

LOW-PRESSURE HYSTERESIS IN MOLECULAR SIEVE CARBONS

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Introduction

The sorption isotherm is effective at revealing information about the equivalent surface area, micropore volume, and pore size distribution of a molecular sieve (MS) carbon. Conventional nitrogen and argon isotherms at 77 K, however, are often limited in their ability to comprehensively characterize the porous network of the carbon adsorbent. To achieve a greater understanding of the microporosity of MS carbons, we have explored the interactions of a variety of probe molecules with polyvinylidene chloride (PVDC)-based carbons. PVDC chars are highly microporous (slit-like pores with widths less than 2 nm) [1], and their isotherms with various adsorbates exhibit different characteristics depending on the system studied, including, in some cases, low-pressure hysteresis (LPH). Although not nearly as well understood as its high-pressure cousin, LPH, or hysteresis that persists to low pressures, is attributable to certain key factors, including activated entry through narrow constrictions in the microporous network, adsorbent swelling and trapping, and surface modification [2,3]. The existence of LPH in specific adsorbent/adsorbate systems provides critical porosity and structural details about the adsorbent that may be overlooked using more conventional characterization methods. In this paper, we evaluate the adsorption behavior of an ATMI PVDC carbon with sulfur hexafluoride (SF_6) and ammonia (NH_3). In both systems, we observe LPH, but the widely different minimum critical dimensions of these two molecules (0.49 nm [4] vs. 0.31 nm [5]) and their chemical properties can be used to distinguish among the factors responsible for LPH in the two systems.

Experimental

PVDC carbon powder samples were prepared by pyrolysis of a Saran resin (Dow Chemical Company) in a nitrogen stream to at least 973 K. High-density PVDC carbon monoliths were prepared by first compacting Dow Saran resin at 25,000 lb/in² and then pyrolyzing the compacted samples. Sulfur hexafluoride, 99.75+% (Sigma-Aldrich) and anhydrous NH_3 (Solkatronic) were used as received. Adsorption-desorption isotherms of the PVDC carbon samples with SF_6 and NH_3 were collected at 294 K up to 0.115 MPa on a VTI Corporation GHP-300 Gravimetric Magnetic Suspension Balance. High vacuum was achieved via an Adixen turbomolecular drag pump ATH31C with ACT201H controller back-up by an ACP28G dry roughing pump vented to a dry scrubber. Samples were evacuated at 453 K for up to six hours prior to isotherm evaluation, and data were subjected to a helium buoyancy correction.

Results and Discussion

Adsorption-desorption isotherms of SF_6 on pyrolyzed Saran powders at 294 K are shown in Fig. 1 along with the corresponding integrated areas for each hysteresis loop. Powder samples heated to T0 (gray squares) show little evidence for LPH with SF_6 , and the isotherm is nearly reversible. Subsequent activation of the carbon powders to higher temperatures gives isotherms with increasing LPH, and once a threshold temperature is reached, the SF_6 capacity decreases.

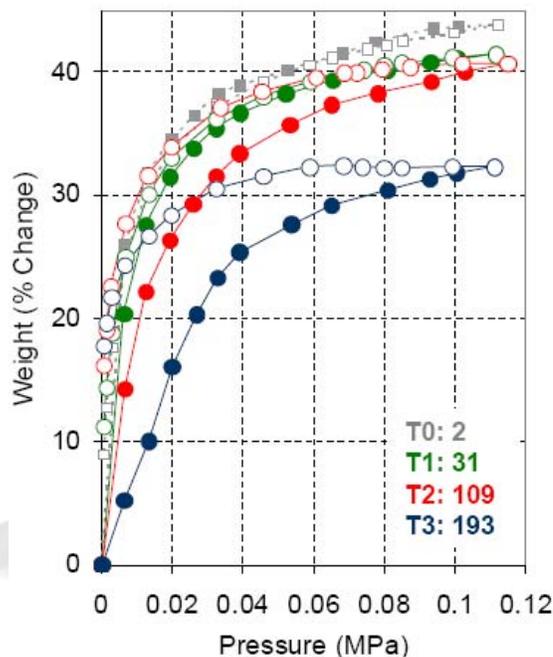


Fig. 1. Adsorption (filled symbols)–desorption (open symbols) isotherms of SF_6 at 294 K on powdered Saran char activated to different temperatures. Activation temperatures increase in the order gray (T0)<green (T1)<red (T2)<blue (T3).

In the carbon/ SF_6 system, the existence of LPH in samples subjected to increasingly higher activation temperatures is consistent with activated entry. Similar to other MS carbons, PVDC carbons comprise a network of micropores and cavities linked by passageways or ‘pore portals’. In this case, the minimum critical dimension of SF_6 , 0.49 nm, is close to the diameter of these entryways, and increasing activation temperatures further constrict these portals, making it more difficult for SF_6 to penetrate the system. Travel of the adsorbate molecule throughout the network proceeds at a limited rate, and a true equilibrium is not reached within the timeframe of the experiment, leading to LPH. Eventually, the diameter of the portals is small enough to prohibit entry to the adsorbate, causing a decrease in capacity (blue isotherm, T3).

Adsorption-desorption isotherms of NH_3 on PVDC carbon monoliths also show LPH, an example of which is depicted by the blue isotherm in Fig. 2. Ammonia is much smaller than SF_6 , and it is unlikely that passage of NH_3

through the porous network is hindered because of constrictions. As a point of reference, neither nitrogen isotherms at 77 K nor CO₂ at 273 or 294 K show evidence for LPH, and their minimum critical dimensions are similar to ammonia at 0.30 and 0.33 nm, respectively [4]. Furthermore, in the case of activated entry, we might expect that thermal activation of carbon samples with CO₂ would enlarge constrictions and reduce LPH, but LPH values remain nearly constant in this carbon/NH₃ system, even after burn-off levels as high as 19%. Rather, swelling of the adsorbent in the presence of NH₃ dominates this interaction, causing LPH. This behavior, which is typical of the interaction of organic vapors with carbon, has also been seen in adsorption isotherms of CO₂ on activated carbon samples taken to much higher pressures; in these experiments, isotherms of nitrogen, a poor swelling agent, showed no evidence of LPH [6].

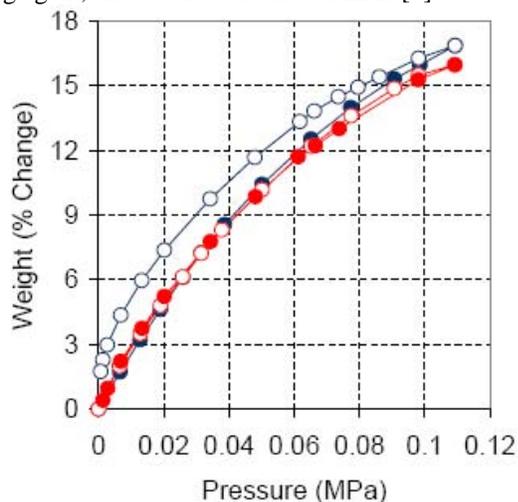


Fig. 2. Adsorption (filled symbols)–desorption (open symbols) isotherms of NH₃ on PVDC monoliths at 294 K. Initial (blue) and after an ammonia isotherm at 413 K (red).

Bailey et al. discuss LPH in PVDC chars in terms of a swelling mechanism in which the structure transforms to a new configuration [3]. For LPH to occur in this case, i) the carbon must be of intermediate rigidity such that the structure can be transformed; ii) there exists some threshold pressure below which this irreversible change does not occur; and iii) the pores that are available in this structural change are of molecular dimensions. From iii) it follows that activation conditions that increase pore size would decrease or eliminate LPH; this is not the case for our system under the conditions studied. Still it is likely that swelling of the carbon during the course of the experiment allows ammonia to penetrate previously inaccessible pore volume; during desorption, the structure collapses, forcing the adsorbate to exit more slowly or by another route. It is also possible that NH₃ molecules, because of their potential for hydrogen bonding, form an extended condensate within the porous network that facilitates swelling and/or restricts entry to additional NH₃ molecules. Such extended networks are observed during water adsorption

[6], although they are expected to occur to a much weaker extent with NH₃. At this stage, the exact mechanism for hysteresis warrants further investigation.

Carbons that exhibit LPH because of swelling can be manipulated to provide continuous access to this additional pore volume. If we condition PVDC carbon with an even better swelling agent, e.g., water, we initially observe the same NH₃ isotherm exhibiting LPH (Fig. 2). Next we cycle to 413 K for a second NH₃ isotherm. Upon returning to 294 K for our third isotherm, we find that the hysteresis has completely disappeared, with both the adsorption and desorption curves following the original adsorption curve. In a similar experiment in which the carbon was not initially exposed to moisture, the LPH remains nearly constant after the high-temperature run. In this example, pre-treating the carbon with water may increase its elasticity, allowing NH₃ to more easily open up the structure so that with each cycle the ‘new’ structure becomes increasingly more stable within the timeframe of the experiment. This approach could lead to a new adsorbent platform for increased storage capacity.

Conclusions

LPH is characteristic of different adsorbent/adsorbate systems and provides additional information about the adsorbent structure beyond what can be gleaned from conventional nitrogen and argon isotherm data. When the constrictions in the porous network are of molecular width, as in the case with SF₆, we observe LPH with loops that become larger as pore portals become more constricted. In contrast, in the presence of NH₃, LPH results from swelling of the carbon structure during adsorption. Collapse of the structure at reduced pressures traps gas molecules, causing irreversibility in the isotherm. Repeated adsorption–desorption steps decrease the hysteresis until the isotherm is nearly reversible. Our results with this system are indicative of underutilized pore volume that can be made available by conditioning the MS carbon.

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