EVALUATING POROSITY: LOW PRESSURE HYSTERESIS, ACTIVATED ENTRY AND CARBON SWELLING

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Abstract

When attempting to fully characterize the microporous structure of a molecular sieve (MS) activated carbon using sorption experiments, it is essential to take into account those factors which are influenced by the size of the adsorptive, the temperature and pressure. Results are shown for a series of MS carbons subjected to adsorption of methane, carbon dioxide, arsine, phosphine and boron trifluoride at 294°K, and nitrogen and hydrogen at 77.4°K. Activated entry effects can be identified, particularly for the larger arsine molecules, resulting in low pressure hysteresis over a wide pressure range, carbon swelling at the higher pressure and trapping of these larger arsine molecules. For small molecules, such as the flat BF3 molecule, low pressure hysteresis can also be seen as these molecules move into groups of even smaller micro-pores. While analysis of nitrogen isotherms (critical dimension 0.30nm)using D-R/D-A or even alpha-S procedures can provide useful information, evidence of activated entry due to the low temperature may be suppressed. Carbon dioxide (critical dimension 0.29nm)isotherms at 294K reveal porosity that constrains the similar-sized nitrogen molecules at 77.4K.

Keywords: Adsorption, Gas Storage, Molecular Sieves

Introduction

A review of physisorption hysteresis and the characterization of nanoporous materials has recently appeared (Sing, 2004a). The article does an excellent job of reviewing the historical experiences and summarizing the present level of understanding of hysteresis during physisorption of gases on nanoporous solids. However, the questions surrounding sorption hysteresis which occurs at low relative gas pressures...so called 'low pressure hysteresis' falls outside of the scope of the paper. Explanations for low pressure hysteresis include intercalation and expansion of layer structures and the 'activated entry' of molecules through narrow pore entrances (Gregg, 1982). For those of us interested in gas storage in 'molecular sieve' activated carbons, this topic is one which needs more attention.

Model pore systems developed in silica or alumina-silica systems (e.g. MCM-41 and SBA-16) have greatly improved our ability to interpret hysteresis loops of mesoporous materials and along with the recent application of computer assisted statistical mechanics of confined liquids (MonteCarlo and molecular dynamics methods with the use of density functional theory) improved pore size distribution analysis. These statistical mechanical techniques have also been applied to elucidate micropore size distributions (Gubbins, 1997; Olivier, 1995). However, in applying these simulations, most investigators have not allowed for pore blocking, 'activated entry' or any other form of diffusion control (Rouquerol, 1999). The same can be deduced for other approaches using for example the framework of Dubinin's theory (Stoeckli, 2001). Lopez-Ramon (1997) attempted to use percolation theory along with Grand Canonical Monte Carlo simulations to interpret the isotherms of CH_4 , CF_4 and SF_6 given by a microporous carbon.

The use of a variety of probe adsorptives at different temperatures is believed to be an ideal way of characterizing microporous materials (Webster, 1999). The higher adsorption temperatures used with these adsorptives, in contrast to N_2 at 77°K, results in larger kinetic energies and these molecules are then able to enter the narrow pores, avoiding diffusional problems (Garrido, 1987). Gregg (1970) reported a significant increase in n-butane adsorption on an activated carbon as the temperature of adsorption increased from 196°K to 273°K, each isotherm showing extensive low pressure hysteresis, providing clear evidence of an activated entry process. Lozano-Castello, (2004) showed benefits for the use of CO_2 at 273K to characterize a molecular sieve carbon. Sing (2004b) adopted the concept of effective minimum dimensions for probe adsorptives from Webster (1999). The ability of a molecule to enter a slit-shaped pore in a

molecular sieve carbon is dependent on the molecule's smallest diameter, referred to as MIN-1 and a listing of such dimensions shows water having the smallest MIN-1 at 0.29 nm with CO₂ next at 0.32 nm.

Nitrogen has a MIN-1 of 0.30nm but, adding to the fact that the molecule will be subject to diffusional limitations in small-pored carbons at the adsorption temperature of 77K, another possible disadvantage of nitrogen is that, because of its diatomic molecular shape and quadrupolar nature, it is an unrepresentative adsorptive for the investigation of micropore filling (Rouquerol, 1999). A comparison of the micropore filling of a molecular sieve carbon (Carbosieve) using a number of non-polar vapors of different molecular size was followed by Carrott (1988). Nitrogen, propane, isobutane and neopentane adsorptives were each compared and a striking feature of the isobutane and neopentane isotherms was their pronounced low pressure hysteresis. Since the rate of uptake of the bulky isobutane and neopentane molecules was very slow, thermodynamic equilibration was not established and therefore the isotherms are not amenable to detailed analysis. The smaller nitrogen and propane molecules were more rapidly adsorbed and their isotherms on the same sample were reversible. Nevertheless, the low pressure hysteresis loops demonstrate molecular sieve carbon.

Activated carbon which develops from pyrolysis of polyvinylidene chloride is a good example of a molecular sieve carbon (MacDonald, 1998). It is highly microporous (slit-like pores of width < 2nm) with little or no mesoporosity and often can be prepared as a monolithic piece with very little macroporosity. For gas storage applications the PVDC char is quite remarkable since, even with all of its microporosity, it can be surprisingly dense. Furthermore, on activation, the microporosity tends to be distributed within a fairly narrow range of pore sizes. Dubinin (1978) suggested that the microporosity of activated carbons is closely related to the micrographitic structure.

The work reported here describes adsorption of a variety of small probe adsorptives on PVDC chars processed in various ways. One adsorptive which is of significant commercial interest to the semiconductor industry is boron trifluoride. It is also unusual since it is one of a very few small planar, non-polar molecules available which is supercritical at room temperature. It's MIN-1 dimension has not yet been reported but it is probably even smaller than CO_2 .

Experimental

Gaseous hydride adsorption measurements were obtained up to 0.1MPa pressure and at 294.3°K using a modified Micromeritics ASAP 2405 porosimeter, replacing the supplied vacuum pump with an Adixen MDP 5011 Molecular Drag Pump and an Adixen Pascal 2005C1 Rotary Vane roughing pump vented to a Metron Technologies Novapure[®] S520 dry scrubber. Delivery of the hazardous gases under pressure to the porosimeter was achieved via a gas manifold with pneumatic isolation valves actuated by a Honeywell Zellweger Analytics MDA TLD-1 Toxic Gas Detector. N₂ & H₂ measurements at 77.4°K and up to 0.1MPa were obtained via the ASAP 2405.

Gaseous inorganic fluoride adsorption measurements again up to 0.1MPa pressure and at 294.3°K were obtained using a VTI Corp. GHP-300 Gravimetric Magnetic Suspension Balance and a gas delivery manifold with certain isolation valves actuated by a Honeywell Zellweger Analytics MDA TLD-1 Toxic Gas Detector. High vacuum was achieved via an Adixen turbo-molecular drag pump ATH31C with ACT201H controller backed up by an ACP28G dry roughing pump each vented to an Metron Technologies Novapure® S451D dry scrubber.

High-density PVDC carbon samples were prepared by compacting Dow (Dow Chemical Co., Midland, MI) Saran A homopolymer or other copolymers in a pre-heated (to 90°C) 13mm die at 15,000 lbs force followed by pyrolysis in a nitrogen gas stream at temperatures up to 850°C.

X-Ray Diffraction measurements were obtained using an automated powder diffractometer (Rigaku Model VS-DXR3000) with Ni-filtered, Cu-K α radiation at 40KV and 30mA.

Results and Discussion

The volumetric gas storage benefits of PVDC carbon can be readily understood by reference to Fig.1. AsH_3 adsorption-desorption isotherms are shown for an ATMI® PVDC monolith carbon and those of Kureha BAC G70R and Kansai Maxsorb (PX-21). The low densities of the two non-monolith carbons severely limit their storage capacities when compared to the PVDC carbon. Note that some low-pressure hysteresis can be identified for both the PVDC and the Maxsorb carbon.

Low pressure hysteresis is rarely detected in N_2 at 77°K or CO_2 at 294°K isotherms of PVDC carbon, yet, as the molecules for storage increase in size (Table 1), the likelihood of low pressure hysteresis increases. In Fig. 2 isotherms of these gases are shown for a PVDC carbon sample 'A' with no evidence of hysteresis. The same sample when adsorbing PH₃ and AsH₃, however, shows increasing levels of low pressure hysteresis. This is consistent with activated entry affecting the progressively larger sizes of the adsorptive molecules. Diffusion of the larger molecules into the structure is limited by pore constrictions. Hence the adsorption isotherm does not reach full equilibration. Furthermore, desorption loops do not close



AsH3 Isotherms on SDS3 carbon, Kureha, Maxosorb

Figure 1. Arsine adsorption (closed markers) and desorption (open markers) isotherms for three commercially available carbons.

| Table 1. Table of | of molecu | lar sizes ac | cording to | Webster (| 1999 |) |
|-------------------|-----------|--------------|------------|-----------|------|---|
|-------------------|-----------|--------------|------------|-----------|------|---|

| Molecule | σ, /nm | MIN-1 | MIN-2 | |
|------------------|--------|-------|-------|--|
| H ₂ | 0.289 | | | |
| H ₂ O | 0.27 | 0.29 | 0.32 | |
| CO ₂ | 0.33 | 0.32 | 0.33 | |
| N ₂ | 0.36 | 0.3 | 0.31 | |
| CH ₄ | 0.38 | 0.38 | 0.39 | |
| PH ₃ | 0.375 | | | |
| BF ₃ | 0.29? | | | |
| AsH ₃ | 0.375 | | | |

at the lowest pressures reached. Since the highest pressures of the PH₃ and AsH₃ isotherms (0.1MPa) equate to 0.024Po and 0.067Po respectively for these gases, a region of pore filling which encompasses much of the microporosity, some swelling of the carbon structure can be envisioned at the top pressure allowing molecules to penetrate deeper (intercalate) into the porous structure to fill larger 'shadowed' pores (Goldstein, 1997). The structure only relaxes when the pressure is sufficiently reduced, trapping molecules in these 'shadowed' pores. The presence of low pressure hysteresis does not feature in every AsH₃ isotherm of PVDC carbon but depends markedly on the specific activation conditions applied (compare those in Fig. 3 for the reference sample 'B').



N2, CO2, PH3 and AsH3 Isotherms - PVDC char 'A'

Figure 2. Adsorption (filled markers) and desorption (open markers) isotherms for nitrogen, arsine, phosphine and carbon dioxide on PVDC carbon sample 'A'.





Figure 3. Arsine adsorption (filled) and desorption (open) isotherms for PVDC chars 'A' and 'B'. Special activation conditions were selected in an attempt to enhance the level of (UMPV) ultramicropore volume, (i.e. pores of a width below about 0.7 nm) in certain samples of PVDC carbon. In Table 2, analyses are provided for the reference PVDC char sample, 'B' and the five attempts, 'C' through 'G' from nitrogen adsorption isotherms. Various mathematical approaches are listed, H-K, D-R, D-A, Stoeckli, t-plot and Alpha-S. The Stoeckli assessment of micropore widths and the UMP volume measurements using the Alpha-S method indicate that the five have smaller pore-widths than that of the reference sample 'B' with samples 'E' and 'F' showing the smallest pores.

| Sample ID | Ref. 'B' | С | D | E | F | G |
|-----------------------------|----------|---------|---------|---------|---------|---------|
| BET SA m2/g | 1014 | 1339 | 1417 | 1171 | 1227 | 1256 |
| t-plot microPV ml/g | 0.378 | 0.497 | 0.526 | 0.439 | 0.460 | 0.465 |
| Horvath -Kawazoe slit size | 0.77 | 0.780 | 0.760 | 0.78 | 0.77 | 0.76 |
| Dubinin-Radushkevich Eo | 23.2558 | 25.2309 | 24.1702 | 29.9578 | 28.1939 | 23.9402 |
| Dubinin-Astakov microPV | 0.386 | 0.541 | 0.554 | 0.462 | 0.481 | 0.521 |
| Dubinin-Astakov <i>Eo</i> | 18.446 | 26.629 | 22.118 | 30.655 | 27.066 | 26.4258 |
| D-A Exponent | 3.386 | 1.774 | 2.477 | 1.927 | 2.148 | 1.5488 |
| Stoeckli Pore width, Lo nm | 0.91 | 0.78 | 0.85 | 0.58 | 0.64 | 0.86 |
| Alpha-S Total Micro PV ml/g | 0.415 | 0.529 | 0.559 | 0.459 | 0.481 | 0.498 |
| Alpha-S Super Micro PV | 0.063 | 0.081 | 0.079 | 0.037 | 0.035 | 0.042 |
| Alpha-S Mid-Micro PV ml/g | 0.043 | 0.096 | 0.097 | 0.060 | 0.074 | 0.100 |
| Alpha-S Ultra-Micro PV ml/g | 0.309 | 0.352 | 0.383 | 0.362 | 0.372 | 0.338 |

Table 2. Nitrogen adsorption-desorption parameters for PVDC MS carbons

Since adsorption of CH₄ at 294K and pressures up to 0.1MPa represents micropore volume filling in the $<25 \times 10^{-4}$ Po region, the isotherms should reveal differences between the samples in this ultra-micropore region. Indeed they do, matching the expectations from the Stoeckli –derived results. Isotherms for just three of the six are shown for clarity in Fig. 4.



CH4 Isotherms at 294K for PVDC char 'B', 'C' and 'E'

Figure 4. Methane isotherms at 294K adsorption (filled) and desorption (open) for three PVDC chars, 'B', 'C', 'E'.

A higher level of volume filling is seen to occur at the lowest pressures for sample 'E' (and 'F', not shown) compared to those of samples 'B', 'C' (and 'D' and 'G' not shown). None of the isotherms in Fig.4 exhibit low pressure hysteresis. However, that is not the case for the isotherm for sample 'G' reported in Fig.5 alongside the CH_4 isotherm for sample 'F'. Low pressure hysteresis was evident throughout the pressure region but loop closure occurred at low pressure. In this case the top pressure was sufficiently low so that the low pressure hysteresis does not include carbon swelling and molecular entrapment. The hysteresis indicates some extent of constricted entry.



CH4 Isotherms at 294K for PVDC chars 'F', 'G'

Figure 5. Methane adsorption isotherms at 294K for PVDC chars 'F' and 'G': adsorption (filled), desorption (open).

Similar results were seen when CO₂ was the probe molecule. When BF₃ adsorbed on these same two samples at 294K and up to 0.1MPa (~0.01Po), low pressure hysteresis was clearly present in the isotherms for both samples and loop closures did not occur (Fig. 6). As expected, sample 'F' had distinct advantages for BF₃ storage over 'G'.

The swelling of carbons during vapor adsorption is a well known phenomenon (Dacey, 1971). Kaneko (1991) reported carbon swelling during increased levels of water adsorption and monitored the swelling of micropores using X-ray Diffraction. Changes in the XRD patterns with desorption of water from the PVDC carbon can be seen in Fig. 7. Following adsorption, on reaching the 24 wt.% water content, a sharp peak appears at 27° two-theta, corresponding to some ordering of the structure and reflections from the (002) planes. Kaneko describes this as due to a change from disordered wedge-shaped pores without adsorbed water to parallel slit-shaped pores filled with water. As the water leaves the structure, the XRD feature at 27° gradually drops in intensity.

Swelling of the carbon is retained sufficiently long so that if outgassing and bake-out occurs within hours of removal from the high humidity environment, micropore volume measured by N_2 adsorption increases; the enhanced adsorption is in ultra-micropore volume as detected by BF₃ adsorption (Fig. 8) and H_2 adsorption at 77K (Fig. 9). However, the BF₃ molecules adsorbed into swollen micropores become trapped and are not released at low pressure, following the structural relaxation. Further supporting evidence for the structural changes suggested by Kaneko.



BF3 Isotherms at 294K PVDC chars 'F', 'G'

Figure 6. BF₃ isotherms on PVDC chars 'F' and 'G': adsorption (filled) desorption (open)



Figure 7. XRD patterns in air of PVDC carbon: dry (Normal puck), hydrated to 24 wt.% H_2O and gradually drying in dry air for 5, 16, 37 and 159 hrs.



BF3 Isotherms at 294K, PVDC char 'B' hydrated & outgassed

Figure 8. BF₃ isotherms on PVDC char 'B' initially hydrated to 1.5, 7.5 and 23.7 wt.% H_2O followed by outgassing at 1 x 10⁻⁵Pa and 453°K: adsorption (filled), desorption (open).



H2 Isotherms at 77K for PVDC char 'B'

Figure 9. Hydrogen isotherms at 77°K for PVDC char 'B' hydrated initially to 1.5, 23.7 wt.% before outgassing at 1×10^{-5} Pa and 453°K: adsorption (filled) and desorption (open).

Conclusions

Molecular Sieve carbons, such as those generated from pyrolysis and activation of PVDC, exhibit porosity in a narrow micropore size region with much of the pores in the ultra-micropore region. Using small gas molecules as adsorptives, the porosity can be probed and reveal evidence of low pressure hysteresis. The low pressure hysteresis is attributed to activated entry effects (pore constrictions) which may or may not involve intercalation of the adsorbent molecules in the slit-like pores. Swelling of the carbon structure under conditions of volume filling can also contribute to the appearance of low pressure hysteresis. The carbon , post-swelling, usually traps/intercalates molecules preventing their release during desorption.

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Acknowledgements

The author wishes to recognize the contribution of Ms. Sue DiMascio for the x-ray diffraction studies and ATMI for permission to present this work.

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