High Pressure Methane Adsorption on a Series of MOF-74: Molecular Simulation Study

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Abstract
Metal-Organic Frameworks (MOFs) are the most promising materials which could reach to DOE target on methane adsorption in practical situations. So finding the best combination of metals and linkers that show the highest adsorption capacity is the most important step in MOFs production process. In this article, the methane storage capacity on a series of the metal-organic frameworks known as M-MOF-74 (M=Mg, Mn, Zn, Co, Ni) has been investigated by using molecular simulation method. Grand Canonical Monte Carlo (GCMC) simulation is employed to predict methane adsorption isotherms at ambient temperature and up to 45 bar pressure. Simulation results show Ni-MOF-74 has the highest methane capacity amongst others (Ni>Co>Zn>Mn>Mg). Finally, the obtained results are compared with experimental adsorption isotherms data and another simulation study, borrowed from literature, to determine the validity of the proposed simulation. Use of universal force field instead TraPPE force field to extract the Lenard-Jones parameters for methane is the main difference between present simulation and another existing simulation (Ye et al.). Results demonstrate high fitness between our simulation and experimental data.

Keywords: Methane, Adsorption, Molecular Simulation, GCMC, High Pressure

Research Highlights
- Methane isotherms on various MOF-74 by using GCMC.
- UFF force field was employed for adsorption system.
- Imperative performances in comparison with experiments.
1. Introduction

Since Yaghi et al. introduced Metal-Organic frameworks (MOFs) in 1999 [1], many efforts have been implemented to produce various MOFs that are appropriate in practical situations. Gas storage, especially methane, carbon dioxide and hydrogen, gas separation, catalysis, drug delivery, membranes, luminescent and sensor are some of the most important practical applications of MOFs, amongst many others [2-5]. Among mentioned applications, adsorption of methane, carbon dioxide and hydrogen have gained many attention in recent decades. Focus on the adsorption of methane and hydrogen as two vehicle fuel alternatives and CO\textsubscript{2} as one of the most hazardous greenhouse gases have been more rather than other gases. Molecular simulation is one the most robust and least cost demanding procedures which can be employed to predict capacity of adsorption of various adsorption systems (various adsorbents and adsorbates) in comparison with adsorption experiments (from synthesizing to measuring adsorption isotherms). Monte Carlo simulation in Grand Canonical ensemble or Grand Canonical Monte Carlo (GCMC) simulation has been utilized to predict adsorption isotherms in equilibrium conditions in many works [6-8]. For example, Ye et al in 2010 [7], investigated methane adsorption in several series of newly synthesised metal-organic frameworks by using GCMC. They also investigated several factors in wide range of pressure which influence on the methane adsorption. Based on their simulation results, they found heat of adsorption at infinite dilute, the accessible surface area and the free volume of materials play important roles in methane adsorption, while the main factors are different in different ranges of pressure. Furthermore, they used 14 MOFs and found that, in the MOFs with the same pore topology, there are evident linear relationships between adsorption capacity and the accessible surface area at moderate pressure as well as the free volume at high pressure. Among all simulation and experimental works, Zhou et al, in 2009 [9], claimed that they have reached to the highest methane adsorption capacity among all existing adsorbents. They produced a MOF known as PCN-14 and showed the methane adsorption can be achieved to 230 V/V at DOE target condition. DOE target condition has been identified as 180 V/V\textsuperscript{1} for methane at 35 bar and 298 K. After PCN-14 which has shown highest capacity for methane adsorption, a series of MOFs known as M-MOF-74\textsuperscript{2} reveal highest methane adsorption capacity. These group of MOFs have been thoroughly synthesized and characterized by many research groups in the recent years [10-12]. In this article, the effect of various metals in the structure of MOF-74 on the methane adsorption capacity will be studied. Subsequently, to validate the simulation, obtained results are compared with experimental adsorption isotherms and another one simulation work presented by Ye et al [7].

2. Simulation method

As it was mentioned earlier, Monte Carlo simulation in Grand Canonical (\(\mu, V, T\)) ensemble can be employed to simulate the equilibrium amount of adsorbate in a certain adsorbent at constant chemical potential, volume and temperature. In this study GCMC along Metropolis sampling scheme was used to predict all adsorption isotherms on MOFs. The important point to note is that three types of move, insert, displacement and remove with equal probability were considered while the Metropolis algorithm was used to decide on the acceptance or rejection of the move [13,14]. Furthermore, \(1 \times 10^6\) cycles were performed to reach

\textsuperscript{1} Adsorbate volume at STP condition to volume of adsorbent.

\textsuperscript{2} MOF-74 has been known with other names as M\textsubscript{2}(dhtp) or CPO-26 [10,12].
equilibrium. The simulation box for all MOFs consists eight unit cells. In other words, a construction of (2×2×2) cells was established for simulations. Besides, periodic boundary conditions in three-dimensions with cutoff radius equal to 12.5Å was used for all samples. It should be noted, the cutoff radius cannot be more than the shortest length of simulation box.

In the present simulation the universal force field (UFF) was employed to calculate the Lenard-Jones (LJ) potential parameters of methane and also the framework atoms [15]. More details regarding to the UFF can be found in literature [15-17]. It must be emphasized, the parameters used to generate the universal force field are summation of a set of hybridization dependent atomic bond radii, a set of hybridization angles, van der Waals parameters, torsional and inversion barriers, and a set of effective nuclear charges [15]. Moreover, in this study the charges of each atoms in the adsorbents structures (atomic partial charges) were calculated via Q equation [18]. Eventually, Peng-Robinson equation of state was employed for conversion of fugacity to pressure of pure methane gas.

3. Results and discussions

The calculated adsorption isotherms of methane on all MOF-74 adsorbents are depicted in Figure 1a. All Isotherms are in room temperature (298K) and up to 45 bar pressure. As it can be observed, like experimental isotherms, showed in Figure 1b, the Ni-MOF-74 discloses the highest adsorption capacity for methane at 298K and 45 bar. After that, Co, Zn, Mn and Mg-MOF-74 reveals the highest methane capacities respectively.

Furthermore in Figure 2, GCMC simulation performances are compared with the experimental results of Wu et al. [10] and simulation consequences of Ye et al. [7]. The narrow solid line is the simulation results of Ye et al.[7], the filled square symbols are experimentally obtained isotherms [10] and the diamond non-filled symbols show the results of the present GCMC simulation. As mentioned before, the UFF was employed for calculating the LJ potential parameters for both adsorbent and adsorbate while Ye et al. employed UFF for only adsorbent atoms and used TraPPE force field for adsorbate. In the other words, they have supposed the methane as a united atom in their own simulation.

Fig.1. Simulated a) and Experimental [10] b) adsorption isotherms of methane on various MOF-74 at 298k
As it can be obtained from Figure 4, the computed methane isotherms show fair agreement with experimental data and also generally better performances in comparison with Ye et al. simulation outcomes, especially, in high pressure range. Almost in all cases an over-prediction on the methane capacity has been occurred in the predicted isotherms of Ye et al simulation. This failure might is because of omitting the atomic partial charges from the adsorbents structure. It seems they didn’t consider the atomic partial charges of MOFs while this parameter has a main effect on the simulation results [19].

Among all obtained simulation performances, predicted methane isotherm on Co-MOF-74 shows the highest agreement with experimental data and better result than Ye et al work while simulated methane isotherm on Ni-MOF-74 reveals poorest fitness in comparison with both experimental and Ye et al. simulation result. In other case studies, the results of present simulation demonstrate better performances in high pressure range while the Ye et al simulation has better fitness in low pressure range. Therefore, it can be induced, although TraPPE force field can be used for simulation of methane adsorption on MOF-74 adsorbents in pressure range up to 10 bar, universal force field must be substituted in higher pressures up to 45 bar. So the combination of two TraPPE and Universal force field seems necessary to reach the best simulation results in case of methane adsorption.

4. Conclusion
Simulation of methane adsorption isotherms on a series of MOF-74 adsorbents at room temperature via Grand Canonical Monte Carlo ensemble was implemented (Figure 1). Universal force field was selected to calculate the LJ potential parameters of both methane adsorbents. The Ni-MOF-74 showed the highest methane capacity while the Mg-MOF-74 has the lowest capacity for methane at 298K and up to 45 bar. The obtained isotherms also were compared with experimental data and another one simulation effort (Figure 2). Although the
obtained simulation results were in good agreement with experimental data, by resorting to another simulation study, the combination of universal force field in high pressure range and TraPPE force field in low pressures for simulation of methane on MOF-74 adsorbents at room temperature is recommended.

References


