Adsorption (2010) 16: 559–565
DOI 10.1007/s10450-010-9260-z

Metal organic frameworks showing hydrocarbon adsorption properties commensurate with their pore structure

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Published online: 14 August 2010

Abstract Commensurate adsorption occurs when the number of molecules adsorbed per unit cell relates to the symmetry of the framework and its topology. While rare in zeolite materials, commensurate adsorption has been observed in several MOF materials. In some MOF materials, several molecules having dimensions within a limited size range show this effect. This paper describes the commensurate adsorption properties of three MOF materials and also two MOFs showing unusual combined structure-composition adsorption features.

Keywords Metal organic framework · MOF · Commensurate · Adsorption

1 Introduction

Typically, adsorption in zeolites and metal organic frameworks (MOFs) takes place with the adsorbate molecules filling channels and cavities that are significantly larger than their molecular size, resulting in random orientation of the molecules in the channels and cavities. In addition, the number of molecules adsorbed does not relate to the crystal symmetry or structure of the zeolite. This random packing is demonstrated via simulated benzene adsorption in zeolite Y, the most important and widely used zeolite (see Fig. 1). Five benzene molecules are seen as randomly occupying the large cavity. In a very limited number of zeolite structures the number and arrangement or packing of the molecules are commensurate with the structure and symmetry of the channels.

The term commensurate adsorption refers to those cases where adsorption levels and location of the molecules are controlled by specific channel features, such as channel segment lengths, cavity shape and size, and relate to crystal symmetry and multiplicity of general or special crystallographic positions. Thus in cases of commensurate adsorption, the ordering of molecules reflect the channel topography and the number of adsorbed molecules relate to the sym-

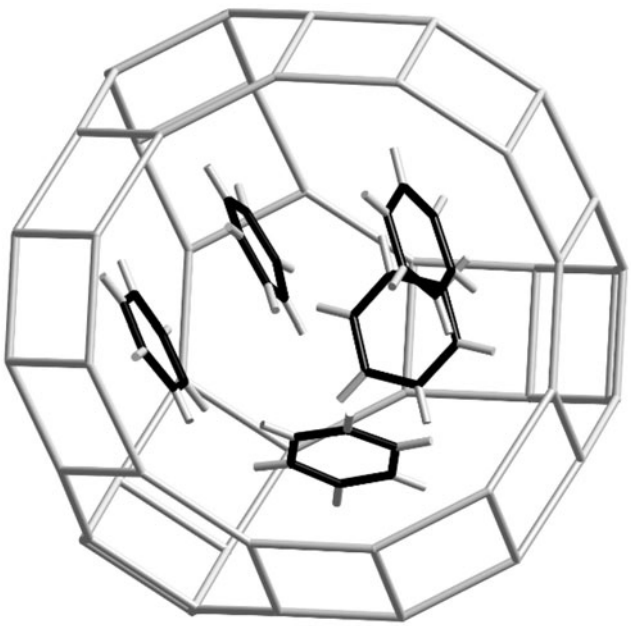

Fig. 1 Five benzene molecules in the supercage of zeolite Y. Positions from adsorption simulation

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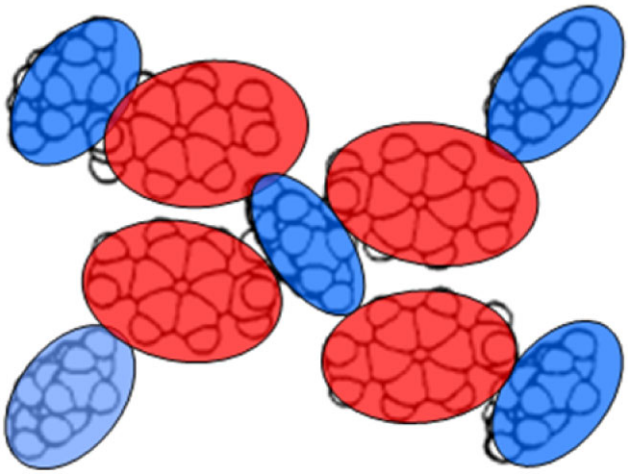

Fig. 2 (Color online) Packing of p-xylene in the ZSM-5 structure. View down [010] the direction of straight channels. The blue p-xylene molecules, in channel intersections, pack parallel to [010]. Red p-xylene site in sinusoidal links between channel interections. Packing from simulations (Reischman et al. 1988)

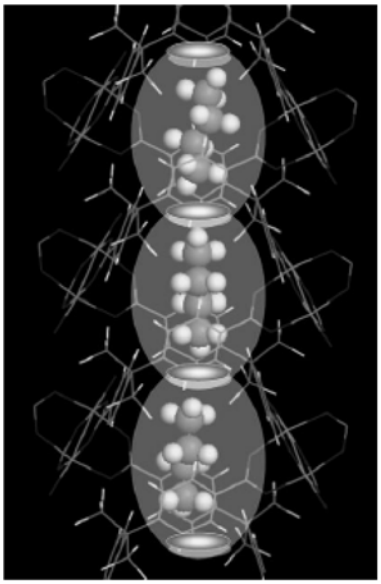

Fig. 3 Packing of butane, one molecule per cage in the oval shaped cages of Cu(hfipbb). Shape of cage is illustrated by the 3 *grey ovals*

metry of the adsorbent (Smit and Maesen 1995; van Well et al. 1995). Herein, we also propose to extend this terminology to cases where the composition of the adsorbate and adsorbent lead to unique properties.

Commensurate adsorption in zeolites is quite rare. An early example is the adsorption of p-xylene in ZSM-5, where adsorption isotherms revealed two distinct adsorption levels having loadings of 4 and 8 molecules of p-xylene per unit cell, respectively (Fig. 2, Olson et al. 1981). The ZSM-5 channel structure has 4 channel intersections per unit cell and 4 straight channel and 4 sinusoidal channel links connecting these intersections. Simulated adsorption studies (Reischman et al. 1988) and crystal structure determinations (Mentzen 1987) revealed that the first 4 molecules of p-xylene adsorbed are located in the channel intersections and next 4 occupy the 4 sinusoidal channel links (Fig. 3). The adsorption of benzene in ZSM-5 show similar behavior (Shah et al. 1995).

While metal organic framework materials (MOFs) are relatively new, numerous examples of commensurate adsorption have been observed. Below, we will describe three examples.

2 Experimental

Adsorption measurements were made using a computer-controlled thermogravimetric balance consisting of a TA51electrobalance and associated TA-2000/PC control system. This one atmosphere, gas flow through electrobalance system was controlled via Macintosh based LabView control software, Kinetic Systems interface, mass flow controllers, and Eurotherm temperature controller. The adsorbents were activated at 100 to 200 °C for 1 h in dry nitrogen prior to the sorption measurement.

Simulated adsorptions were computed using Accelrys Cerius2 Sorption software (Accelrys). This Sorption module employs a Monte Carlo method of generating positions for the adsorbate molecules and accepts their insertions when they are energetically favored. Burchard-Universal forcefield were used (Burchard 1993).

The composition and brief description of the MOF materials are as follows.

Cu-hfipbb is [Cu(hfipbb)(H_2hfipbb)$_{0.5}$], where H_2hfipbb = 4,4′-(hexafluoroisopropylidene bis(benzoic acid)), (Pan et al. 2004, 2006). It has 1-dimensional (1D) channels consisting of oval-shaped "supercages" ∼7.3 Å in length connected via narrow "necks" (∼3.2 Å in diameter).

Zn-bpdc-bpee is [Zn_2(bpdc)$_2$(bpee)]·2DMF where H_2bpdc = 4,4′-biphenyldicarboxylic acid, bpee = 1,2-bipyridylethene and DMF = *N*,*N*-dimethylformamide), (Lan et al. 2009). The channel features 1D tubular, essentially straight channels with rectangular-shaped ∼5 × 10 Å openings.

Co-FA is [Co_3(HCOO)$_6$]·DMF, (Li et al. 2008a). It has 1D zig-zag channels of irregular shape (∼5–6 Å).

Zn-bpdc-apy is [Zn_3(bpdc)$_3$(apy)]·*x*DMF, where apy = 4,4′azopyridine, *x* not determined by single crystal X-ray diffraction due to disorder of the guest DMF molecules). Its 1D channels contain "supercages", ∼11 × 11 × 5 Å in size interconnected through small windows, roughly triangular in shape, with an effective maximum dimension of ∼8 Å.

Ni-bodc-ted is $Ni_2[bodc)_2(ted)]\cdot 3.5DMF$, where H_2bodc = bicyclo[2.2.2]octane-1,4-dicarboxylic and ted = triethylenediamine) (Li et al. 2008b). Its complex channel system has three sets of tubular channels with square and close-to-square openings of ∼7.0–7.3 Å in size that are perpendicular to each other and are interconnected to form the overall 3D pore system.

3 Results and discussion

3.1 Commensurate adsorption in Cu-hfipbb

One of the simplest cases of commensurate adsorption in MOF's is the adsorption of light hydrocarbons in Cu-hfipbb (Pan et al. 2006). The channel of this MOF is 1-dimensional and made up of small oval cages with a diameter of ∼5.8 Å, a narrow ∼3.2 Å neck, and a length (unit cell repeat) of 7.3 Å. Propane and butane, having a length of ∼5.7 and 6.9 Å, respectively, have an adsorption limit of 1 molecule per cage. Pentane, with a length of ∼8.1 Å is not adsorbed. This exclusion is not based on molecular sieving but on the basis of the size of the cavities in the adsorption channels, in particular, the small size of the windows (3.2 Å) separating the cages. These observations are illustrated in Fig. 3. The adsorption of propene and propane in the pure silica ITQ-12, where one molecule per cage is adsorbed, is similar, however for this zeolite temperature dependant total molecular exclusion of propane occurs above ∼80 °C (Olson et al. 2004).

3.2 Commensurate adsorption in Zn-bpdc-bpee

Simulated He adsorption in Zn-bpdc-bpee reveals one-dimensional rectangular channels with dimensions ∼4.5 × 7.0 Å (Fig. 4, Lan et al. 2009). Simulated adsorption of benzene and p-xylene further define the channel shape. Benzene, p- and o-xylene all show adsorption levels indicative of commensurate adsorption, having adsorption maxima of 8, 4 and 4 molecules per unit cell, respectively.

Both experimental and simulated benzene adsorption reveal an adsorption limit of 8 molecules per unit cell and the later a zig-zag packing of benzene within each of the 1-d channels (Fig. 5). Because of its greater length, 8.3 versus 6.8 Å for benzene, p-xylene has an adsorption limit of 4 molecules/uc, one half that of benzene. Simulations show that it packs in either a "zig" or a "zag" orientation (Fig. 6). It is likely that within a given channel, once the first molecule is adsorbed, subsequent p-xylene molecules in that channel take up the same orientation, i.e. either "zig" or "zag". It is possible that over an extended channel length, e.g. ∼1000 unit cells, within one channel in one crystal, this ordering may not be maintained. In the simulation, with a length of ∼40 Å, the p-xylene is essentially all "zig" or "zag" within a single channel but adjacent channels appear to pack independent of the packing of the neighboring channels.

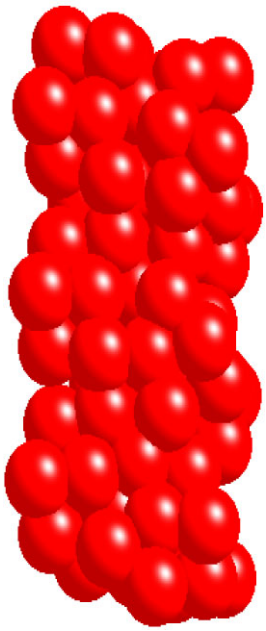

Fig. 4 (Color online) Shape of channels in Zn-bpdc-bpee as indicated by simulated He adsorption. The view is along [100]; the [010] direction is vertical. The Zn-bpdc-bpee structure is not shown

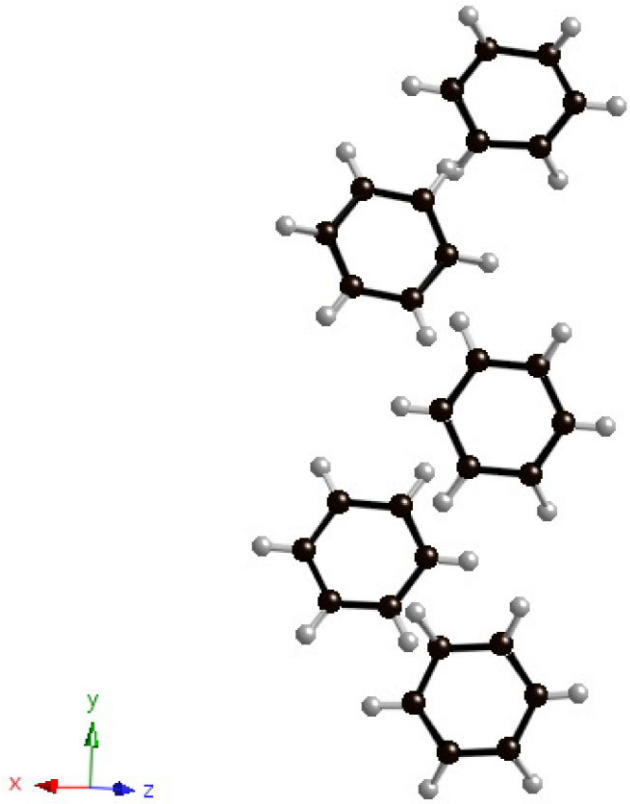

Fig. 5 Zig-zag packing of benzene in the channels of Zn-bpdc-bpee as indicated by simulated adsorption. The view is down [100]; the [010] direction is vertical. The Zn-bpdc-bpee structure is not shown

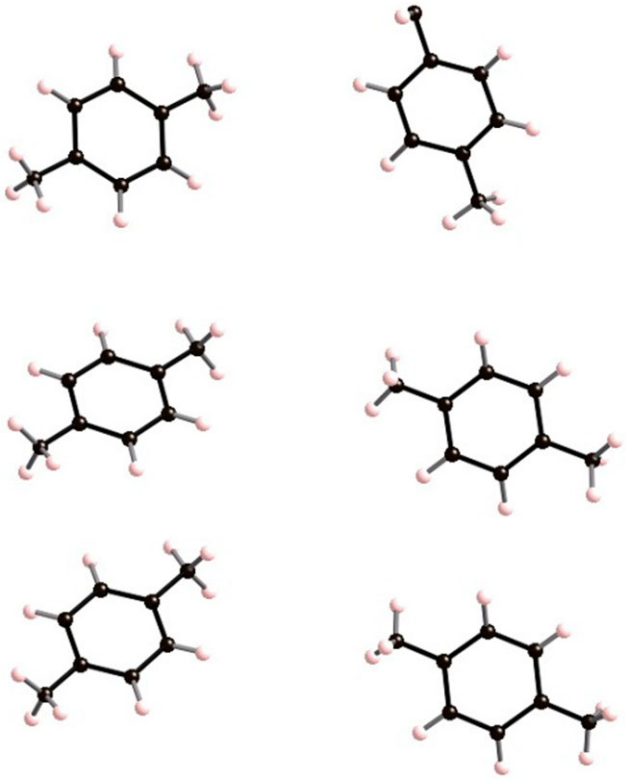

Fig. 6 Packing of p-xylene in the channels of Zn-bpdc-bpee as indicated by simulated adsorption. A majority of molecules have either a zig or zag orientation. The view is down [100]; the [010] direction is vertical. The Zn-bpdc-bpee structure is not shown

Because of its shorter length, 7.3 Å, and lower symmetry, o-xylene does not appear to order, with respect to the ortho methyl groups, within each of the channels but does tend to maintain either a "zig" or "zag" orientation.

The adsorption curves for propanol and butanol are particularly interesting (Fig. 7). Isotherms at 30 and 25 °C, respectively, show a clear adsorption limit of 8 molecules per unit cell. Propanol, having a molecular length of 6.8 Å, is close to the size of benzene and the unit cell repeat distance, adsorbs 8 molecules per unit cell. Note that the 50 °C propanol adsorption curve exhibits the hint of a break in the curve at about 2 molecules; the reason for this step is not known.

The 25 °C adsorption curve for butanol shows a classical type I adsortpion but at 30 °C type II type curves begin to develop and are more clearly observed at 35 and 40 °C. At 45 ° and above the curves are essentially type I with an adsorption limit of 5.6 (6?) molecules per unit cell. The linear butanol molecule has a length of 8.0 Å, seemingly too long for the adsorption of 8 molecules per unit cell based on the observations of 4 molecules adsorbed for the similar length p-xylene. We propose that at the lower temperature, 25 °C, the butane molecule adopts a non-linear conformation allowing it to pack 8 per unit cell but that at higher temperature this confirmation is not stable, reducing the amount adsorbed. Further work is needed to clarify this point.

The effect of the length of the alcohol molecules, in the series from methanol to pentanol, is demonstrated in Fig. 8. Molecules having lengths between 5.7 and 9.1 have capacities of 8 molecules per unit cell, commensurate with the number of equivalent channel segments.

3.3 Commensurate adsorption in Co-FA

Co-FA has a 1-dimensional, medium size pore system (∼5.5 Å channels), whose zig-zag shape can be seen from the results of the simulated He adsorption (Fig. 9, Li et al. 2008a, 2008b). Its repeat distance is 9.9 Å and the multiplicity of the general positions is 4. The adsorption properties for a series of light alcohols are shown in Table 2. By inspection we note that molecules having a length of ∼5.7 to 8.0 Å have commensurate adsorption, with an adsorption limit of 4. The smaller methanol adsorbs 5.5 molecules per unit cell and the larger molecules, pentanol and n-hexane adsorb less than 4 per unit cell.

Both simulated adsorption and a crystal structure determination of the benzene loaded isostructural MOF, Mn-FA (Fig. 8, Wang et al. 2004) reveals zig-zag packing of benzene in the channels in perfect agreement with the channel shape shown by the simulated He adsorption.

3.4 Composition and structural effects

We have also observed two examples of an unusual phenomenon which appears to be the result of a combination of composition and structure. The two MOF's are Zn-bpdc-apy) and Ni-bodc-ted having aromatic and non-aromatic surfaces, respectively. Both have relatively high adsorption capacity and could be classified as large pore zeolites. The unusual affect occurs for the aromatic adsorbate o-xylene with Zn-bpdc-apy and non-aromatic *cyclo*-hexane with Ni-bodc-ted, i.e. with aromatic adsorbate/aromatic adsorbent and with non-aromatic adsorbate/non-aromatic adsorbent. Figure 10 shows families of adsorption curves for each of two materials. In each case, an apparent transition occurs between a monolayer region and the pore filling high loading region.

While the source of this effect is not known, it does reflect a discontinuity in a smooth transition between the monolayer region the high loading region.

However, this effect is not observed for all pairings of adsorbate and adsorbent. For Zn-bpdc-bpee in addition to n-hexane and c-hexane, the aromatic benzene also shows

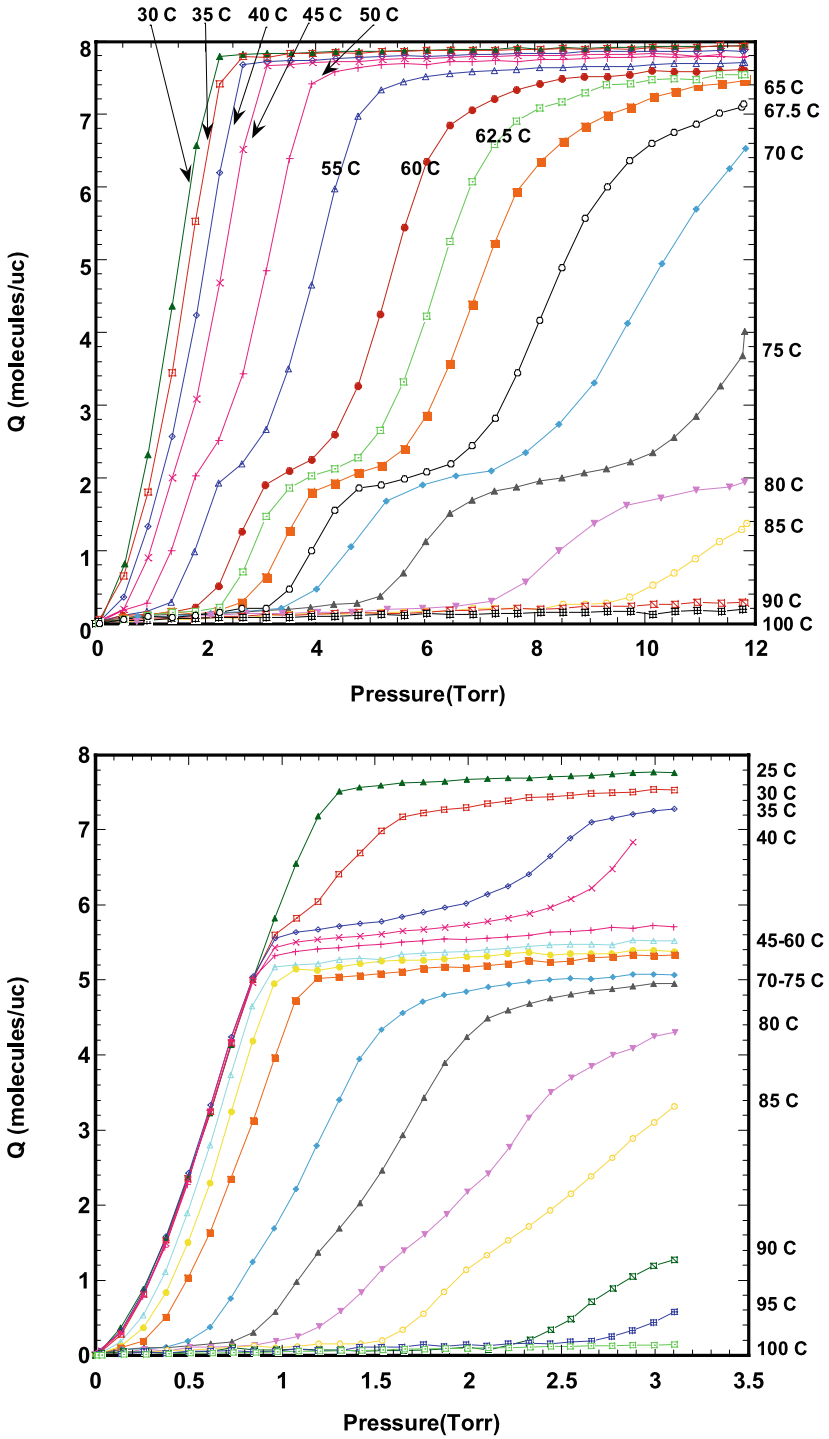

Fig. 7 (Color online) Adsorption curves for propanol (*top*) and butanol (*bottom*) in Zn-bpdc-bpee

type I adsorption curves over the entire range of temperatures and loadings measured. As discussed above, a transition region is observed for o-xylene. Similarly for non-aromatic surface MOF NI-bodc-ted, benzene and the non-aromatic n-hexane have type I adsorption curves whereas c-hexane exhibits the transition behavior. Thus it appears that structure as well as composition plays a role in controlling this phenomenon.

4 Conclusions

Above we have demonstrated commensurate adsorption in 3 MOF materials. In Cu-hfipbb only one molecule of propane or butane can be adsorbed in its small cages. Because of its greater length, pentane is excluded. In Zn-bpdc-bpee, 8 molecules of benzene are adsorbed per unit cell adsorb in channel regions consistent with its 8-fold general position

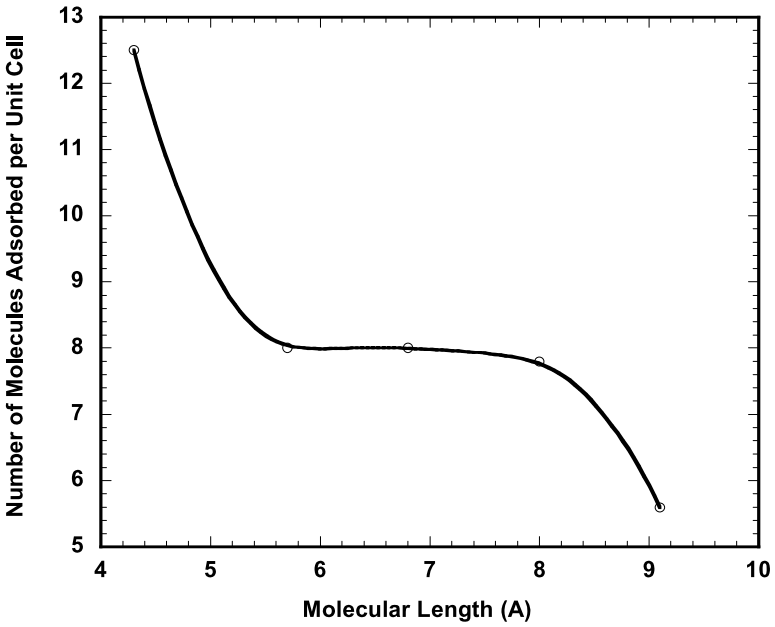

Fig. 8 Adsorption of light alcohols in Zn-bpdc-bpee. Number of molecules adsorbed per unit cell versus molecular length (methanol-left → pentanol-right)

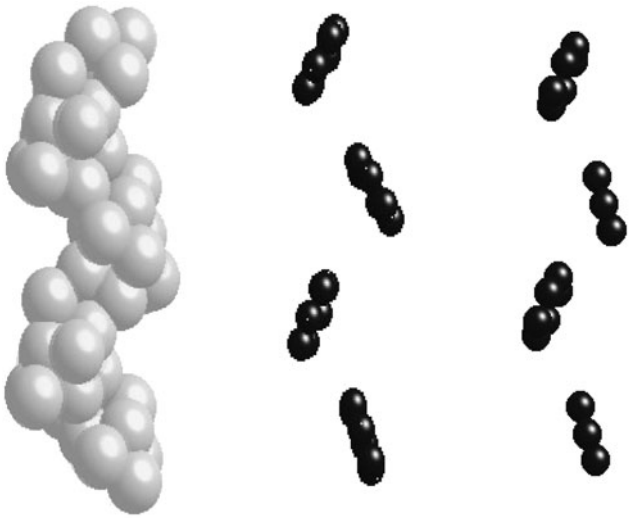

Fig. 9 Packing of helium and benzene in Co-FA (The MOF framework is not shown). Simulated He adsorption (*left*), simulated benzene adsorption (*center*), crystal structure of Benzene-Mn-FA

Table 1 Hydrocarbon adsorption in Zn-bpdc-bpee

	Q^{obs} (mg/g)	Q^{obs} (mol/uc)	Volume (cc/g)	Length (Å)
Benzene	192	7.8	0.221	6.7
p-xylene	124	3.7	0.143	8.3
o-xylene	130	3.9	0.151	7.3
Methanol	126	12.5	0.159	4.3
Ethanol	115	8.0	0.146	5.7
Propanol	143	8.0	0.189	6.8
Butanol	152	7.8	0.225	8.0
Pentanol	155	5.6	0.190	9.1

Table 2 Light hydrocarbon adsorption in Co-FA

	Q^{obs} (mg/g)	Q^{obs} (mol/uc)	Length (Å)
Methanol	99	5.47	4.3
Ethanol	106	4.06	5.7
Propanol	143	4.20	6.8
Butanol	168	4.00	8.0
Pentanol	108	2.20	9.1
n-Hexane	102	2.10	10.2
Benzene	174	3.94	6.7

symmetry. Because of its greater length, only 4 molecules of p-xylene are adsorbed. Light alcohols show similar effects. The zigzag channels of Co-FA accommodate 4 molecules per unit cell of benzene, and para and ortho-xylene.

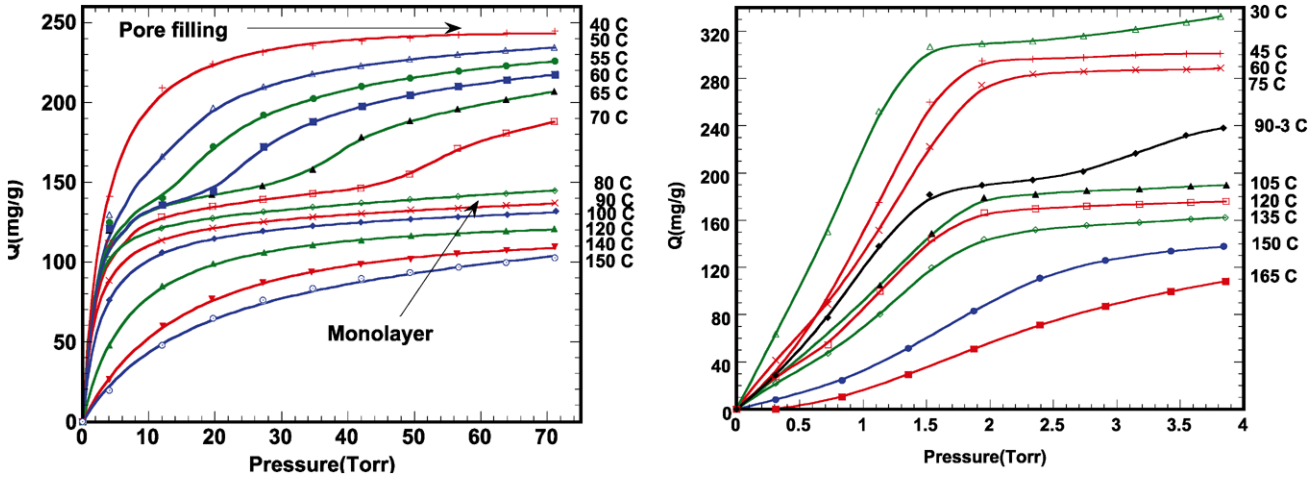

Fig. 10 (Color online) Two MOF's showing apparent composition based adsorption effects. Adsorption of c-hexane in Ni-bodc-ted (*left*) and o-xylene adsorption in Zn-bpdc-apy (*right*)

We also report two MOF's exhibiting adsorbate-adsorbent composition and structure effects. Aromatic adsorbent-aromatic MOF channel and non-aromatic adsorbent and structure lead to a transition region in adsorption curves separating a monolayer region from the pore filling region.

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