Chapter 6

Conclusions

6.1 Summary of Results

The motivation of the studies presented in this thesis was twofold: to gain thermodynamic insights into the mechanism of physical adsorption at the solid-gas interface that can be effectively applied to the design of future energy storage materials, and to accurately determine the adsorptive properties of key materials that have received attention for their reported extraordinary physisorptive storage of hydrogen toward understanding the key material properties that can be tuned to reach maximum adsorption densities. We seek to assist in determining if physisorptive materials can be developed to meet the needs of the transportation sector.

It is long established that physisorptive hydrogen uptake is well approximated as proportional to surface area in carbonaceous materials, and thus specific surface area is the benchmark material property for determining the “ballpark” hydrogen capacity of a new material. The relationship depends on temperature and pressure, and is commonly stated at 77 K and the surface excess maximum pressure. This specific relationship, “Chahine’s rule,” roughly predicts 1 wt% H_2 uptake per 500 m^2 g^{-1} of specific surface area, corresponding to 6 molecules per square nm. The prediction is inexact, as we find the precise description of this relationship to be 0.009±0.001 mmol m^{-2}, or 5.6±0.8 molecules per square nanometer (see Section 4.5.2). A caveat is that, for carbonaceous materials, the relationship reaches a limit at ~3000 m^2 g^{-1}: relatively few higher surface area materials have been reported and the trend seems to level off.

Finding a material that deviates from this trend (significantly higher than scatter) has been the goal of the physisorptive hydrogen storage community in recent years. Two notable reports of enhanced uptake that have drawn significant attention are those of (atomic) hydrogen sorption by metal-assisted spillover and anomalous hydrogen adsorption densities in zeolite templated-carbons at high pressure (>10 MPa). We have focused on both of these systems in this study to understand the underlying principles of their anomalous behaviors, and presented a detailed assessment of their hydrogen storage properties in Chapters 3 and 4.

Toward new materials which could realize significantly higher adsorptive storage than that of typical activated carbons, we focused on methane adsorption since it is possible to perform extremely detailed thermodynamic studies in a region beyond that of the ideal gas. We collected a very large data set of high-pressure methane isotherms between 238-526 K up to 9 MPa, and with careful treatment of the data, were able to shed remarkable insight into the thermodynamics of adsorption in the carbon materials studied. Specifically, we showed that in zeolite-templated carbon ZTC-3, a combination of tuned material properties and strong, attractive methane-methane interactions in the adsorbed phase contributed to an anomalous increase in isosteric enthalpy of adsorption with increased site occupancy at high pressure, presented in Chapter 5. We employed a simple and effective model to estimate the absolute adsorption from high-pressure experimental data, a key technique for extracting the level of detail from adsorption data that was necessary for this study (detailed in Chapter 2).

In summary, three primary results are presented in this thesis:

i. the addition of platinum nanoparticles to the surface of activated carbon, while creating suitable conditions for metal-assisted hydrogen spillover, does not appreciably enhance reversible hydrogen uptake above the pure supporting material,

ii. the physisorptive hydrogen storage capacity of zeolite-templated carbon is among the highest known for pure carbonaceous materials, but is ultimately proportional to surface area at all conditions measured, and

iii. the adsorption of methane on zeolite-templated carbon is anomalous compared to other physisorptive materials, showing an increase in isosteric enthalpy with uptake, a result of enhanced adsorbate-adsorbate interactions in the adsorption phase.

6.1.1 Hydrogen Spillover for Storage Applications

At the time of our investigation of metal-assisted hydrogen spillover materials, the factor of 2 enhancement reported for the Pt/AX-21 system and, similarly, the 8 times enhancement reported for “bridged” IRMOF-8 were perhaps the most prominent experimental results that suggested reversible hydrogen adsorption could be accomplished at significant capacities at room temperature. At the same time, these results were poorly understood theoretically, sometimes referred to as “weak chemisorption” rather than physisorption, and the experimental evidence was limited to volumetric hydrogen sorption measurements that was unreproduced by other groups. Our efforts were to be initially focused on the simplest possible spillover system, since exposed transition metal sites (such as in MOFs), hydrogen absorbing metals (e.g., palladium nanoparticles), and organic molecule “bridges” were seen to be complicating variables and were reported as unnecessary to achieve significant enhancement of hydrogen uptake capacity. Platinum nanoparticles supported by a well-characterized support material was the chosen system for initial studies, equivalent to the previously reported Pt/AX-21. We synthesized materials, optimized the material properties for spillover (especially reducing nanoparticle size and increasing dispersion), and ultimately achieved products, referred to as Pt-MSC-30, which could not be differentiated from others in the literature based on typical characterization techniques: XRD, TEM, and TGA. Hydrogen sorption properties were assessed, first by standard techniques, and due to large uncertainties in the results, also by significantly more accurate methods. One unique quality of spillover compared to traditional physisorption is its long duration, reported to be 1-2 orders of magnitude longer in equilibration time due to surface diffusion of the atomic hydrogen, requiring alterations to our standard measurement apparatus and techniques to minimize numerous sources for substantial errors.

Our ultimate results, assured by increasing the signal to noise capabilities of our Sieverts instrument by a factor of 10-16, showed that the enhancement of hydrogen uptake capacity by spillover was below the detection limit of volumetric adsorption measurements in Pt-MSC-30. We were not able to confirm the 100% increase associated with an otherwise identical system, Pt/AX-21, but were able to pinpoint possible sources of error accumulation in the methods of its measurement. Further work, including measurements from our lab as well as collaborators, has supported our initial results and refined our estimate of the magnitude of this effect in terms of storage. Details are provided in Appendix B.

6.1.2 Anomalous Adsorption Properties of Zeolite-Templated Carbons

Zeolite-templated carbons (ZTCs), a class of materials with extremely high surface area and narrow microporosity, received enthusiastic attention after the report of significantly increased hydrogen storage capacities at pressures between 10-34 MPa. To investigate the reported unique properties of adsorption in ZTCs at high pressure, where few instruments are capable of adsorption measurements, we designed, constructed, and commissioned an apparatus capable of measurements up to 70 MPa. In addition, we succeeded at synthesizing relatively large quantities of high surface area, high template-fidelity ZTCs comparable in quality to those reported in the literature. However, hydrogen adsorption characteristics of ZTCs were consistent with other carbonaceous materials, even beyond 10 MPa where it had previously been reported to differ. We established a "Chahine's rule" relation of excess hydrogen capacity at 298 K and 30 MPa, 2.3 mmol g^{-1} per 1000 m^2 of BET surface area, or 1.4 H_2 per square nanometer for carbonaceous materials. The enthalpy of adsorption of hydrogen in ZTCs was also shown to be similar to other carbons, but interestingly, skeletal density was significantly lower in ZTCs due to a high H content as determined by elemental analysis experiments. While the hydrogen adsorption properties of ZTCs are typical of other carbons, the unique periodic pore spacing, extremely high surface area, and practical synthetic procedures make ZTCs a highly interesting class of materials for adsorption applications beyond high-pressure hydrogen storage.

Following hydrogen, we investigated the methane adsorption properties of ZTCs with the motivation that strong, attractive intermolecular interactions would significantly alter the chemical potential environment, even at temperatures and pressures near ambient conditions. This was a convenient realization since extremely detailed thermodynamic information could be harvested with relative ease for methane, where hydrogen studies are much more limited (unless a helium cryostat is available). We measured methane adsorption uptake as a function of pressure at 13 temperatures between 238-526 K, the regime of practical importance for methane storage applications, and amassed one of the largest data sets for methane adsorption on high surface area carbonaceous materials. Combined with a simple and effective model for determining the absolute quantity of adsorption, this study lead to the central result presented in this thesis: the increasing isosteric enthalpy of methane adsorption with increasing uptake in faujasite-templated carbon, ZTC-3. This is an interesting and highly desirable deviation from the typical properties of high surface area carbonaceous materials, where the isosteric enthalpy of adsorption is usually observed to decline with uptake. It is intuitive that binding heterogeneities in high surface area carbons (where edge terminations, defects, and surface roughness typically contribute to the extremely high surface area quality of the material) ensure that high energy sites are filled preferentially to low energy ones. However, it is precisely the homogeneous distribution of extremely narrow channels in ZTCs that lend the unique property of enhanced binding as fractional occupancy in the adsorbed phase increases.

The direct cause of this effect is not ascertainable without a better understanding of the relative roles of the strong lateral interactions of methane in the adsorbed phase and the extent of binding site homogeneity in ZTC. However, we can estimate that the lateral interactions are quite important in light of their importance to gas-phase properties of methane in this pressure and temperature regime. We cannot rule out entropic contributions, and analysis showed that the entropy of the adsorbed phase resembled that of liquid methane in the high-pressure region. In any case, templated-carbons remain an exciting class of materials and much remains to be investigated in this area.

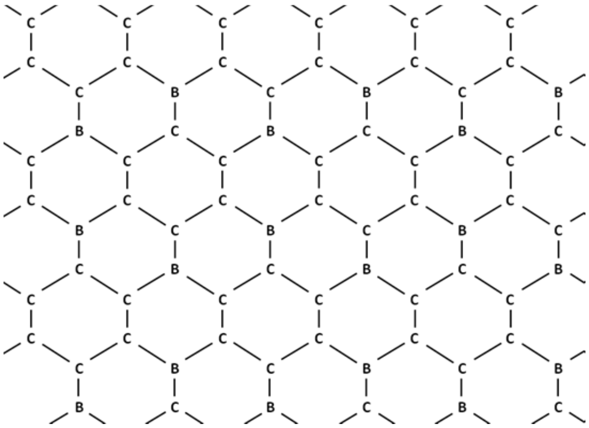
6.2 Future Work

6.2.1 Zeolite-Templated BC_x Materials

Substitutional doping of carbon with beryllium, boron, and other light elements by solid-state diffusion has been discussed as a promising route toward increasing hydrogen binding energy. In particular, computational analysis shows that the strongly localized empty p_z orbitals at a Be or B site substituted within a graphite-like surface interacts with the occupied orbital of H_2, leading to a partial charge transfer from H_2 to the surface. Significantly higher hydrogen binding energy (~11 kJ mol^{-1}) has been reported experimentally for boron-doped carbon (BC_x) materials,[1] though surface areas in these systems are limited to < 1000 m^2/g. As a result of stronger binding, hydrogen uptake is found to be increased by up to 50% in microporous BC_x materials compared to pure carbon materials of similar surface area. Compounds of beryllium-doped carbon are expected to have even higher hydrogen binding energy, but are unknown experimentally.

In practice, it is difficult to obtain boron levels in carbon greater than ~10 wt% by standard synthesis techniques.[1] Alternatively, graphite-like BC_3 (shown in Figure 6.1) has a high B:C ratio, but its synthesis is typically performed on the surface of a thin substrate inside a flow-through tube furnace.[2-4] Fabrication of high surface area sorbents with a chemical structure resembling BC_3 would be of significant interest for hydrogen physisorption. The precursors necessary for producing graphite-like BC_3 (boron trichloride and benzene) are both readily adsorbed by zeolites, and we suggest that under the right conditions, a BC_3-like coating could be formed on the inner surface of the zeolite template. Subsequent removal of the zeolite template as in ZTC synthesis should yield an amorphous BC_x ($x \approx 3$) material that exhibits extremely high surface area, narrow microporosity, and a homogeneous distribution of elevated hydrogen binding energies.

Our initial attempts at producing BC_3 are shown in Figure 6.2, where we have collected the product on a silicon substrate. The energy-loss spectrum shows boron and carbon K-edges with a boron concentration over twice that of the known solubility limit, but still half of that expected for pure BC_3. With the substantial potential for refinement of the processing technique (involving the careful handling of corrosive gas precursors) in mind, this is a promising first result.



$$C_6H_6 + 2\,BCl_3 \rightarrow 2\,BC_3 + 6\,HCl$$

Figure 6.1. BC_3 synthesis reaction and chemical structure.

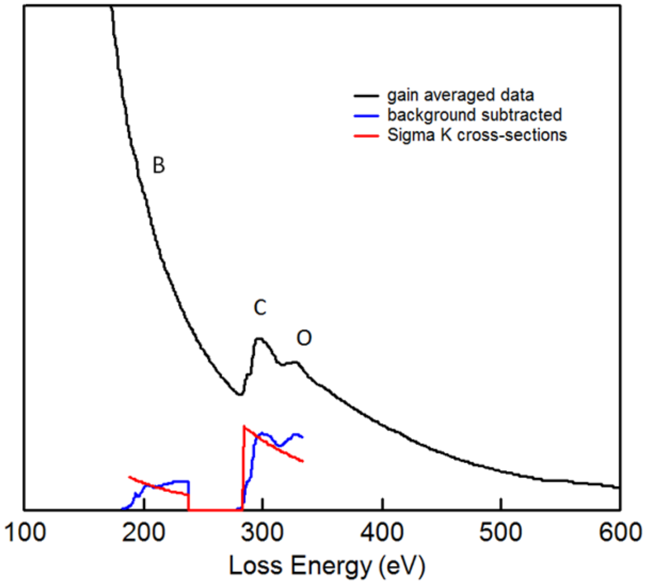


Figure 6.2. EELS spectrum of an early attempt to synthesize BC_3 on a silicon substrate.

6.2.2 Pressure to Change Chemical Potential: Carbon Nanotubes

Pressure can be used as a dial to tune the chemical energy environment of a gas-solid system. The chemical potential, μ, of a single-component gas held at a fixed temperature (the molar Gibbs free energy) increases proportional to ln P, that is, until the ideal gas limit is surpassed. The nature of the chemical potential in the non-ideal gas region for hydrogen and methane is plotted as a function of pressure in Figure 6.3, with reference to an arbitrary state so that $\mu(P,T)$ is 0 at P = 0.001 MPa. The deviation from ideality is positive for H_2 at all temperatures between 77-523 K, due to Pauli repulsion, while it has a negative initial deviation for CH_4 at low temperatures due to attractive intermolecular forces. Both gases show a positive deviation at high temperatures and pressures.

The proposed future work concerns using the change in chemical potential associated with a decrease in pressure to drive a phase transition between different states of surface exposure in a material. Single-walled carbon nanotubes are known to form bundled structures, bound by weak van der Waals forces between nanotubes, analogous to the inter-planar forces between graphene sheets in the structure of graphite. , bound by weak van der Waals forces between nanotubes, analogous to the inter-planar forces between graphene sheets in the structure of graphite. The magnitude of the binding interaction between planar carbon surfaces is not precisely known, but is often estimated to be ~50 meV per C in pure graphite. Within the last 10 years, the binding energy has been calculated to fall within the range of 8-200 meV per C. Misalignments, curvature, and defects in nanotubes could result in a lower value. It is possible to probe this interaction using adsorption; if the chemical potential of the adsorptive phase exceeds that between self-interacting surfaces, it is plausible that a phase transition will proceed to expose a larger area for adsorption. The change in state from bundles to individual nanotubes would be accompanied by a large change in available surface for adsorption, and it is possible to design an experiment to test this.

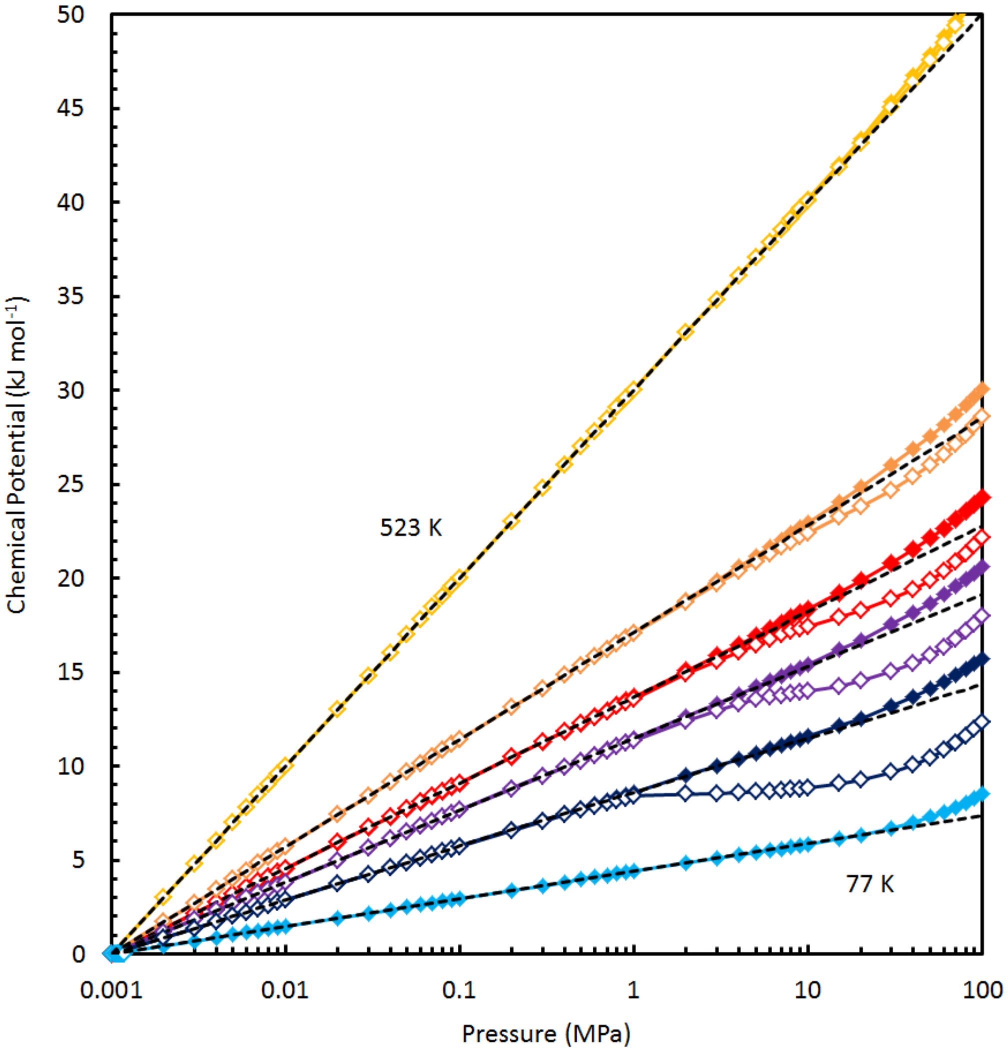


Figure 6.3. Chemical potential of methane (unfilled diamond) and hydrogen (filled diamond) at 77 K (light blue), 150 K (dark blue), 200 K (purple), 238 K (red), 298 K (orange), and 523 K (yellow). The reference state has been adjusted so that all curves intersect at P = 0.001 MPa and μ = 0 kJ mol^{-1}, for clarity.

The regime where the most chemical potential is available for driving this transition is one where the change in chemical potential with pressure is steepest. Adsorption on the large exposed area would result in a significantly lower final pressure of the system, a state with lower free energy than that in which the nanotubes remain bundled.

With some simple approximations, and using actual measured data for the amount of adsorbed hydrogen or methane as a function of pressure, we can predict the conditions which are most likely to result in un-bundling. It seems hydrogen, with its large positive slope in chemical potential with pressure, would be the better candidate gas. Secondly, lower temperatures, despite having a more gradual change in chemical potential with pressure, yield much higher surface coverages at the final pressure of the adsorption system, giving the highest values of change in chemical potential per C. A practical temperature would be 77 K. First approximations of the magnitude of this effect achievable in our laboratory predict at least 1-2 meV per C is possible within acceptable pressures, but would benefit from a specifically designed apparatus with carefully adjusted volumes (refer to Appendix E). An ideal setup would be to have a large sample with as much exposable surface as possible contained in the smallest void, thus giving the largest possible change in pressure on adsorption and exploiting the maximum chemical potential available in the gas phase.

While applications of this proposed idea are not obvious, it is possible that a material which undergoes such a pressure driven transition to a high surface area phase could have promising applications for energy storage since large changes in adsorption uptake would be possible with small changes in system pressure.

6.3 References

(1) T. C. M. Chung, Y. Jeong, Q. Chen, A. Kleinhammes, and Y. Wu, 'Synthesis of microporous boron-substituted carbon (B/C) materials using polymeric precursors for hydrogen physisorption', *J. Am. Chem. Soc.,* **130**, 6668-6669 (2008).

(2) J. Kouvetakis, R. B. Kaner, M. L. Sattler, and N. Bartlett, 'A novel graphite-like material of composition BC3, and nitrogen-carbon graphites', *J. Chem. Soc., Chem. Commun.*, 1758-1759 (1986).

(3) R. B. Kaner, J. Kouvetakis, C. E. Warble, M. L. Sattler, and N. Bartlett, 'Boron-carbon-nitrogen materials of graphite-like structure', *Mat. Res. Bull.,* **22**, 399-404 (1987).

(4) K. M. Krishnan, J. Kouvetakis, T. Sasaki, and N. Bartlett, 'Characterization of newly synthesized novel graphite films', *Mat. Res. Soc. Symp. Proc.,* **121**, 527-530 (1988).