Dubinin-Astakhov Model for Acetylene Adsorption on Metal-Organic Frameworks

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Abstract

Acetylene (C_2H_2) is explosive at a pressure above 29 psi, causing a safety issue for its storage and applications. C_2H_2 adsorption on metal-organic frameworks (MOFs) has been explored to solve the issue. However, a suitable isotherm equation for C_2H_2 adsorption on various MOFs has not been found. In this paper, it was demonstrated that Dubinin-Astakhov equation can be exploited as a general isotherm model to depict C_2H_2 adsorption on MOF-5, ZIF-8, HKUST-1, and MIL-53. In contrast, commonly used Langmuir and BET models exhibited their inapplicability for C_2H_2 adsorption on those MOFs.

Keywords

C_2H_2 · adsorption · Dubinin-Astakhov equation · metal-organic frameworks

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1. Introduction

Acetylene (C_2H_2), which is the simplest unsaturated hydrocarbon with a triple bond [1], is an energy-rich fuel for oxy-acetylene welding and metal cutting and an important chemical building block for catalytic synthesis of fine-chemicals [2,3]. However, acetylene is explosive at pressures above 29 psi, which constitutes a critical safety issue [3,4]. To solve this issue, acetylene is usually dissolved in acetone or dimethylformamide (DMF) and transported by gas cylinders with a porous material (Agamassan). Unfortunately, this storage system has low storage capacity and low gas withdrawal rate [1]. Although microporous materials (such as zeolites, molecular sieves, and activated carbon) are also employed to purify and store acetylene, they possess a low uptake capacity and a poor selectivity and catalyze acetylene polymerization [5–9].

As a new type of porous materials, metal-organic frameworks (MOFs) have attracted much attention for gas separation and storage due to their low density structures, ultra-high surface areas, and tunable frameworks [10–22]. MOFs have been explored to enhance acetylene uptake capacity, improve its selectivity, and inhibit its polymerization [1,4,23–36]. Furthermore, various adsorption models (such as Dual-site Langmuir equation [37], Langmuir equation [33], Virial expression [25], and so on [27,31,35,36,38]) were exploited for acetylene adsorption isotherms. However, none of them can well depict acetylene adsorption on various MOFs. Thus it is necessary to find an equation as a general model for acetylene adsorption on various MOFs.

As early as 1947, Dubinin and Radushkevich proposed Dubinin-Radushkevich

equation (DR equation) [39] incorporating Polanyi's Potential Theory [40] with the affinity coefficient to describe physical adsorption on heterogeneous surfaces. Based on DR equation, Dubinin developed the theory of volume filling of micropores (TVFM) [41], which made a considerable contribution in classification of microporous adsorbents and understanding the differences between physical adsorptions on porous and nonporous adsorbents. DA equation (Eq. 1), which is a more generalized version, can linearize gas adsorption on a wider variety of materials [42,43].

$$\theta = \exp\left[-\left(\frac{A}{E}\right)^n\right] \quad (1)$$

where $A=-RT\ln(p/p_0)$ and is the differential molar work of adsorption, E is the characteristic energy of adsorption, and n is the Astakhov exponent. Though DA equation is semi-empirical in nature, it can be used to obtain information about micropore structures from a single adsorption isotherm [44]. Furthermore, Chen and Yang derived Dubinin-Astakhov equation from statistical mechanical principles [45]. A unique advantage of DA equation over others is that the Dubinin-Astakhov parameters are independent on temperature [46]. DA equation was employed to evaluate benzene and cyclohexane adsorption on steam gasified humic acid chars from brown coal [47]. We found that Dubinin-Astakhov equation could well describe CO₂ adsorption on SWCNTs [48]. In this paper, we demonstrated that Dubinin-Astakhov equation can be used as a general model for acetylene adsorption on metal-organic frameworks (MOFs). This finding would be important for C₂H₂ storage in and its catalytic conversion on MOFs.

2. Experimental Section

2.1. Preparation of samples

MOF-5 was synthesized via the approach developed by Yaghi and his co-workers [49], and briefly described as follows: 0.45 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.083 g terephthalic acid were dissolved in a 100 ml Pyrex media bottle with 49 ml of dimethylformamide (DMF) and 1 ml distilled H_2O , and sealed by a Teflon lined lid. The obtained mixture was heated at 100 °C for 7 h to yield large crystals. The bottle was then cooled to room temperature and transferred to an argon-filled glove bag. All subsequent manipulations were performed in this glove bag under argon atmosphere using oven-dried glassware and anhydrous solvents. The obtained solid was washed six times with anhydrous DMF and anhydrous CH_2Cl_2 (each time soaking the solid for 8 h), respectively. Finally, after filtering the mixture, the remained product was heated at 115 °C for 24 h to yield $\text{Zn}_4\text{O}(\text{BDC})_3$ as colorless cube-shaped crystals.

ZIF-8, HKUST-1, and MIL-53 (Al) were purchased from Sigma-Aldrich.

2.2. Standard measurements of surface areas

N_2 adsorption on MOF-5, ZIF-8, HKUST-1, or MIL-53 was measured at 77 K using Micromeritics ASAP 2000 sorptometer. The samples were degassed under vacuum at 120 °C for 12 hours before the measurement. The surface areas from the N_2 adsorption were calculated by Brunauer-Emmett-Teller (BET) model [50].

2.3. C_2H_2 adsorption measurements

C₂H₂ adsorption isotherms on MOF-5, ZIF-8, HKUST-1, and MIL-53 were measured by volumetric method [19] at a selected temperature (273 K or 298 K) as follows: 200 mg of samples were loaded into a reactor and degassed under vacuum at 100 °C for 12 h. Then, C₂H₂ was introduced into the reactor for adsorption. The C₂H₂ pressure change during adsorption and desorption were monitored with a digital pressure gauge (Accu-Cal Plus 75514-29B55 with a precision of 1 Torr), generating the adsorption/desorption isotherm of pressure vs. amount of adsorbed/desorbed C₂H₂.

3. Results and Discussion

3.1. Applicability evaluation of Langmuir, BET, and Dubinin-Astakhov models for acetylene adsorption

Acetylene adsorption on MOF-5, ZIF-8, HKUST-1, and MIL-53 was carried out at 273 and 298 K, generating adsorption isotherms (Fig. 1a, 2a, 3a, and 4a). Models of Langmuir (Eq. 2), BET (Eq. 3), and Dubinin-Astakhov (Eq. 4) were employed to fit those isotherms.

$$\frac{(p/p_0)}{V} = \frac{1}{V_0 b} + \frac{1}{V_0} \left(\frac{p}{p_0} \right) \quad (2)$$

$$\frac{\left(\frac{p}{p_0} \right)}{\left(1 - \frac{p}{p_0} \right) V} = \frac{1}{V_0 c} + \left(\frac{c-1}{V_0 c} \right) \left(\frac{p}{p_0} \right) \quad (3)$$

$$\ln V = \ln V_0 - \left(\frac{RT}{E} \right)^n \left[\ln \left(\frac{p_0}{p} \right) \right]^n \quad (4)$$

where V , V_0 , P , P_0 , R , T , E , n , b , and c are the total volume adsorbed, the monolayer capacity, the equilibrium pressure, the saturation vapor pressure of the gas, the ideal gas constant, temperature, the characteristic energy of adsorption, the Astakhov exponent, the adsorption equilibrium constant, and the BET constant, respectively. As shown in

Fig. 1–4, one can see that Langmuir and BET equations provide a good-fitting line for C₂H₂ adsorption isotherms on HKUST-1 and MIL-53, but not for those on MOF-5 and ZIF-8. In contrast, Dubinin-Astakhov model can well depict all C₂H₂ adsorption isotherms on MOF-5, ZIF-8, HKUST-1 and MIL-53 (Fig. 1–4).

It is well-known that the standard method for surface area measurements is N₂ adsorption at its liquid temperature (77K) with BET model. Although BET model is generally unsuitable for the surface area estimation of microporous materials, Monte Carlo simulations revealed that BET surface areas of MOFs calculated from the simulated N₂ isotherms at 77K agree very well with the accessible surface areas calculated directly from the crystal structures in a geometric fashion [51]. This provides a validation that the BET theory can be used for N₂ adsorption at its liquid temperature to obtain reliable surface areas of MOFs. The surface areas, which were obtained with the standard N₂ adsorption approach, are 3450, 1505, 1998, and 1005 m²/g for MOF-5, ZIF-8, HKUST-1, and MIL-53, respectively (Table 1). Those accurate surface areas will be compared with those obtained from C₂H₂ adsorption isotherms at 273 and 298K using Langmuir, BET, and Dubinin-Astakhov equations. This can allow us to further evaluate the applicability of those models for C₂H₂ adsorption on MOFs.

The monolayer capacities (*V*₀) of C₂H₂ on MOFs, which were obtained by fitting isotherms with Langmuir, BET, and Dubinin-Astakhov models (Table 1), were exploited to calculate surface areas of MOFs with Eq. 5.

$$SA(m^2/g) = \frac{6.022 \times 10^{23} \sigma V_0}{22414 cm^3 \times 10^{18} nm^2/m^2} \quad (5)$$

where *SA* is the calculated surface area of the adsorbent (MOFs), *V*₀ is the monolayer

capacity, and σ is the cross-sectional area of the gas (C_2H_2) that was calculated with Eq. 6.

$$\sigma = f \left(\frac{M}{\rho N_a} \right)^{2/3} \quad (6)$$

where f is the packing factor (for hexagonal-close-packed, then f equals 1.091), ρ the density of liquid adsorbate (C_2H_2), M the molar mass of the adsorbate (C_2H_2), and N_a Avogadro's number. At 273 and 298 K, the densities of liquid C_2H_2 are 0.451 and 0.406 g/cm³ [52] and thus the cross-sectional areas of C_2H_2 are 0.2283 and 0.2449 nm², respectively. As shown in Table 1, the application of Dubinin-Astakhov model to C_2H_2 adsorption isotherms (at 273 and 298 K) produced the surface areas of 3479 and 3583 m²/g for MOF-5, 1493 and 1578 m²/g for ZIF-8, 2004 and 2006 m²/g for HUKST-1, and 966 and 1006 m²/g for MIL-53. This indicates that the surface areas from Dubinin-Astakhov model are well consistent with the accurate surface areas (3450, 1505, 1998, and 1005 m²/g for MOF-5, ZIF-8, HUKST-1, and MIL-53, respectively) obtained from N_2 adsorption at 77K. Using Langmuir model for C_2H_2 adsorption isotherms (at 273 and 298 K) gave the surface areas as follows: -6860 and 3274 m²/g for MOF-5, -2239 and -1385 m²/g for ZIF-8, 1728 and 1548 m²/g for HUKST-1, and 833 and 818 m²/g for MIL-53. The surface areas for the MOFs were also obtained using BET model for C_2H_2 adsorption isotherms (at 273 and 298 K), namely, 8588 and 1777 m²/g for MOF-5, -6918 and -2289 for ZIF-8, 1651 and 1508 for HUKST-1, 779 and 778 for MIL-53. Those indicates that all surface areas of the MOFs from C_2H_2 adsorption isotherms with Langmuir and BET models are far from their accurate surface areas. Therefore, one can see that only Dubinin-Astakhov model for C_2H_2 adsorption isotherms can produce

reliable surface areas. Since Langmuir equation is based on a chemical adsorption on uniform surface, the unsuitability of Langmuir model for C_2H_2 indicates that C_2H_2 on MOFs is not a chemical adsorption on a single type of active sites (please see more discussion in the next section). In contrast, BET model is for physical adsorption that mainly occurs near the condensation point. When the temperature of gas adsorption is much higher than its condensation temperature, the BET model cannot be used for the surface area calculation [48]. In other words, the very low melting point ($-80\text{ }^{\circ}\text{C}$) of C_2H_2 makes the BET model unsuitable for its adsorption on MOFs at room temperature. Therefore, only Dubinin-Astakhov equation can be used as a general model for C_2H_2 adsorption on MOFs.

3.2. Evaluation of acetylene adsorption by Dubinin-Astakhov model

The characteristic energy (E) of C_2H_2 adsorption on MOFs was calculated with Dubinin-Astakhov model. The obtained E value decreases in the order: 13.6 kJ/mol (HKUST-1) $> 10.4\text{ kJ/mol}$ (MIL-53) $> 5.0\text{ kJ/mol}$ (ZIF-8) $> 3.7\text{ kJ/mol}$ (MOF-5). It was demonstrated that the pore size is inversely proportional to the characteristic energy for physical adsorption of gas molecules on porous materials [53,54]. The pore sizes of MOF-5 [49], ZIF-8 [55], HKUST-1 [56], and MIL-53 [57] are 12.94 , 11.6 , 9 , and $7.7\text{ \AA}$, respectively. The correlation of the pore sizes with the characteristic energies generates a linear relationship (except HKUST-1) with a negative slope (Fig. 5a). This indicates that C_2H_2 on MOF-5, ZIF-8, and MIL-53 is a typical physical adsorption.

Furthermore, the adsorption heats were calculated with Clausius-Clapeyron equation. As shown in Fig. 5b, the initial adsorption heats of C₂H₂ on HKUST-1, MIL-53, ZIF-8, and MOF-5 are 35.6, 20.3, 15.0, and 13.5 kJ/mol, respectively. The adsorption heats are linearly proportional to the Dubinin-Astakhov characteristic energies for all MOFs except HKUST-1 (Fig. 5b). The exception of HKUST-1 for the above two linear relationships would be due to C₂H₂ chemical adsorption. Different from other MOFs, HKUST-1 possesses open Cu²⁺ sites, which can be bound by gas molecules to form chemical adsorption [58]. The high adsorption heat of C₂H₂ on HKUST-1 originated from a chemical bond between C₂H₂ and an open Cu²⁺ site [31].

4. Conclusions

C₂H₂ adsorption on MOF-5, ZIF-8, HKUST-1, and MIL-53 were fitted by Dubinin-Astakhov, Langmuir, and BET models. Only Dubinin-Astakhov equation can provide a perfect-fit for all four MOFs. The application of the Dubinin-Astakhov equation to C₂H₂ adsorption produced reliable surface areas for MOFs. Furthermore, the relationship between Dubinin-Astakhov characteristic energies and pore sizes revealed that C₂H₂ adsorption on MOF-5, ZIF-8, and MIL-53 is a typical physical adsorption, whereas C₂H₂ adsorption on HKUST-1 contains a chemical adsorption.

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Table 1

The surface areas obtained from the Langmuir, BET, Dubinin-Astakhov equations at 273 and 298 K and measured from N₂ BET at 77 K.

Sample	Langmuir (m ² /g)		BET (m ² /g)		Dubinin-Astakhov (m ² /g)		Standard measurement (m ² /g)
	273 K	298 K	273 K	298 K	273 K	298 K	
MOF-5	-6860	3274	8588	1777	3479	3583	3450
ZIF-8	-2239	-1385	-6918	-2289	1493	1578	1505
HKUST-1	1728	1548	1651	1508	2004	2006	1998
MIL-53	833	818	779	778	966	1006	1005

Fig. 1. (a) C₂H₂ adsorption isotherms on MOF-5 at 273 and 298 K. Application of the (b) Langmuir, (c) BET, and (d) Dubinin-Astakhov equations to C₂H₂ adsorption on MOF-5 at 273 and 298 K (the squares and circles represent experimental data and the solid lines represent modeling predictions).

Fig. 2. (a) C_2H_2 adsorption isotherms on ZIF-8 at 273 and 298 K. Application of the (b) Langmuir, (c) BET, and (d) Dubinin-Astakhov equations to C_2H_2 adsorption on ZIF-8 at 273 and 298 K (the squares and circles represent experimental data and the solid lines represent modeling predictions).

Fig. 3. (a) C_2H_2 adsorption isotherms on HKUST-1 at 273 and 298 K. Application of the (b) Langmuir, (c) BET, and (d) Dubinin-Astakhov equations to C_2H_2 adsorption on HKUST-1 at 273 and 298 K (the squares and circles represent experimental data and the solid lines represent modeling predictions).

Fig. 4. (a) C_2H_2 adsorption isotherms on MIL-53 at 273 and 298 K. Application of the (b) Langmuir, (c) BET, and (d) Dubinin-Astakhov equations to C_2H_2 adsorption on MIL-53 at 273 and 298 K (the squares and circles represent experimental data and the solid lines represent modeling predictions).

Fig. 5. (a) The correlation of the pore sizes with the characteristic energies on MOFs. (b) The correlation of the characteristic energies with the initial adsorption heats on MOFs.

Graphical abstract

It was demonstrated that Dubinin-Astakhov equation can be exploited as a general isotherm model for C_2H_2 adsorption on metal-organic frameworks (MOFs), including MOF-5, ZIF-8, HKUST-1, and MIL-53.