

A new adsorption isotherm for C5 hydrocarbons on metal–organic framework $\text{Cu}_3(\text{BTC})_2$

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Abstract A new equation describing isotherms of C5 hydrocarbons on metal–organic framework $\text{Cu}_3(\text{BTC})_2$ in the temperature range from 273 to 333 K was developed. The isotherms of *n*-pentane, isopentane and cyclopentane on $\text{Cu}_3(\text{BTC})_2$ belonging to the Type 5 according to the IUPAC classification are characterized by a long vertical part in the low pressure region. An analysis of isosteric adsorption heats has revealed that lateral interactions among pentane molecules adsorbed on $\text{Cu}_3(\text{BTC})_2$ dominate over gas–solid interactions. Because there is no equation in the literature, which can be used for the description of isotherms under investigation, equation based on the Dubinin theory of S-shaped adsorption isotherms was developed. According to this theory each adsorbed molecule is a secondary center, which is capable to adsorb other molecules. The equation was suggested with respect to the leveling-off of the isotherms as at the end of the adsorption process the whole adsorption volume becomes filled with adsorbed molecules. Despite only three constants included in the equation, its accuracy in experimental data description is satisfactory.

Keywords $\text{Cu}_3(\text{BTC})_2$ · Adsorption · C5 hydrocarbons · Isosteric adsorption heats · Isotherm equation

1 Introduction

Metal–organic frameworks (MOFs) are novel materials constructed from multi-dentate organic ligands and metal atoms or small metal-containing clusters. Most of the MOF materials have three-dimensional structures of uniform pores possessing extremely large surface areas and pore volumes (Millward and Yaghi 2005). The number of potential MOFs is virtually unlimited as variations in metals or metal cluster nodes linked together through organic moieties produce novel MOFs with distinct properties. Particularities of MOFs make these materials attractive for investigations in catalysis (Dhakshinamoorthy et al. 2013) and adsorption (Rouquerol et al. 2014). Due to large variety of available MOFs the number of adsorption studies is highly diverse. In the cited monograph (Rouquerol et al. 2014) examples are given that are able to highlight the adsorption properties of MOFs.

Among various MOFs, Cu-BTC [$\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$, BTC = benzene-1,3,5-tricarboxylate], first reported by Chui (Chui et al. 1999), is one of the most-studied MOFs for gas adsorption and storage. The network of $\text{Cu}_3(\text{BTC})_2$ has a simple face-centered cubic symmetry (Vishnyakov et al. 2003). The unit cell consists of 48 copper atoms, 192 oxygen atoms, 288 carbon atoms and 96 hydrogen atoms, *i.e.* its composition corresponds to the formula $[\text{Cu}_3(\text{BTC})_2]_{16}$. The structure of the unit cell is shown in Fig. 1. This Figure demonstrates two Cu atoms connected to eight oxygen atoms of tetra-carboxylate units forming a dimeric paddle wheel. Each BTC ligand holds three dimeric Cu paddle wheels to constitute a microporous open framework. The pore system consists of two types of cages: (i) large main cavities connected to each other by nearly square windows of ca. 0.9 nm edge (8 per unit cell) and (ii) small octahedral-shaped pockets accessible from the main cavities through small triangular

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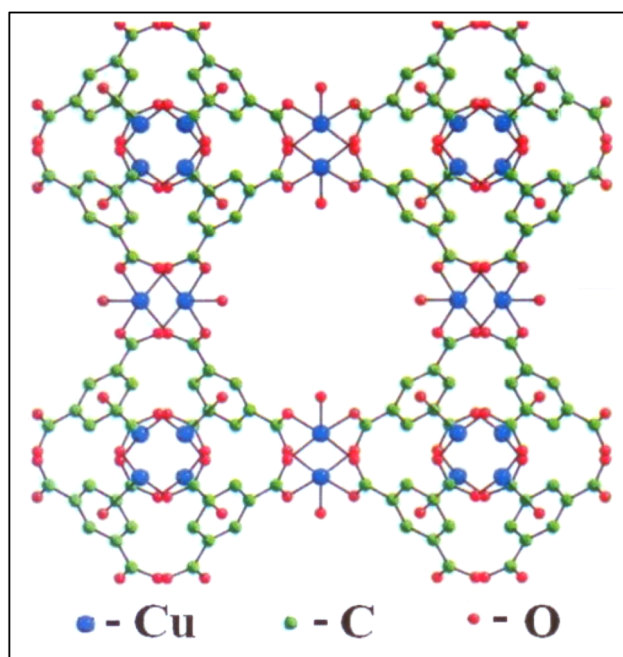


Fig. 1 Structure of $\text{Cu}_3(\text{BTC})_2$ metal–organic framework

windows inscribing circle of approximately 0.35 nm in diameter (8 per unit cell). The key structural characteristics are copper dimers being coordinated to the oxygen atoms of the BTC linkers. The remaining coordination sites (one per Cu atom) are occupied by water molecules. Prior to experimental measurements of adsorption, the water molecules are to be removed by a careful degassing procedure. The dehydration leaves unsaturated Cu sites being accessible to the adsorbed molecules. The partial positive charges on these sites, called the open metal sites, have a potential to enhance the strength of interaction with adsorbed molecules.

Investigation of adsorption of organic molecules on $\text{Cu}_3(\text{BTC})_2$ was performed foremost with C1 or C3–C6 hydrocarbons (Lamia et al. 2009; Chmelik et al. 2009; Klein et al. 2010; Jorge et al. 2010; Chen et al. 2011; Ruběš et al. 2013). As the understanding of adsorption equilibrium of hydrocarbon vapors on $\text{Cu}_3(\text{BTC})_2$ is of importance for both the fundamental investigation of adsorption equilibrium and for application of MOFs in hydrocarbon separation, the adsorption of C5 hydrocarbon vapors on $\text{Cu}_3(\text{BTC})_2$ at temperatures 273–333 K was recently investigated (Zukal et al. 2015). It was shown that pentane isotherms belonging to the Type 5 according to the IUPAC classification are characterized by unusual rectangular course with a long vertical part in a low pressure region. To our best knowledge there is no isotherm equation in the literature, which can be used for the description of these isotherms. Therefore, we have proposed a new equation based on the Dubinin model of adsorption onto sites of which concentration increases with loading.

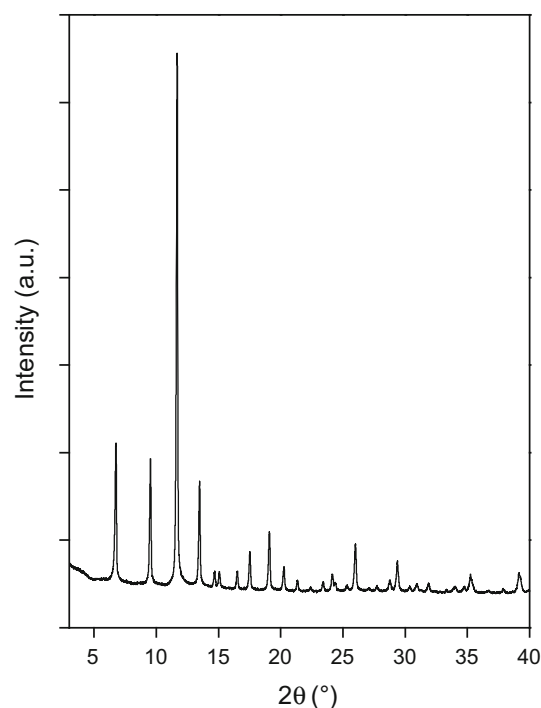


Fig. 2 X-ray pattern of $\text{Cu}_3(\text{BTC})_2$

2 Experimental

2.1 Materials

High-purity anhydrous *n*-pentane, isopentane and cyclopentane from Aldrich were used for adsorption measurements. The metal–organic framework $\text{Cu}_3(\text{BTC})_2$ was purchased from Aldrich under trademark Basolite C300.

To verify the structure of $\text{Cu}_3(\text{BTC})_2$, the X-ray diffraction (Bruker D8 X ray powder diffractometer) and nitrogen adsorption (ASAP 2020 instrument, Micromeritics) were recorded. XRD pattern of $\text{Cu}_3(\text{BTC})_2$ (Fig. 2) shows well resolved diffraction lines corresponding to those reported by Dhakshinamoorthy (Dhakshinamoorthy et al. 2010). Pore volume and surface area were determined from nitrogen adsorption isotherm at 77 K (Fig. 3). The BET area of 1,718 m^2/g and micropore volume of $= 0.64 \text{ cm}^3/\text{g}$ are comparable with those reported by Millward and Rowsell (Millward and Yaghi 2005; Rowsell and Yaghi 2006).

2.2 Adsorption

All adsorption measurements were performed with an ASAP 2020 instrument. In order to measure isotherms of vapors of liquid C5 hydrocarbons, the instrument was equipped with vapor accessory kit. Before adsorption experiments, possible contaminants such as atmospheric

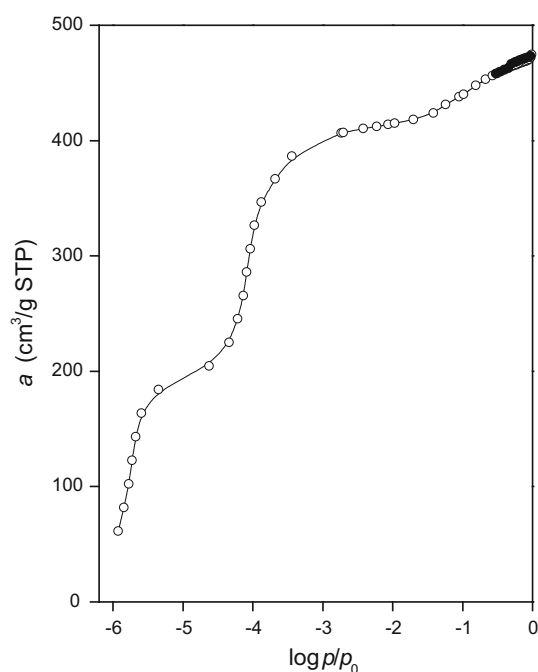


Fig. 3 Adsorption isotherm of nitrogen at 77 K for $\text{Cu}_3(\text{BTC})_2$. Solid points denote desorption

gases or traces of moisture were removed from liquid adsorptives. The fresh MOF sample was degassed starting at an ambient temperature up to 353 K (temperature ramp of 0.5 K min^{-1}) until the residual pressure of 1 Pa was attained. After further heating at 353 K for 3 h, the temperature was increased up to 383 K (temperature ramp of 1 K min^{-1}). At this temperature, degassing continued under the turbomolecular pump vacuum for 12 h. Prior to the repeated adsorption measurement on the same sample, $\text{Cu}_3(\text{BTC})_2$ was degassed directly on the sample port at 383 K (temperature ramp of 1 K min^{-1}) for 12 h under turbomolecular pump vacuum.

Adsorption isotherms of *n*-pentane, isopentane and cyclopentane vapors were recorded using equilibration time interval of 5 s. (Equilibration time interval represents the number of seconds between successive pressure readings during equilibration. The usual practice of adsorption measurements supposes that equilibration is reached when the pressure change per equilibration time interval is less than 0.01 % of the average pressure during this interval.) To verify adsorption equilibrium, the isotherms at 293 K were measured using equilibration time intervals of 10 and 20 s. It was established that a lengthening of equilibration time interval practically does not play any role, i.e. the equilibrium is reached if the time interval of 5 s is applied.

Adsorption isotherm of nitrogen was recorded at 77.3 K using liquid bath of N_2 . The Iso-Therm thermostat (e-Lab Services, Czech Republic) maintaining temperature of the sample with accuracy of $\pm 0.01 \text{ K}$ was used for the

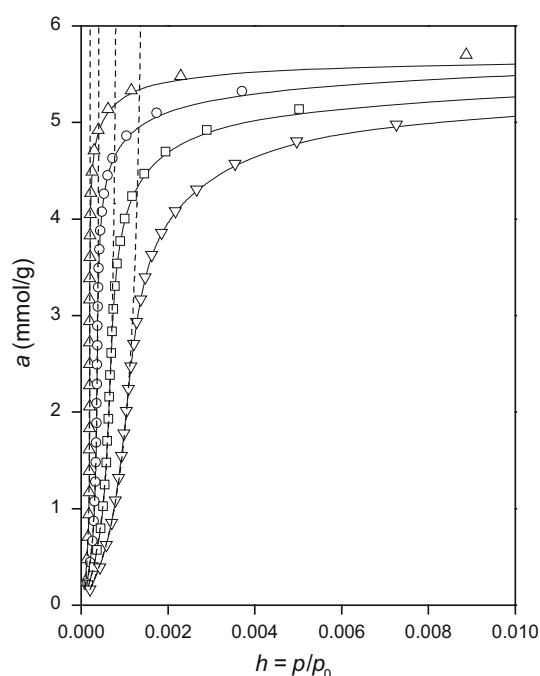


Fig. 4 Adsorption isotherms of *n*-pentane on $\text{Cu}_3(\text{BTC})_2$ at 273 K (open triangle), 293 K (open circle), 313 K (open square) and 333 K (open inverted triangle) in linear coordinates. Dashed curves are calculated from Eq. (3b)

measurement of adsorption of *n*-pentane, isopentane and cyclopentane vapors. Isotherms were subsequently recorded on the same sample at temperatures 273, 293, 313 and 333 K. For measurement of isotherms of each adsorptives a fresh $\text{Cu}_3(\text{BTC})_2$ sample was used.

Experimental details are given in paper by Zukal (Zukal et al. 2015).

3 Results and discussion

Adsorption isotherms of *n*-pentane on $\text{Cu}_3(\text{BTC})_2$ at 273, 293, 313 and 333 K are shown in Fig. 4 in linear coordinates. To achieve good resolution, isotherms are displayed in semi-logarithmic coordinates in Fig. 5. Isotherms of isopentane and cyclopentane on $\text{Cu}_3(\text{BTC})_2$ are similar. They are shown in Supplementary Information, Figures SI 1–SI 4. All recorded isotherms belong to the Type 5 according to the IUPAC classification; they are convex to the p/p_0 axis at low pressures. The isotherms display unusual long vertical part especially at 273 and 293 K revealing that the micropore filling takes place in very narrow pressure interval.

Based on the temperature dependence of adsorption isotherms, the isosteric heats of adsorption, Q_{st} , were calculated. This fundamental thermodynamic function provides information about the adsorbate-adsorbent and

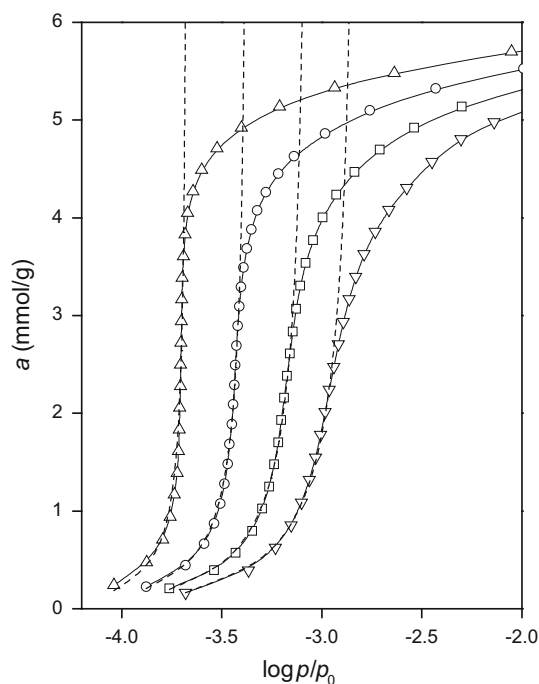


Fig. 5 Adsorption isotherms of *n*-pentane on $\text{Cu}_3(\text{BTC})_2$ at 273 K (open triangle), 293 K (open circle), 313 K (open square) and 333 K (open inverted triangle) in semi-logarithmic coordinates. Dashed curves are calculated from Eq. (3b)

adsorbate–adsorbate interactions. The isosteric adsorption heat was determined according to the Clausius–Clapeyron equation:

$$\frac{Q_{st}}{R} = - \left(\frac{\partial \ln p}{\partial 1/T} \right)_a, \quad (1)$$

where R is gas constant. The Q_{st} values in Fig. 6 show for *n*-pentane and isopentane increasing trends up to the loading of ~ 5 mmol/g. This indicates that the lateral interactions between adsorbed molecules dominate over the gas–solid interactions. The domination of the lateral interactions becomes more pronounced for cyclopentane. From 1.5 to 4.0 mmol/g of adsorbed cyclopentane, isosteric adsorption heat does not depend on the amount adsorbed. Its value 46.1 kJ/mol is somewhat higher than molar heat 42.3 kJ/mol of cyclopentane sublimation. It is obvious that the horizontal part of the dependence Q_{st} versus a corresponds to the vertical part of adsorption isotherm. Therefore, it can be supposed that the filling of micropores of $\text{Cu}_3(\text{BTC})_2$ takes place due to lateral interactions of cyclopentane molecules practically regardless of cyclopentane– $\text{Cu}_3(\text{BTC})_2$ interactions. At the end of micropore filling, isosteric adsorption heat of pentanes increases owing to enhanced lateral interactions. It is obvious that Q_{st} reaches the maximum value at loadings of 5 mmol/g (*n*-pentane, isopentane) or 6 mmol/g (cyclopentane) which correspond to fully filled micropores.

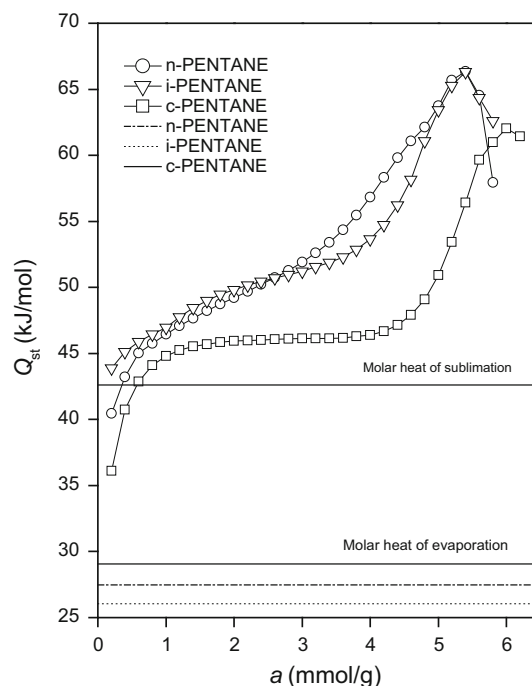


Fig. 6 Isosteric adsorption heats of pentane isomers on $\text{Cu}_3(\text{BTC})_2$. Horizontal lines denote molar heat of evaporation of pentane isomers and molar heat of sublimation of cyclopentane, respectively

The domination of lateral interactions, which gives rise to S-shaped isotherms, is typical for the adsorption of water vapor on hydrophobic materials, especially on carbonaceous adsorbents (McCallum et al. 1999). The paper by Dubinin represents one of the early attempts to analyze the water adsorption data (Dubinin 1980). Suggested equation is based on a kinetic model of water adsorption onto sites of which concentration increases linearly with loading. According to this model each adsorbed water molecule is a secondary center, which is capable to adsorb other water molecule. If constant a_0 is the number of primary adsorption centers, at the dynamic equilibrium

$$k_1(a_0 + a)h = k_2a, \quad (2)$$

where a is amount adsorbed and h relative pressure p/p_0 ; k_1 and k_2 are adsorption and desorption rate constants, respectively. From the condition (2) we obtain

$$h = \frac{a}{c(a_0 + a)}, \quad (3a)$$

or

$$a = a_0 \frac{ch}{1 - ch}, \quad (3b)$$

where $c = k_1/k_2$ is dimensionless constant. Rearrangement of Eqs. (3a) or (3b) gives linear form $a/h = a_0c + ac$; therefore, both constants a_0 and c can be simply calculated from the plot a/h versus a .

Table 1 Values of constants in the Eqs. (3) and (6)

Adsorptive	Temperature (K)	a_0 (mmol/g)	c	$1,000/c$	a_s (mmol/g)
<i>n</i> -pentane	273	0.256	4,587	0.218	6.0
	293	0.486	2,246	0.445	5.8
	313	0.859	1,088	0.919	5.6
	333	1.153	607	1.647	5.4
<i>i</i> -pentane	273	0.179	7,648	0.131	5.9
	293	0.286	3,574	0.280	5.8
	313	0.555	1,765	0.567	5.7
	333	0.885	898	1.113	5.6
<i>c</i> -pentane	273	0.0181	1,985	0.504	6.7
	293	0.0493	1,302	0.768	6.6
	313	0.142	779	1.284	6.5
	333	0.268	499	2.004	6.4

Equations (3a) or (3b) describe only the initial region and the main part of the isotherm rise. In order to describe the end of adsorption process, where the isotherm levels off, Dubinin (Dubinin and Serpinsky 1981) has modified Eq. (3a) using third constant k representing the loss of adsorption sites upon adsorption:

$$h = \frac{a}{c(a_0 + a)(1 - ka)}. \quad (4)$$

In order to gain better description of the water adsorption on activated carbon, four-parameter modification of the Dubinin equation was developed by Barton (Barton et al. 1991). This equation can be represented by

$$h = \frac{a}{ca_0 + ca \left[1 - \exp(-k^2(a - a_c)^2) \right]}, \quad (5)$$

where a_0 , a_c , c and k are fitting parameters (Cal 1997). Later on, more sophisticated models were proposed by Talu and Meunier (1996), Qi et al. (1998), McCallum et al. (1999), Do and Do (2000) and Kim et al. (2008). These models were proposed to describe the adsorption equilibrium of water on different carbonaceous adsorbents; however, they are not applicable on pentane isotherms on $\text{Cu}_3(\text{BTC})_2$ due to their special features. It is typical for pentane isotherms that nearly vertical increase in the amount adsorbed takes place in the region of relative pressures p/p_0 lower than 0.001–0.002 while increase of loading of water on carbonaceous materials occurs in the broad region of relative pressures higher than ~ 0.2 .

Although Eqs. (4) and (5) or more complicated models were not suitable for description on adsorption of pentane vapors on $\text{Cu}_3(\text{BTC})_2$, the simple Eqs. (3a) or (3b) surprisingly fits experimental points in the initial and the steep parts of the pentane isotherms with a high accuracy. The constants a_0 and c in these equations obtained from linear form are listed in Table 1. The Figs. 4 and 5 illustrate the fit for *n*-pentane isotherms in linear and semi-logarithmic

coordinates, respectively. The similar fits for isopentane and cyclopentane are shown in Supplementary Information (Figures SI 1–SI 4).

The presented fits of experimental data with Eq. (3) give further support for the decisive role of lateral interactions during the filling $\text{Cu}_3(\text{BTC})_2$ micropores. It follows from the Eq. (3b) that calculated isotherms asymptotically approach the vertical line when the product $c \cdot h \rightarrow 1$, i.e. when $h \rightarrow 1/c$. (The values of $1,000/c$ are given in Table 1.) Since vertical parts of isotherms gradually shift to higher values of h with increasing temperature, the constant c decreases with increasing temperature. With respect to the definition of c this clearly indicates expected decrease in the adsorption rate constant k_1 and increase in the desorption rate constant k_2 with increasing temperature.

In the original Dubinin model the constant a_0 as a number of primary adsorption centers does not depend on the temperature. In our interpretation the constant a_0 expresses the amount of pentane molecules (in mmol/g) which are adsorbed directly on the $\text{Cu}_3(\text{BTC})_2$ surface at beginning of micropore filling. As shown in Table 1, with all pentane isomers a_0 increases with increasing temperature. Since adsorption rate constant k_1 decreases with increasing temperature, we can speculate that the decrease of k_1 is compensated by the increase of a_0 .

At the end of the adsorption process, the whole adsorption volume becomes filled with pentane molecules. With respect to the leveling-off of the isotherms we have suggested following modification of Eq. (3a):

$$h = \frac{p}{p_0} = \frac{a}{c(a_0 + a)} \left[1 + \frac{1}{(a_s - a)^2} \right]. \quad (6)$$

The empirical term $\left[1 + \frac{1}{(a_s - a)^2} \right]$ involves the constant a_s , which represents the limiting amount adsorbed. This term is practically negligible at small amounts adsorbed; therefore, it does not affect the initial adsorption behavior.

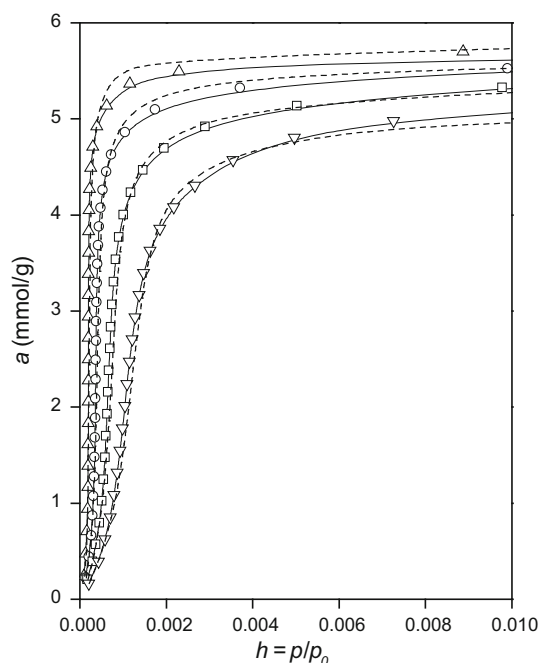


Fig. 7 Adsorption isotherms of *n*-pentane on $\text{Cu}_3(\text{BTC})_2$ at 273 K (open triangle), 293 K (open circle), 313 K (open square) and 333 K (open inverted triangle) in linear coordinates. Dashed curves are calculated from Eq. (6)

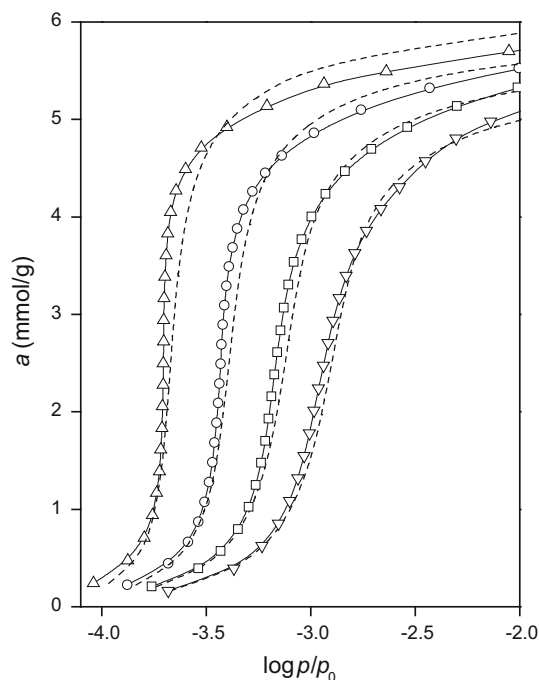


Fig. 8 Adsorption isotherms of *n*-pentane on $\text{Cu}_3(\text{BTC})_2$ at 273 K (open triangle), 293 K (open circle), 313 K (open square) and 333 K (open inverted triangle) in semi-logarithmic coordinates. Dashed curves are calculated from Eq. (6)

Since the constant a_s affects the maximum amount of pentane that can adsorb on the $\text{Cu}_3(\text{BTC})_2$, it causes the leveling-off of the isotherm with increasing loading.

The values of the constant a_s determined using least square method are listed in Table 1. It is evident that the small decrease of this constant corresponds to the decrease of finite adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ micropores with increasing temperature. The fit of *n*-pentane isotherms is displayed in Figs. 7 and 8 in linear and semi-logarithmic coordinates, respectively. Similar fits for isopentane and cyclopentane isotherms are displayed in Supplementary Information. All Figures show that Eq. (6) describes adsorption isotherms of *n*-pentane, isopentane and cyclopentane with satisfactory precision. Small discrepancies between experimental and calculated data are evidently due to simplicity of suggested equation. It is obvious that more complicated equations containing more constants provide better fit of experimental data. However, in this case we lose straightforward meaning of such equations and constants used.

4 Conclusions

Adsorption isotherms of pentane isomers on $\text{Cu}_3(\text{BTC})_2$ belong to the Type 5 of the IUPAC classification. Because these isotherms display unusual rectangular course with long vertical part at low equilibrium pressures, the models proposed in the literature fail. As determined isosteric adsorption heats increase with the amount adsorbed, the lateral interactions among pentane molecules adsorbed on $\text{Cu}_3(\text{BTC})_2$ dominate over the gas–solid interactions. For this reason, we have suggested here for the description of pentane isotherms on $\text{Cu}_3(\text{BTC})_2$ an equation based on the Dubinin model. This model takes into account adsorption onto sites of which concentration increases linearly with loading. Suggested equation containing three constants describes experimental data with satisfactory precision.

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