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Multivariable linear models of structural parameters to predict methane uptake in metal–organic frameworks

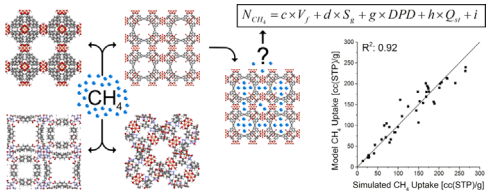
Kutay Berk Sezginel [a,b], Alper Uzun [a,b,*], Seda Keskin [a,b,**]

[a] Department of Chemical and Biological Engineering, Koc University, Rumelifeneri Yolu, Sariyer 34450, Istanbul, Turkey
[b] KÜTEM (Koc University TUPRAS Energy Center), Koc University, Rumelifeneri Yolu, Sariyer 34450, Istanbul, Turkey

HIGHLIGHTS

- CH_4 uptake and structural/chemical parameters were calculated for 45 MOFs.
- Simulation results were validated with experimental results.
- QSPR analysis was performed to investigate properties that affect CH_4 uptake.
- Pressure dependent multivariable linear models were constructed to predict CH_4 uptake.
- Models show good agreement with experimental data and outperform previous models.

GRAPHICAL ABSTRACT



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ABSTRACT

A key challenge preventing CH_4-driven energy future is the lack of effective, economic and safe on-board CH_4 storage systems. In this study, computational tools were utilized to examine CH_4 storage capacity of metal–organic frameworks (MOFs) under practical operating conditions. Grand Canonical Monte Carlo (GCMC) simulations were performed to calculate CH_4 uptake capacity of 45 MOFs. Results were confirmed with experimental data available in the literature. Motivated from the good agreement between experiments and simulations, a quantitative structure–property relationship (QSPR) analysis was performed. Making use of this analysis, multivariable linear models with one-, two-, three-, and four-variables that can accurately predict CH_4 uptake of MOFs at room temperature and pressures ranging from 1 to 65 bar were developed. Model parameters were based on easily measurable/computable structural properties, such as pore volume, surface area, and density. Models that predict CH_4 uptake at 5 and 35 bar were studied in detail to investigate the viability of reaching CH_4 storage target for vehicular systems set by DOE. At both pressures the models with four-variables outperformed other models at the same pressures, and void fraction (V_f) and isosteric heat of adsorption (Q_{st}) were found to be the most significant parameters. In order for a material to exceed the DOE target of 0.5 g/g CH_4 uptake at a storage pressure of 35 bar, the material should have high gravimetric surface area (S_g), reaching 6000 m^2/g, void fraction (V_f), as high as 0.9, dominant pore diameter (DPD) approximately 30 Å, and Q_{st} value around 30 kJ/mol. Results of this work reveal the structural properties controlling the CH_4 storage capacity of MOFs. Such information can guide experimental studies to tune the MOFs in the way of designing new materials with desirable structural properties that will reach the storage targets.

1. Introduction

Natural gas, consisting mainly of CH_4, has potential to replace petroleum and to become the primary transportation fuel source.

* Corresponding author. Tel.: +90 212 338 1754.
** Corresponding author. Tel.: +90 212 338 1362.
E-mail addresses: auzun@ku.edu.tr (A. Uzun), skeskin@ku.edu.tr (S. Keskin).

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It is naturally abundant and it has the highest H/C ratio among all hydrocarbons, therefore emits less carbon compared to other fossil fuels (Mason et al., 2014). The major challenge of utilizing CH_4 as a fuel is its efficient room temperature storage and delivery because of its low volumetric energy density compared to gasoline. There are several ways to store high densities of CH_4. Adsorbed natural gas (ANG) is one of the promising options since it offers a safer and relatively inexpensive solution compared to other methods, such as compressed natural gas (CNG) and liquefied natural gas (LNG) (He et al., 2014). In order to successfully implement ANG, adsorbent materials that can efficiently store and deliver CH_4 must be developed. For this purpose, various studies focused on porous materials such as zeolites (Antoniou et al., 2014), activated carbon (Matranga et al., 1992), carbon nanotubes (CNTs) (Cao et al., 2003), porous polymer networks (PPNs) (Lu et al., 2010) and metal–organic frameworks (MOFs) (He et al., 2014; Mason et al., 2014). Among these porous materials MOFs have been examined extensively for their CH_4 storage applications. MOFs are a type of highly porous materials formed typically from metal clusters and organic linkers and they show high potential for a wide range of applications, such as gas storage (Sumida et al., 2011; Chen et al., 2012; Suh et al., 2012; He et al., 2014), gas separations (Li et al., 2009, 2014; Kim and Nair, 2013; Ferreira et al., in press) and catalysis (Lee et al., 2009). Compared to traditional nanoporous materials MOFs exhibit several advantages, such as ease of synthesis, good thermal and mechanical stability, high permanent porosity, and large surface area. Moreover, as a result of their tunable chemistry it is possible to obtain almost unlimited number of different MOFs with a wide range of pore size and framework structure by changing the combination of metal centers and organic linkers (Sarkisov and Kim, in press).

Advanced Research Projects Agency-Energy (2014) of the U.S. Department of Energy (DOE) has set targets for adsorbent working capacity as the difference between the adsorbed CH_4 amounts at storage and delivery pressures at 298 K. The target corresponds to a volumetric working capacity of 350 cm^3(STP)/cm^3 CH_4 and when the adsorbent material packing loss is ignored the target becomes 263 cm^3(STP)/cm^3 (corresponding to CNG at 250 bar and 298 K) between a delivery pressure of 5 bar and moderate storage pressures (He et al., 2014). Two storage pressures of 35 and 65 bar were considered in previous studies as they correspond to upper limits achievable with single-stage and two-stage compressors, respectively (Peng et al., 2013; Wilmer et al., 2013). Both pressures require relatively inexpensive equipment compared to multi-stage compressors necessary to reach high pressures (250 bar) of CNG tanks. Up to date no MOFs have been identified to reach this working capacity target at either of these storage pressures. The highest working capacity recorded for a delivery pressure of 5 bar was 197 and 151 cm^3(STP)/cm^3 for UTSA-76a (Li et al., 2014) followed by 190 and 150 cm^3(STP)/cm^3 for HKUST-1 (Peng et al., 2013) for storage pressures of 65 and 35 bar, respectively. Even though, the target has not been reached yet, the highly tunable nature of MOFs provides opportunities to design materials that may reach the target. For optimal material design, it is required to examine structural and chemical properties that are controlling CH_4 storage and working capacity. Previously, relations between structural properties in MOFs and CH_4 uptake were studied experimentally by several groups. He et al. (2013) investigated five MOFs of the same family (NOTT-100, NOTT-101, NOTT-102, NOTT-103 and NOTT-109) having variable open Cu sites and porosities for CH_4 storage at 35 bar. They found a linear correlation between gravimetric CH_4 uptake and pore volume (V_p). Peng et al. (2013) studied six promising MOFs for CH_4 storage (PCN-14, UTSA-20, HKUST-1, CPO-27-Ni, NU-111, and NU-125) at 65 bar and found another linear correlation between gravimetric CH_4 uptake and V_p, and between gravimetric surface area (S_g) and total volume V_{total} (i.e. one over crystal density $1/\rho_{cryst}$). Moreover, the corresponding values for S_g, V_p, and ρ_{cryst} of MOFs were suggested to be in the order of 7500 m^2/g, 3.2 cm^3/g and, 0.28 g/cm^3, respectively, to exceed the DOE target. Kong et al. (2013) investigated the relation between S_g and CH_4 uptake at 60 bar using previously reported experimental results for 25 MOFs and reported that CH_4 uptake is linearly correlated with S_g and, V_p linearly varies with $1/\rho_{cryst}$. These studies give valuable information about the relation of structural properties and CH_4 uptake, however, the limited number of MOFs (≤ 25) used in these studies and the fact that these studies focused solely on storage pressures prevent utilization of these outcomes extensively.

Large scale computational screening studies were also performed to predict CH_4 uptake at storage and delivery pressures as well as the working capacity. Fernandez et al. (2013) performed a large-scale quantitative structure–property relationship (QSPR) analysis on approximately 130,000 hypothetical MOFs to predict CH_4 uptake at 1, 35 and, 100 bar focusing on structural properties, such as dominant pore diameter (DPD), S_g, and void fraction (V_f). They concluded that for high CH_4 storage at 35 bar, ρ_{cryst} and V_f should be greater than 0.43 g/cm^3 and 0.52, respectively. Gómez-Gualdrón et al. (2014) followed this study by performing simulations on 122,835 hypothetical MOFs to elucidate the viability of reaching volumetric CH_4 storage and delivery targets (between 5.8 and 65 bar). Their results revealed the recommended parameters as volumetric surface area (S_v) between 2100–2300 m^2/cm^3, largest cavity diameter (LCD) between 10–12 Å and, isosteric heat of adsorption (Q_{st}) between 10.5–13.0 kJ/mol. Recently another large scale screening study (Martin et al., 2014) was performed for porous polymer networks (PPNs), where structure–property relationships for CH_4 storage performance was investigated on approximately 18,000 hypothetical PPN structures. They found out that pore size is the primary structural property that determines the CH_4 uptake performance of PPNs and they also discovered that in all best-performing materials cooperative CH_4–CH_4 interactions were present, therefore they suggested CH_4 adsorption sites should be optimized by adjusting the pore size to enhance CH_4 uptake. These large scale studies provide very important information regarding which routes to take to design new materials that can reach CH_4 storage target. However, the structures considered in these studies are hypothetical, thus these works are limited in accurately representing the performance of actual synthesized MOFs. One successful approach on this regard is reported by Farha et al. (2010) which uses computational modelling to design and characterize a hypothetical MOF followed by synthesis of the designed structure. After synthesis of the tailored material they found very similar characterization and uptake properties (H_2 and CO_2) with the predicted structure. Even though this is a very promising result, CH_4 uptake properties of the synthesized material was not measured and to the best of our knowledge no other hypothetical MOF structure has been investigated experimentally for CH_4 storage purposes.

In this work, a detailed investigation on structural properties determining the CH_4 storage performance of MOFs focusing on 45 real MOF structures is provided. The MOFs were chosen to represent a diverse set of MOFs with pore diameters large enough to accommodate CH_4 molecules including the current record holding MOF materials in CH_4 storage, such as HKUST-1, CPO-27-Ni, NU-125, and PCN-14. The gravimetric CH_4 uptake and Q_{st} values were calculated at 298 K and at a wide range of pressures 1, 5, 10, 15, 20, 25, 30, 35, 50, and 65 bar using grand canonical Monte Carlo (GCMC) simulations. The validity of these simulations was tested by comparing the results with available experimental data from the literature. In order to understand the most prominent factors affecting the CH_4 storage performance of MOFs, seven structural characteristics (ρ_{cryst}, V_f, V_p, S_g, pore limiting diameter