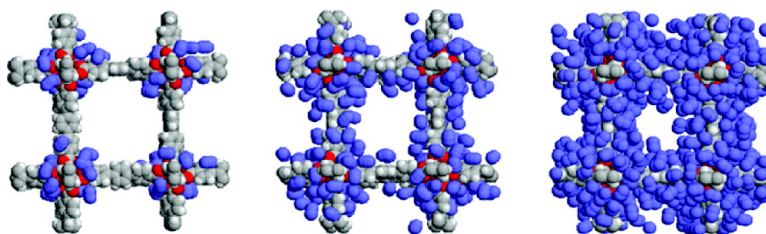


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Applicability of the BET Method for Determining Surface Areas of Microporous Metal–Organic Frameworks

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Abstract: The surface area is one of the most important quantities for characterizing novel porous materials. The BET analysis is the standard method for determining surface areas from nitrogen adsorption isotherms and was originally derived for multilayer gas adsorption onto flat surfaces. Metal–organic frameworks (MOFs) are a relatively new class of crystalline, porous materials that have been shown to exhibit very large BET surface areas. These materials are microporous and possess surfaces that are far from flat. In some MOFs, adsorption occurs through a pore-filling mechanism rather than by layer formation. Thus, it is unclear whether BET surface area numbers reported for these materials are truly meaningful. Given the standard practice of reporting BET surface areas for novel porous materials, a critical test of the BET method is much needed. In this work, grand canonical Monte Carlo simulations were used to predict adsorption isotherms for nitrogen in a series of MOFs. The predicted isotherms were used as pseudoexperimental data to test the applicability of the BET theory for obtaining surface areas of microporous MOFs. BET surface areas calculated from the simulated isotherms agree very well with the accessible surface areas calculated directly from the crystal structures in a geometric fashion. In addition, the surface areas agree well with experimental reports in the literature. These results provide a strong validation that the BET theory can be used to obtain surface areas of MOFs.

Introduction

Over the past decade, metal–organic frameworks (MOFs) have emerged as an important new class of nanoporous materials with the potential for making a significant impact in separations, gas storage, catalysis, and chemical sensing.^{1–10} MOFs are synthesized by a self-assembly process in which metal or metal oxide vertices are connected by functionalized organic linker molecules to form extended, crystalline, porous materials. Different combinations of vertices and linkers lead to materials with varying topologies, pore sizes, and functionalities, and indeed, a large variety of metal–organic materials have been produced.^{11–13}

Some MOFs have incredibly high surface areas. For example, the widely studied Cu–BTC¹⁴ possesses a surface area of roughly 1800 m²/g, MIL-101¹⁵ is reported to have a surface area of 4100 m²/g, and MOF-177 has a surface area of 4500 m²/g.¹⁶ These are some of the highest surface areas reported for any material to date. The surface area is an important characteristic of porous materials, especially for applications in adsorption separations and gas storage. For physisorption, the energetic interaction of guest molecules with surface atoms is usually much more important than guest–guest interactions, so it is expected that a higher surface area per mass of material should correlate with a higher amount adsorbed (per mass). Several groups have reported a linear relationship between surface area and the amount adsorbed for different types of porous materials.^{17–19} For a series of MOFs all having the same framework topology, Frost et al.¹⁹ used molecular modeling to show that the amount of hydrogen adsorbed at 77 K correlates with the heat of adsorption at low loading and the pore volume

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- (1) Millward, A. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *127*, 17998.
- (2) Pan, L.; Olson, D. H.; Ciemnomolonski, L. R.; Heddy, R.; Li, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 616.
- (3) Wang, Q. M.; Shen, D.; Bülow, M.; Lau, M. L.; Deng, S.; Fitch, F. R.; Lemcoff, N. O.; Semancin, J. *Microporous Mesoporous Mater.* **2002**, *55*, 217.
- (4) Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T. *AIChE J.* **2004**, *50*, 1090.
- (5) Dinca, M.; Yu, A. F.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 8904.
- (6) Panella, B.; Hirscher, M.; Pütter, H.; Müller, U. *Adv. Funct. Mater.* **2006**, *16*, 520.
- (7) Cho, S. H.; Ma, B. Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, *24*, 2563.
- (8) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238.
- (9) Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jung, S. H.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8227.
- (10) Mueller, U.; Schubert, M.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastre, J. *J. Mater. Chem.* **2006**, *16*, 626.
- (11) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276.

- (12) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- (13) Rosseinsky, M. J. *Microporous Mesoporous Mater.* **2004**, *73*, 15.
- (14) Chui, S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *5405*, 1148–1150.
- (15) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *307*, 2040–2042.
- (16) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494.
- (17) Texier-Mandoki, N.; Dentzer, J.; Piquero, T.; Saadallah, S.; David, P.; Vix-Guterl, C. *Carbon* **2004**, *42*, 2744.
- (18) Langmi, H. W.; Walton, A.; Al-Mamouri, M. M.; Johnson, S. R.; Book, D.; Speight, J. D.; Edwards, P. P.; Gameson, I.; Anderson, P. A.; Harris, I. R. *J. Alloys Compd.* **2003**, *356*, 710.
- (19) Frost, H.; Düren, T.; Snurr, R. Q. *J. Phys. Chem. B* **2006**, *110*, 9565.

at very high loading. However, in a significant intermediate coverage range the amount adsorbed correlates with the surface area.

Surface areas are commonly reported as BET surface areas obtained by applying the theory of Brunauer, Emmett, and Teller²⁰ to nitrogen adsorption isotherms measured at 77 K. This is a standard procedure that allows for comparisons among different materials and with benchmark materials from the literature. However, the BET method^{20–23} relies on several assumptions that may break down for microporous materials with very open structures and ultrahigh surface areas such as MOFs. The BET analysis assumes that adsorption occurs by multilayer formation and that the number of adsorbed layers is infinite at the saturation pressure, i.e., adsorption occurs as if on a free surface.²³ Appreciable overlap of monolayer and multilayer adsorption would invalidate this assumption. In addition, it has been suggested that adsorption in MOFs occurs through a pore-filling mechanism rather than by layer formation.²⁴ Thus, while the BET method allows for a ranking of different materials, it is far from clear whether the surface area numbers reported are really meaningful in an absolute sense. Given the increasing numbers of papers that report BET surface areas for novel, microporous MOFs, a critical test of the BET method as applied to MOFs is very much needed.

The crystallinity of MOFs offers the possibility to test the applicability of the BET method. Because the positions of the framework atoms are known from crystallography, the surface area can be calculated directly from the crystal structure as a geometric problem. The “accessible” surface area²⁵ is calculated by considering the center of mass of an adsorbate molecule rolling along the surface of the MOF. A significant difficulty in using the accessible surface area to test the BET results from experimental isotherms is that real materials may have defects. For example, portions of a crystal may collapse or retain solvent molecules from the synthesis. Such defects will naturally lower the amount of nitrogen that can be adsorbed and thus the BET surface area reported experimentally. In this work, to provide a definitive test of the BET method, we use molecular modeling to calculate nitrogen adsorption isotherms for a series of MOFs. The BET method is then applied to these simulated isotherms to calculate the surface areas, which can be compared with the accessible surface areas calculated from the crystal structures geometrically. In this way, the same precisely known crystal structure is used for calculating both the accessible surface area and the BET surface area (via the simulated isotherm), avoiding the problem of imperfect materials in real experiments.

Methods

Grand canonical Monte Carlo (GCMC) simulations were used to calculate nitrogen adsorption isotherms in a series of isorecticular metal–organic frameworks (IRMOFs) representing a range of pore sizes and apparent surface areas. The six IRMOFs used in this work are shown in Figure 1. These materials all have the same basic framework

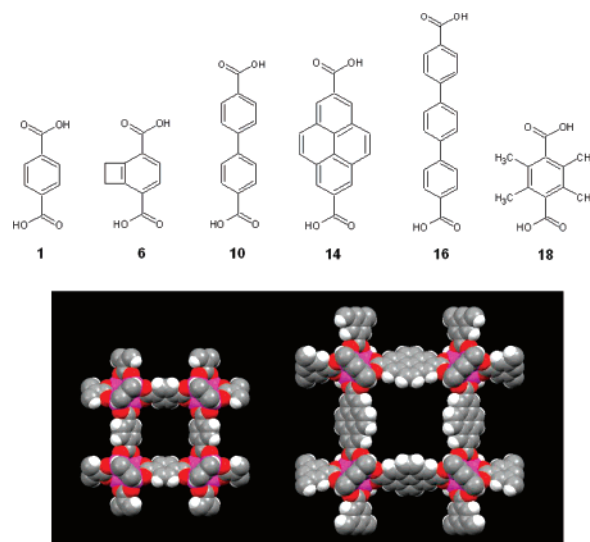


Figure 1. Top: From left to right, organic linkers for IRMOFs-1, -6, -10, -14, -16, and -18. Bottom: IRMOF-1 and IRMOF-14.

topology. The IRMOFs were developed by Yaghi and co-workers^{26–28} and consist of oxide-centered Zn_4O tetrahedra linked by dicarboxylate molecules to form extended cubic networks. Materials with different pore sizes can be synthesized using linker molecules with different lengths.²⁶

Dispersion and repulsion interactions were modeled with a standard Lennard-Jones potential. The Lennard-Jones parameters for the nitrogen atoms were taken from the TraPPE model.²⁹ This model also places a point charge of +0.964 on the center of mass of the molecule and -0.482 on the center of each nitrogen atom to simulate the molecule’s quadrupole moment. The Lennard-Jones parameters for the framework atoms were taken from the DREIDING force field.³⁰ Lorentz–Berthelot mixing rules were employed to calculate sorbate/framework parameters. Interactions beyond 12.8 Å were neglected. The Lennard-Jones parameters and additional simulation details are given in the Supporting Information.

Adsorption isotherms were calculated for nitrogen in the six IRMOFs shown in Figure 1 at 77 K and pressures up to 1 bar, which is the saturation pressure of nitrogen at that temperature. Molecular simulation predicts the absolute number of sorbate molecules within the framework material at the given gas-phase conditions, whereas experimental measurements yield the excess amount adsorbed. The absolute adsorbed amounts were converted to excess adsorption using the procedure described by Frost et al.¹⁹

BET surface areas were determined from the calculated isotherms by the same method used for treating experimental data.^{20,23} The BET analysis is performed by plotting $x/v(1-x)$ vs x , where $x = P/P_0$ ($P_0 = 1$ bar) and v is the volume of nitrogen adsorbed per gram of MOF at STP. This analysis produces a curve typically consisting of three regions: concave to the x axis at low pressures, linear at intermediate pressures, and convex to the x axis at high pressures. Choosing the proper linear region can be somewhat subjective because often several pressure regions will give a roughly linear BET plot. We will revisit this point in the next section. The slope ($[c-1]/v_m c$) and y intercept ($1/v_m c$) of this linear region give the monolayer capacity, v_m , that is then used to calculate the surface area from $A = v_m \sigma_0 N_{AV}$, where σ_0 is the cross-sectional area of the adsorbate at solid or liquid density (16.2

(20) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(21) Rouquerol, J.; Llewellyn, P.; Rouquerol, F. *Stud. Surf. Sci. Catal.* **2007**, *160*, 49–56.

(22) Parra, J. B.; de Sousa, J. C.; Bansal, R. C.; Pis, J. J.; Pajares, J. A. *Adsorpt. Sci. Technol.* **1995**, *12*, 51.

(23) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley & Sons: New York, 1997.

(24) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304.

(25) Leach, A. R. *Molecular Modelling: Principles and Applications*, 2nd ed.; Prentice Hall: New York, 2001.

(26) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keefe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.

(27) Li, H.; Eddaoudi, M.; O’Keefe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

(28) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666.

(29) Potoff, J. J. and Siepmann, J. I. *AIChE J.* **2001**, *47*, 1676–1682.

(30) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897.

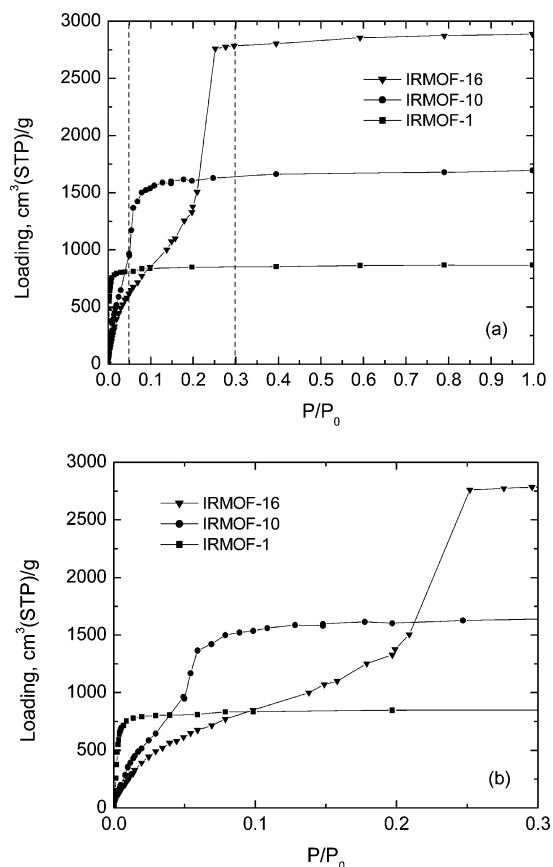


Figure 2. Adsorption isotherms for nitrogen in IRMOFs-1, -10, and -16 at 77 K calculated from GCMC simulations.

\AA^2 for nitrogen²³). An example BET calculation is given in the Supporting Information.

The accessible surface areas were calculated from a simple Monte Carlo integration technique where the probe molecule is “rolled” over the framework surface. A nitrogen-sized (3.681 \AA) probe molecule³¹ was randomly inserted around each of the framework atoms and checked for overlap. The fraction of the probe molecules that did not overlap with other framework atoms was then used to calculate the accessible surface area. The diameters of the framework atoms were taken from the DREIDING force field (H, 2.85 \AA ; C, 3.47 \AA ; O, 3.03 \AA ; Zn, 4.04 \AA).³⁰

Results and Discussion

The adsorption isotherms for IRMOF-1, -10, and -16 are shown in Figure 2. These three materials allow a comparison of the effect of increasing linker size (Figure 1). Increasing linker lengths correspond to more open structures with larger pore volumes per mass,¹⁹ and Figure 2a shows that, as expected, the adsorption saturation capacities increase with increasing pore volume. The most striking feature of these isotherms is an unusual step, which can be seen more clearly in Figure 2b. Eddaoudi et al.²⁶ have reported experimental isotherms for nitrogen in IRMOF-12 and IRMOF-14 that show a similar step, but they do not comment on it. Many of the experimental nitrogen isotherms for MOFs in the literature focus on the saturation region, making it difficult to verify the predicted steps. Additional experimental measurements that focus on the low-pressure portion of the isotherm will be an interesting area for future study. The reasons for the step are discussed below.

(31) Hirschfelder, C. F.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; p 1110.

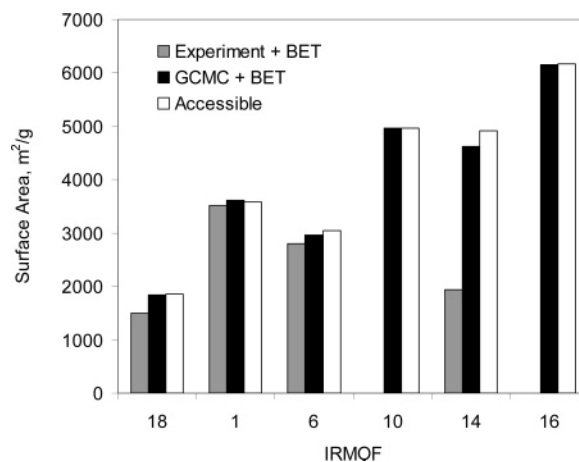


Figure 3. Comparison of IRMOF surface areas obtained from the BET theory applied to experimental nitrogen isotherms,^{24,26,28} the BET theory applied to nitrogen isotherms from GCMC simulation, and the accessible surface area calculations from the crystal structure.

The isotherms from Figure 2 and those calculated for the other IRMOFs were treated with the BET theory, exactly as experimental isotherms are normally treated. Figure 3 shows a comparison of the BET surface areas calculated from the simulated isotherms (black) with the BET surface areas reported in the literature from experimental nitrogen isotherms (gray).^{24,26,28} The agreement is quite good for IRMOFs-1 and -6 and acceptable for IRMOF-18. The simulated results do not agree well with the experimental value for IRMOF-14. However, upon examination of the crystal structures, it does not make sense that IRMOF-14 should have a lower surface area than IRMOF-1. The experimental surface area for this material, thus, appears to be much too low considering the pore size and linker molecules. The low experimental value could be the result of defects in the crystal structure, interpenetration, or blocking of the pores due to incomplete solvent removal.

Figure 3 also shows the accessible surface areas calculated geometrically from the crystal structures (white). There is very good agreement between the (simulated) BET surface areas and the accessible surface areas obtained from the crystal structures. These results show that the BET surface areas obtained from the nitrogen adsorption isotherms are directly related to the geometric surface areas calculated from the crystal structures. This is a remarkable result considering the differences in how these two methods arrive at a surface area. Given the widespread use of the BET model, this comparison provides an important test of the BET method and provides strong support for its continued use to characterize new MOFs and to correlate their performance properties with the BET surface areas.

One of the primary assumptions of the BET theory is that adsorption occurs by multilayer formation. To test this assumption and to understand the steps in the isotherms, snapshots of the adsorbed molecules were examined at various points along the adsorption isotherms. Figure 4 shows the results for IRMOF-16. At low coverage, N_2 molecules populate the corner regions where the interaction energy with the framework is strongest. As loading increases, the snapshots show a gradual layering of adsorbed N_2 molecules and clear formation of a full monolayer before the pores finally fill. Snapshot C indicates that the first layer has been completely filled at $P/P_0 \approx 0.2$. Figure 5 shows the simulation results for IRMOF-1. Again at low loadings, N_2 molecules first populate the corners of the cavities. This

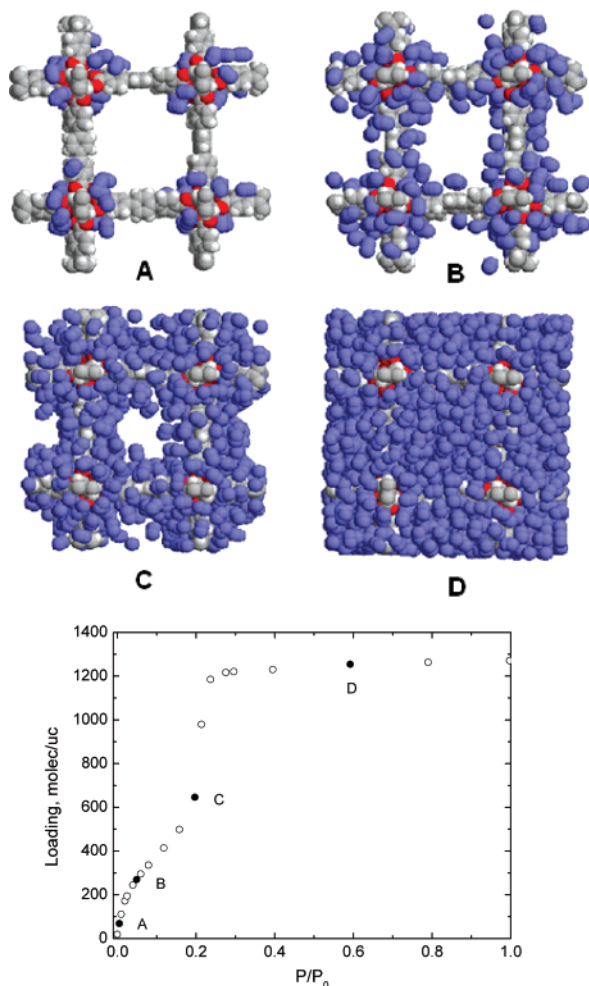


Figure 4. Top: Simulation snapshots of nitrogen adsorption at 77 K in IRMOF-16 at various loadings. Bottom: Nitrogen adsorption isotherm at 77 K for IRMOF-16 with loadings expressed as molecules of N_2 per unit cell.

prediction agrees with the results of X-ray diffraction experiments for nitrogen and argon.³² As the loading increases, the snapshots show that in the smaller pores of IRMOF-1 adsorption does not occur in well-defined layers. The mechanism instead appears to be dominated by pore filling.

The BET analysis is usually performed over the range $0.05 < P/P_0 < 0.3$, with the implicit assumption that monolayer formation occurs in this pressure range. This range, marked in Figure 2a with vertical dashed lines, should correspond to the linear region of the BET plot and works well for materials that do not contain micropores. However, as illustrated in Figure 2b and in the snapshots above, the pores of the smaller MOFs (-1, -6, -18) are completely filled with N_2 at pressures well below the standard BET range. Rouquerol et al.²¹ and Parra et al.²² found similar difficulties when applying the BET analysis to N_2 adsorption in 13X zeolite and microporous carbon, respectively. Adding to this problem is the fact that several pressure ranges on the BET plot may yield a linear region. Thus, two major criteria were established²¹ to aid the choice of pressure range for applying the BET analysis: (1) The pressure range selected should have values of $v(P_0 - P)$ increasing with P/P_0 .

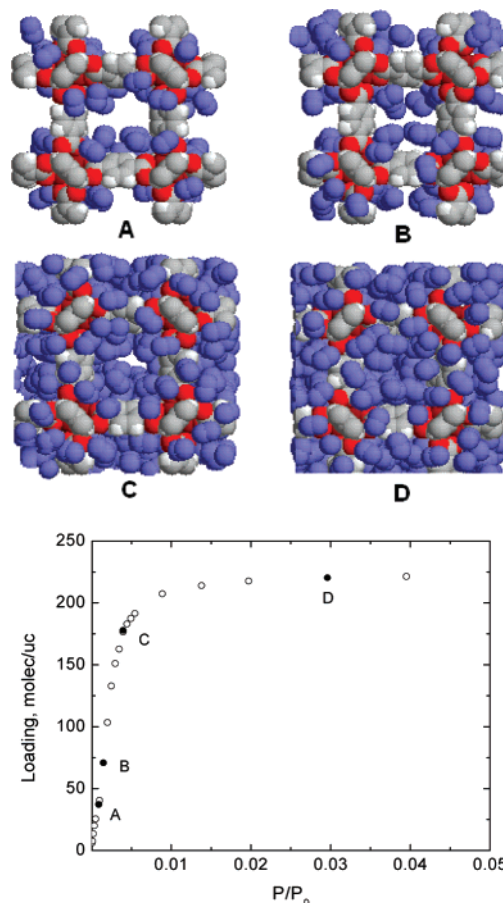


Figure 5. Top: Simulation snapshots of nitrogen adsorption at 77 K in IRMOF-1 at various loadings. Bottom: Nitrogen adsorption isotherm at 77 K for IRMOF-1 with loadings expressed as molecules of N_2 per unit cell.

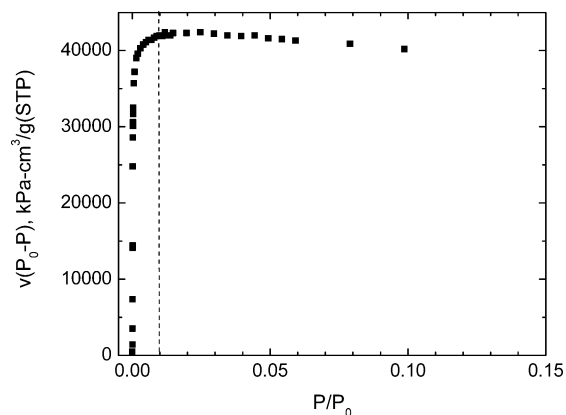


Figure 6. $v(P_0 - P)$ vs P/P_0 for IRMOF-18. Only the range below $P/P_0 = 0.01$ satisfies the first consistency criterion for applying the BET theory.

(2) The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero.

The GCMC BET results shown in Figure 3 were obtained using these consistency criteria. Indeed, when we applied the BET method to the N_2 isotherms over the standard BET range, we obtained BET c parameters that were less than zero for all materials except for the large-pore IRMOF-16. A plot of $v(P_0 - P)$ vs P/P_0 for IRMOF-18 is shown in Figure 6. This figure clearly shows that only the pressure range less than $P/P_0 \approx 0.01$ should be included in the BET analysis to satisfy the first

(32) Rowsell, J. L. C.; Spencer, E. C.; Eckert, J.; Howard, J. A. K.; Yaghi, O. M. *Science* **2005**, *309*, 1350–1354.

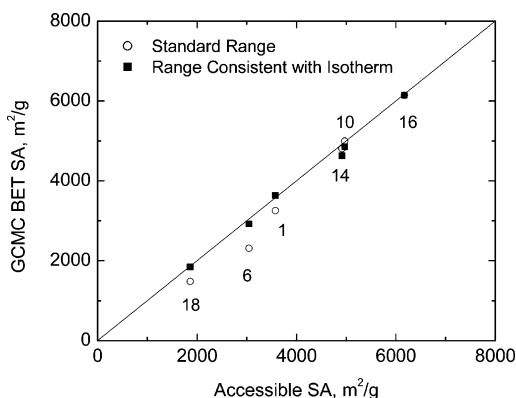


Figure 7. Comparison of BET surface areas (SAs) calculated from the standard range, BET surface areas calculated from the range identified through the consistency criteria, and accessible surface areas.

consistency criterion. For all of the materials, we found that the linear region identified by the criteria above corresponds to the first step in the adsorption isotherm and results in consistent BET surface areas, i.e., c values that are greater than zero. In general, the range identified by criterion 1 is less than $x = 0.05$ for all of the smaller MOFs (-1, -6, -18) but corresponds much closer to the standard range as the pore size of the material increases. The two ranges agree exactly for IRMOF-16. This is reasonable because the larger pores provide an adsorption environment that more closely resembles a free surface, and adsorption on a free surface is an important assumption in the derivation of the BET model. Conversely, the materials with smaller pores, IRMOFs-1, -6, and -18, provide an adsorption environment where an adsorbate molecule will be influenced by the potential energy of more than one wall of the IRMOF cavity. This type of adsorption leads to a pore-filling mechanism that invalidates one of the BET assumptions. Nevertheless, the agreement between BET and accessible surface areas is surprisingly good across the whole series of materials.³³

The surface areas calculated using the range identified from the consistency criteria and those obtained from the standard BET range are compared with the accessible surface areas in Figure 7. We find that the BET surface areas obtained from the consistent pressure range correlate extremely well with the accessible surface areas for all of the IRMOFs, whereas the values from the standard range do not give as good agreement for the three smaller materials. These results underscore the importance of calculating surface areas from the proper pressure region of the adsorption isotherm when the BET method is applied.

(33) The original BET derivation leads to an isotherm equation containing three adjustable parameters: n , v_m , and c . The parameter n is equal to the number of adsorbed layers. When n is infinite, the equation reduces to the typical BET equation that is used for experimental surface area determination. For $n = 1$, the equation reduces to the Langmuir isotherm equation. Because MOFs have a finite volume, it is reasonable to assume that the actual number of adsorbed layers is finite. However, in the original BET paper, the authors state that, for $n = 4$ or 5 , the surface area results are almost identical to the results obtained by assuming $n = \infty$. To maintain consistency with experimental methods, this work only uses the analysis with $n = \infty$.

The agreement between the BET surface areas and the accessible surface areas provides a compelling argument for using the accessible surface area to characterize crystalline nanoporous materials. The accessible surface area can be calculated quickly from the crystal structure. Discrepancies between the accessible surface area and the BET surface area obtained from an experimental nitrogen isotherm can be used to judge the quality of the experimental sample and may indicate the presence of residual adsorbed solvent molecules or partial collapse of the pores.

We may further infer from these results that the BET analysis also has some general validity for MOFs with topologies that differ from those of the IRMOFs of this study. If the results had indicated that the BET analysis holds only for the very large-pore MOFs, e.g., IRMOF-16, then extending these conclusions to MOFs with other types of pore systems might not be possible. However, it was found that the BET analysis gives consistent surface areas compared to the accessible surface areas, even when the dominating adsorption mechanism is pore filling.

Conclusions

The BET surface areas calculated from simulated nitrogen isotherms agree well with those reported in the literature from experimental nitrogen isotherms for a series of isorecticular MOFs. The simulated isotherms were used as pseudoexperimental data to test the BET theory on “perfectly” crystalline materials by comparing the BET surface areas calculated from the simulated isotherms with the accessible surface areas obtained geometrically from the crystal structures. The results agree very well for all of the IRMOFs. Some of these materials have surface areas of 5000–6000 m²/g. The best results are obtained by applying the BET theory over the pressure range identified by established consistency criteria, rather than simply using the “standard” BET pressure range. The formation of monolayers in the large-pore IRMOFs was indicated by steps in the simulated isotherms and was confirmed by examination of the structure of the adsorbed molecules within the MOF cavities. This study demonstrates that the BET theory applied to experimental nitrogen isotherms is a valuable method for characterizing porous, crystalline materials even for materials having surface areas of thousands of m²/g with pores that are far from the flat surfaces used in deriving the BET theory.

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Supporting Information Available: Simulation details and example BET calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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