Evaluation of the BET Method for Determining Surface Areas of Ultra-Microporous MOFs and Zeolites

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The BET analysis is commonly used for determining surface areas of metal-organic frameworks (MOFs) and zeolites that contain "ultra-micropores" (< 7 Å). However, it is not clear whether the BET surface areas obtained for such small pores are really meaningful in an absolute sense. In this study, nitrogen and argon isotherms in ultra-microporous MOFs and zeolites were predicted by grand canonical Monte Carlo (GCMC) simulations and were used as pseudoexperimental data to evaluate the BET method for determining surface areas of ultra-microporous MOFs and zeolites. The dispersion and repulsion interactions were modeled using the standard Lennard-Jones (LJ) potential. GCMC simulations were performed to calculate nitrogen isotherms at 77 K and argon isotherms at 87 K for all materials. All the isotherms were obtained up to 1 bar, which is the saturation pressure of nitrogen at 77 K as well as that of argon at 87 K. The BET surface areas calculated from simulated nitrogen or argon isotherms agree well with the accessible surface areas obtained directly from the crystal structures in a geometric fashion. These are remarkable results because the BET surface area and the accessible surface area are obtained from totally different strategies. It should be noted that good agreement was only found when the BET analysis was performed using the appropriate pressure range based on "consistency criteria" in the recent literature. The BET analysis underestimates the surface areas of ultra-microporous MOFs and zeolites if it is performed in the "standard" text book BET pressure range. This can explain rather small experimental BET surface areas of MOFs and zeolites reported in the literature compared to the accessible surface areas from crystal structures. Using a zeolite with artificial heterogeneity, we showed that the BET theory can be applied also to materials with heterogeneous surfaces. These results validate the application of the BET method for determining surface areas of ultra-microporous MOFs and zeolites.