Kinetics and Equilibrium of Gas Adsorption on RPM1-Co and Cu-BTC Metal-Organic Frameworks: Potential for Gas Separation Applications

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DOI 10.1002/aic.11422
Published online February 8, 2008 in Wiley InterScience (www.interscience.wiley.com).

We report on the results of kinetic and equilibrium adsorption measurements for two gases, CF_4 and Ar, on RPM1-Co and Cu-BTC metal-organic framework materials. The kinetic experiments were performed at similar relative temperatures ($T/T_{critical} = 0.52$ and 0.597) on both adsorbents. The results show that both gases behave differently on Cu-BTC from the way they do on RPM1-Co. In addition, the equilibrium isotherms indicate that there are some sites on Cu-BTC which are accessible to Ar but not to CF_4. Taken together, our results for the kinetic and equilibrium experiments suggest that these MOFs have high potential for use in gas separation applications. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 918–923, 2008
Keywords: adsorption kinetics, steric exclusion, metal-organic frameworks, kinetic separation

Introduction

Microporous metal-organic frameworks (MOFs).[1–8] are materials that consist of metal clusters connected by the organic linkers forming 1D, 2D, or 3D systems of pores.[1,3,4,8–11] By selecting linkers of specific length and metals of suitable coordination, it is possible to obtain channels of a desired pore structure and size.[1–5,7–9,12–15]

Microporous MOFs captured the attention of researchers in experiment, theory, and simulation after experiments suggested that these materials, as a group, encompass some of the most promising candidates for applications to the gas storage of alternative fuels (hydrogen and methane).[10,11,16–21]

In this letter we want to focus on another significant potential application of adsorption in MOFs. Specifically, their potential for use in the separation of gas mixtures. So far, this issue has been explored only to a more limited extent.[22–24]

There are three different types of physical mechanisms through which the separation of a gas mixture can be accomplished by adsorption[25]: equilibrium, kinetic, and steric mechanisms. Equilibrium mechanisms are based, ultimately, on the strength of the attraction of the gases to the substrate; the kinetic mechanisms are those based on the differences in the rates of adsorption and/or transport of gas on and through a substrate; and the steric mechanisms are based on the incompatibility between the size or shape of the pores in the substrate and those of the adsorbate gas molecules.

In this article we show that two of these types of mechanisms, kinetic and steric, are exhibited by MOFs. We do this

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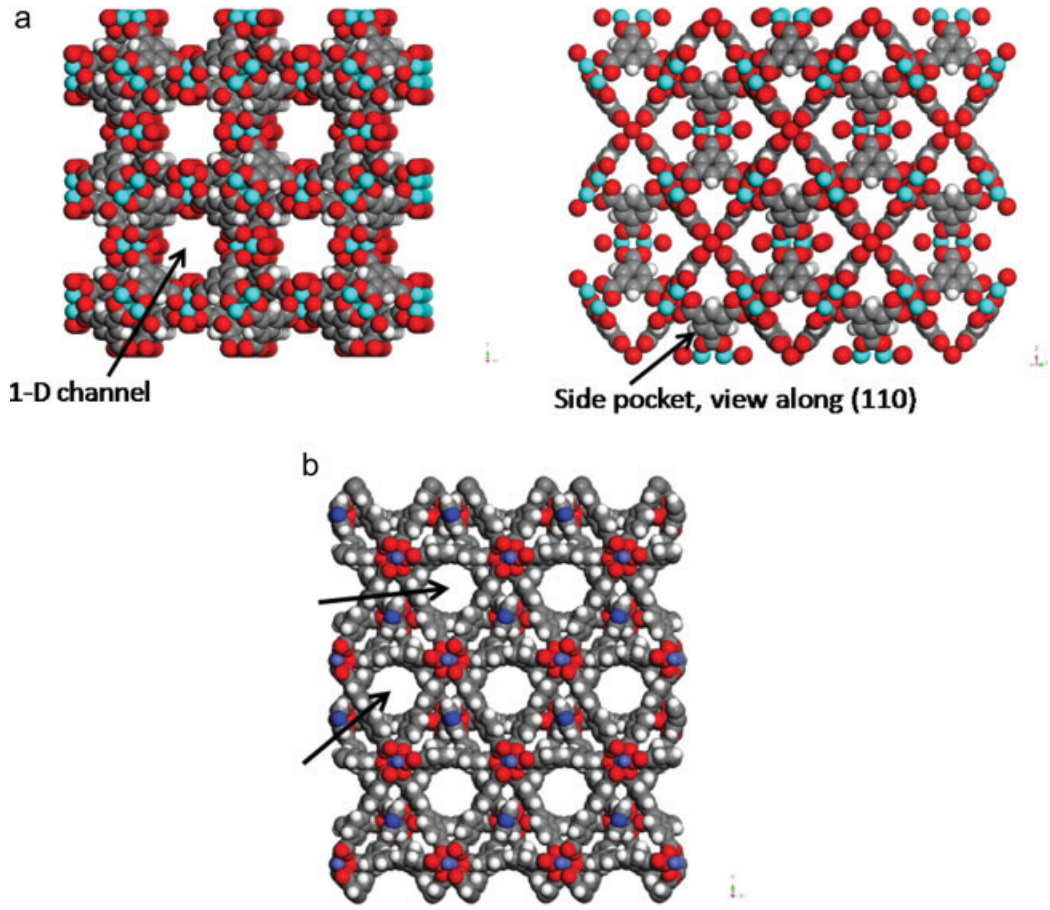

Figure 1. Structure drawings.

(a) Cu-BTC ($Cu_3(BTC)_2(H_2O)_3$ (BTC = Benzene-1,3,5-tricarboxylate). View along the *z*-axis (left), and (110) direction (right). (b) RPM1-Co [$Co_3(bpdc)_3(bpy)$] · 4DMF · H_2O (bpdc = biphenyldicarboxylate, bpy = 4,4′-bipyridine). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by comparing the adsorption behavior of two effectively spherical adsorbates of different diameters (Ar and CF_4) on two different MOF substrates. While the particular pair of adsorbate gases chosen for these measurements is not one of industrial interest, the results obtained with them provide a clear illustration that both kinetic and steric mechanisms are available with MOF substrates, and hence, that these mechanisms can, in principle, be used in cases of practical interest.

Experimental

We used two different metal-organic framework samples: a well-studied 3D metal-organic framework Cu-BTC (see Figure 1a) and a less well-studied material, Rutgers Recyclable Porous Material-1-Co (RPM1-Co) (see Figure 1b) (Ref. 9).

Cu-BTC was first reported by Chui et al. in 1999 (Ref. 26). It has pores of two different sizes: large ~9 Å diameter main channels and tetrahedral-shaped side pockets that are accessible through small triangular windows that are ~3.5 Å in diameter.[26–28] RPM1-Co, on the other hand, has super cages that are ~11 × 11 × 5 Å which are connected with each other through windows that are ~4.0–4.6 Å (Refs. 9 and 29) in diameter and, hence, form one-dimensional channels, as indicated in Figure 1b.

In our adsorption measurements, we first admitted a predetermined amount of gas into a calibrated dosing volume using electropneumatic valves. We then opened a valve to the sample cell (which contained the MOF substrate) and allowed the gas to adsorb onto the substrate at a fixed temperature. We monitored the pressure decrease inside the sample cell as a function of time until equilibrium (i.e., the point in which the pressure does not change with time) was reached. Once the equilibrium pressure was determined, the amount of gas adsorbed on the MOF was obtained.

The adsorption isotherm is the plot of the amount of gas adsorbed on the substrate as a function of the pressure of the gas in the vapor phase in the sample cell. Typical isotherms that we measured have between 50 and 100 points in the pressure interval between the beginning of the measurements (when no gas is adsorbed on the substrate) and the saturated vapor pressure for the gas at the isotherm temperature.

The kinetic adsorption characteristics were determined for each one of the points along the isotherm: for every point in the isotherm we measured the decrease in the pressure in the cell as a function of time (we recorded pressure every 10 s) as equilibrium was approached.

In our custom built adsorption setup: (a) the pressures were measured using 10, 100, and 1000 Torr capacitance

Table 1. Experimental Conditions

Sample	Gas	T (K)	$T/T_{critical}$*	Initial Pressure (Pa)
Cu-BTC	Ar	90.03	0.597	176
	CF_4	118	0.52	149
RPM1-Co	Ar	78.5	0.52	164
	CF_4	118	0.52	153

*Critical temperature values were taken from Ref. 30.

gauges (MKS Baratron); (b) control of the gas dosing, calculations of the amounts of gas adsorbed, recording of the pressures, etc. was achieved using an in-house-developed program written in LabView; and, (c) establishing the low temperatures was achieved through the combined use of a helium closed-cycle refrigerator and two stages of temperature control. Our setup thus allowed us to perform measurements at temperatures other than the ones of liquid cryogens.

Both for the equilibrium as well as for the kinetic measurements, it is important to ensure that the system is leak-free. Vacuum integrity was checked twice: once before the runs were started, using a helium mass spectrometer leak-detector; and a second time after the runs were concluded, by measuring the amount of gas present in the cell and determining whether it agreed with the amount dosed into the cell.

Results

Kinetic results

Our measurements for the adsorption kinetics of Ar and CF_4 on RPM1-Co and Cu-BTC were conducted under comparable scaled conditions (i.e., similar values of $T/T_{critical}$ and similar levels of substrate loading), as well as at similar values of the initial pressure. The experimental conditions are listed in Table 1.

We found that the time it takes for CF_4 to reach equilibrium on RPM1-Co is more than an order of magnitude longer than the time it takes for Ar to reach equilibrium on this same substrate (see Figure 2a). Note, in particular, that for CF_4 the pressure had not reached equilibrium even after 11 days had elapsed after the gas was admitted into the cell. (As noted before, we verified that there were no leaks in our setup by checking how much gas desorbed from the sample).

By contrast, when the measurements for the same two gases were conducted on the other MOF studied, Cu-BTC, the equilibration times (shown in Figure 2b) were very similar.

Clearly, there are very significant differences in the adsorption kinetics of Ar and CF_4 on RPMI-Co. The existence of differences of this order is one of the basis of a mechanism that permits the kinetic separation of gas mixtures.

It should be noted that the experimental conditions we used, (in particular, using similar values of the scaled temperature), are not those that one encounters in a gas separation application (where the gas mixture is, of course, at the same temperature). This does not invalidate the comparison given here: the rates of adsorption decrease with decreasing temperature, so if we were to perform measurements for CF_4 not at the same scaled temperature as that used for Ar as we did, but at the same absolute temperature (which would be lower, as T_c is lower for Ar than for CF_4), we would find that the kinetic differences would be even greater. Unfortunately, the pressures for CF_4 would fall well below the range where we can reliably measure them in our setup; this is, in part, why we chose to compare data measured at the same scaled rather than absolute temperatures.

Equilibrium results

The sieving of molecules from a gas mixture, resulting from the impossibility of some of them to penetrate or adsorb in the pores of a material because of size or shape incompatibilities with the structure of the substrate, is another physical mechanism that allows achieving gas separation through adsorption.[25] The equilibrium isotherm results discussed below provide evidence that this incompatibility is present for a group of pores within Cu-BTC: they are accessible to Ar but are not accessible to the larger adsorbate, CF_4.

Figure 3a displays the results for an equilibrium adsorption isotherm for Ar on Cu-BTC. This system has been the subject of a number of experimental and computer simulation studies.[11,27,28,31] Experiments and simulations indicate that the small steep substep present at lower pressures and lower substrate loadings corresponds to the adsorption of Ar in the small diameter side pockets present in this MOF, see

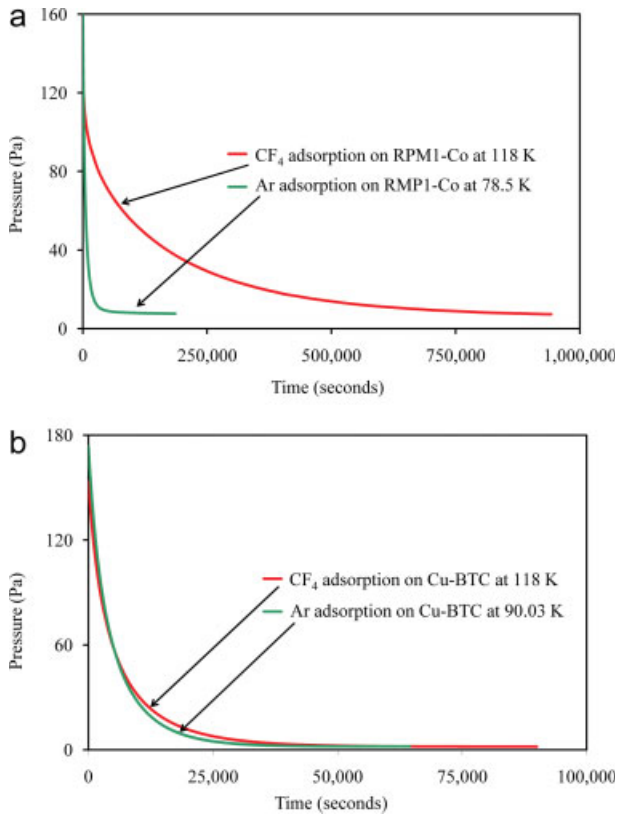

Figure 2. Pressure decrease as a function of time for Ar and CF_4 on (a) RPM1-Co and (b) Cu-BTC metal-organic frameworks.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

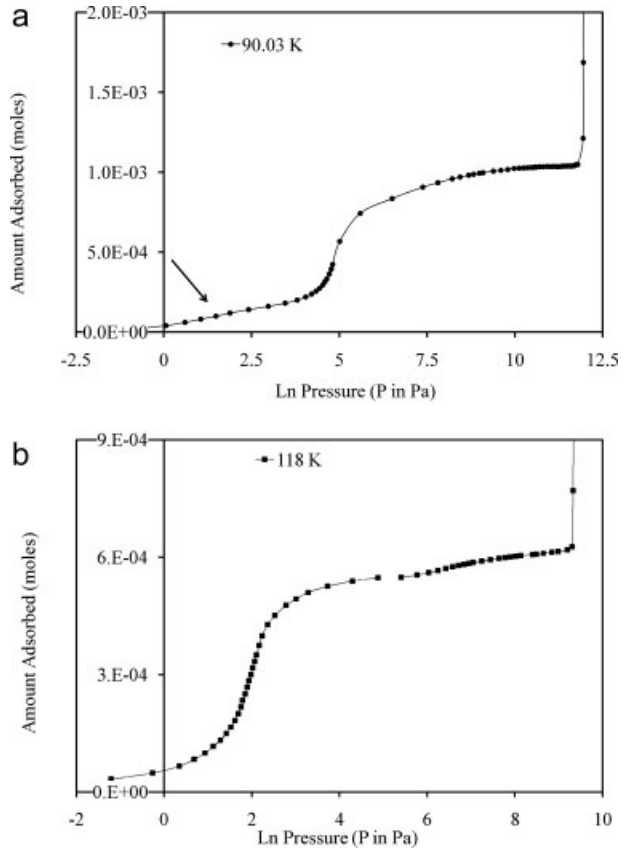

Figure 3. Adsorption isotherms of (a) Ar and (b) CF_4 on Cu-BTC.

Figure 1a (interested readers are directed to Ref. 28 for a more detailed comparison of experimental and simulation data). This feature is indicated by the arrow in Figure 3a. The size of the pockets where this adsorption occurs is ~3.5 Å in diameter.

We note from Figure 3b that such a feature is not present in the adsorption isotherm for CF_4 corresponding to the low coverage substep present in the Ar data. The fact that no discernible feature in the data is observed for the larger adsorbate indicates that CF_4 is sterically prevented from occupying the side pockets.

Discussion

Burde and Calbi[32] have recently described how the kinetics of adsorption of gases on a porous substrate depends on the size of the adsorbate and on the size of the pores present in the adsorbent (they considered, specifically, the interior of a carbon nanotube as their pore).[32] They found that when $R \sim 0.95\sigma_{gc}$ (where R is the pore's radius, and σ_{gc} the adsorbate-carbon length parameter for the Lennard-Jones potential) a potential barrier will develop and gas molecules will have great difficulty adsorbing inside the pore. Below, we discuss our experimental results in light of these theoretical and simulational findings.

We have estimated the LJ length parameters[33] for the systems that we studied. In our LJ parameter calculations, we chose to consider only the gas-carbon interaction, because from the analysis of the structures for both metal-organic framework materials,[9,26–29] we arrived at the conclusion that at the entrance of the main channels and of the tetrahedral-shaped side pockets in Cu-BTC,[26–28] and at the openings of the windows in RPM1-Co,[9,29] the gas molecules come into a closer contact with carbon atoms than they do with any other atom present in either framework. If we look at the σ parameters for the various components of either MOF, their average values are close to 3.40 Å for Ar and 3.99 Å for CF_4.

In Table 2 we present the pore dimensions and σ_{gc} parameters for these systems.

Main pores—kinetic separation mechanism

Taking into account the Burde and Calbi criterion,[32] and the data shown in the Table 2, neither Ar nor CF_4 should have any difficulty in diffusing into the largest pores present in Cu-BTC (i.e. the main channels with 9 Å pore diameter), since for both, Ar and CF_4, the $0.95\ \sigma_{gc}$ parameters are much smaller than the diameter of the main pores. This has been shown to be the case above, in Figure 2b, where the results of the kinetic measurements for both gases show that it takes similar times for them to reach equilibrium. That is, neither gas has difficulties in adsorbing inside the pores.

The situation is different for RPM1-Co.[9,29] In this metal-organic framework the size of the main pore is smaller than in Cu-BTC; $0.95\sigma_{gc}$ for CF_4 is very close to the main pore diameter, while $0.95\sigma_{gc}$ for Ar is smaller than the diameter of the main pore. Thus, the former gas should have great difficulty adsorbing inside those pores while the latter should not. This theoretical expectation is confirmed by our experimental data (Figure 2a). We find that it takes much longer times for the CF_4 molecules than it does for Ar to diffuse into the main pores of RPM1-Co.

It is interesting to compare, even if only qualitatively, the potential effects on gas separation we expect from the kinetic and equilibrium mechanisms for CF_4 on RPM1-Co. As is the

Table 2. Pore Sizes for Cu-BTC and RPM1-Co MOF and Lennard–Jones Parameters for Ar and CF_4

Sample	Gas	σ_{gc} (Å)	$0.95\sigma_{gc}$ (Å)	Diameter of the Main Pores* (Å)	Type of the Pore
Cu-BTC	Ar	3.40[33]	3.3	9.0[27,28]	Main channels
	CF_4	3.99[34]	3.8	9.0[27,28]	Main channels
	Ar	3.40[33]	3.3	3.5[27,28]	Triangular windows to the tetrahedral-shaped side pockets
	CF_4	3.99[34]	3.8	3.5[27,28]	Triangular windows to the tetrahedral-shaped side pockets
RPM1-Co	Ar	3.40[33]	3.3	4.0–4.6[9,29]	Triangular windows to the super cages
	CF_4	3.99[34]	3.8	4.0–4.6[9,29]	Triangular windows to the super cages

*Radius, R, used in the computer simulations is equivalent to the diameter of the pores in the materials.

case on other substrates, the binding energy of CF_4 to the substrate is stronger than that for Ar (a result which can be inferred from the fact that even at higher temperatures the pressures for CF_4 are lower than those for Ar at the same coverage). The strength of the binding energy is what, ultimately, determines the equilibrium separation characteristics (i.e., once equilibrium adsorption for a mixture is attained, the more strongly bound gas will be the one prevailing on the substrate, and the less tightly bound will be prevalent in the vapor phase). Exactly the opposite is the case in the kinetic effect described here: the more weakly bound gas adsorbs faster, and hence, it is initially the prevalent species on the substrate; kinetic and equilibrium effects result in different species adsorbed and in the gas phase.

Small pores—steric separation mechanism

In the case of the smaller, tetrahedral-shaped pores in Cu-BTC MOF,[26–28] applying the Burde and Calbi criterion[32] we expect that Ar should be able to diffuse into the small side-pocket pores, while CF_4 should not be since these openings are smaller than $0.95\sigma_{gc}$ for the larger gas (while they are comparable to the diameter for Ar, see Table 2). Taking into account the data presented in Table 2 and the differences between the isotherms plotted in Figure 3, where the substep corresponding to the adsorption in the tetrahedral-shaped side pockets is present in the Ar data and absent in the CF_4 data, we conclude that CF_4 is sterically forbidden from going into the side pockets of Cu-BTC MOF, while Ar is not.

Conclusions

We measured equilibrium and kinetic adsorption properties for CF_4 and Ar on Cu-BTC and RPM1-Co metal-organic frameworks. Our kinetic results indicate that in Cu-BTC neither gas has any difficulties in diffusing and adsorbing in the main channels. The data for RPM1-Co, on the other hand, suggest that the smaller Ar gas molecules adsorb inside the pores much faster than the larger CF_4, thus, this adsorbent material has the capacity for kinetically selecting between these two gases.

Our equilibrium isotherm results on Cu-BTC indicate that the smaller tetrahedral-shaped side pockets in this microporous MOF are too small for CF_4 to adsorb in them, while they can be readily occupied by Ar.

The presence of kinetic differences in adsorption and of sterically allowed and forbidden adsorption sites in microporous MOFs shows that these adsorbents can, in principle, be used for attaining the separation of gaseous mixtures. Since the properties of these materials (e.g., pore size and geometry, pore connectivity, etc), unlike some other adsorbents, can be tuned and modified to fit or exclude different gases, they offer unique selectivity and substantial potential for applications in gas separation technologies.

Acknowledgments

JYL and JL acknowledge the donors of The Petroleum Research Fund administrated by the ACS (PRF #42614-AC3,10) for the partial support of this work.

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Manuscript received July 18, 2007, and revision received Nov. 12, 2007.