده‌های تجربی مقایسه شد که تطابق نزدیک با مقدار گزارش شده ۰.۰۳۶ گرم متان در هر گرم جاذب نتیجه شد. شبیه‌سازی‌ها همچنین بینش‌هایی را در مورد الگوهای جذب آشکار کردند و نشان دادند که مولکول‌های متان به‌طور انتخابی با مناطق مختلف چارچوب‌ها بر اساس جهت‌گیری‌شان برهمکنش دارند. این مطالعه نشان می‌دهد که MOFها به‌عنوان جاذب‌های مناسب برای ذخیره‌سازی گاز طبیعی در فناوری‌های ANG نوید دارند. در میان سه MOF مورد مطالعه، MIL-100 (Al) به‌عنوان کارآمدترین گزینه ظاهر شد که با توجه به ملاحظات اقتصادی و تولیدی، پتانسیل را برای پیاده‌سازی در مقیاس صنعتی آینده ارائه می‌دهد.

واژگان کلیدی: چارچوب فلز-آلی (MOF)، جذب متان، فناوری گاز طبیعی جذب شده (ANG)، شبیه‌سازی دینامیک مولکولی، شبیه‌سازی مونت‌کارلو