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Chemistry of Materials

Toward New Candidates For Hydrogen Storage: High Surface Area Carbon Aerogels

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A basic understanding of hydrogen sorption behavior of materials will be critical to the transportation sector needs of high gravimetric and volumetric density. An important criterion for effective physisorption is a high surface area that exposes a large number of sorption sites to ad-atom or ad-molecule interaction.[1] Moreover, these sites need to have potential wells that are sufficiently deeper than kT if physisorbents are to operate at engineering temperatures. The dependence of gravimetric density on surface area can be appreciated from studies of activated carbons that show that the amount of surface excess hydrogen adsorbed at 77 K varies linearly with surface area at pressures of ~35 bar.[2-4] We can generally expect a gravimetric density of 1% for every 500 m^2/g of surface area in activated carbons. While metal organic framework materials are also capable of being synthesized with high surface areas, the gravimetric density dependence will be weaker due to the mass associated with the transition metal vertices of these materials.[3]

Carbon aerogels (CAs) represent another class of carbons that can serve as effective physisorbents. CAs are mesoporous materials with a range of properties, such as controllable mass densities, continuous porosities and high surface areas.[6,7] These properties are derived from the aerogel microstructure, a network of interconnected primary particles with characteristic diameters between 3 and 25 nm. Unlike activated carbons, CAs can be prepared in a variety of forms, including monoliths with a high degree of conformability. The hydrogen sorption properties of CAs, however, have not been studied previously. Our understanding of the surface area dependence of sorption behavior in activated carbons has motivated us to prepare a range of high surface area carbon aerogels in order to understand how sorption behavior in these materials scales with surface area. In this communication, we present 77 K isotherm data and sorption enthalpies for activated CA (ACAs) with BET surface areas up to 3200 m^2/g as well as for metal-doped CAs. The BET surface area of 3200 m^2/g is the highest value that we are aware of for a CA.

The CA materials used in this study, both the undoped and metal-doped materials, were prepared as previously described.[6-8] In general, these materials were synthesized through the sol-gel polymerization of resorcinol with formaldehyde in aqueous solution to produce organic gels that are supercritically dried and subsequently pyrolyzed in an inert atmosphere. The undoped CAs were then activated with CO_2 at 950°C.[9] Full synthetic details and structural characterization of the ACAs will be presented elsewhere.

Hydrogen adsorption/desorption excess sorption measurements were performed with a volumetric Sieverts apparatus.[10] The 77 K adsorption isotherm traces from a low surface area (330 m^2/g) organic aerogel prior to carbonization, and from ACA samples with higher surface areas (1460 to 3200 m^2/g), are shown in Figure 1. For clarity, only adsorption isotherm traces are shown. In all instances, the adsorption and desorption data were identical and no hysteresis could be observed. The sample with the surface area of 330 m^2/g adsorbs 0.8 wt% at 20 bar while the 3200 m^2/g sample adsorbs 5.3 wt% hydrogen at 30 bar pressure. The ACAs with surface areas of 1460, 2000 and 2550 m^2/g show saturation values taken from the surface excess adsorption isotherms that are intermediate to these values, as expected. Of interest is the fact that an ACA can be prepared with a surface area of 3200 m^2/g, greater than the surface area of a single graphene sheet (2630 m^2/g, if both graphene surfaces are taken into account) and comparable to high surface area activated carbons. Presumably,

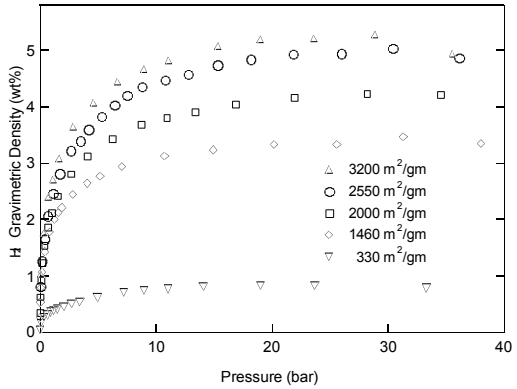

Figure 1. Adsorption isotherms at 77K for the undoped ACAs. The organic aerogel with surface area of 330 m^2/g was not carbonized.

edge terminations make up a substantial fraction of the surface area of the ACAs as is the case for activated carbons.

We have also studied the sorption dependence of nickel and cobalt incorporation into the carbon aerogel framework (Figure 1S). Our previous work has shown that the metal nanoparticles are homogeneously distributed in the CA network and that the accessible surface area of the metal nanoparticles is related to the carbonization temperature.[8] For example, when carbonization is performed at 1050°C, the metal nanoparticles are typically encased in graphitic carbon, while at 800°C, this effect is less pronounced and, as a result, the metal nanoparticles still possess accessible surface area. The adsorption isotherms at 77 K for the Co-modified CAs carbonized at 800°C and 1050°C are similar with saturation values of ~2.1 wt% for each sample. The effect of carbonization temperature on sorption behavior for the Ni-modified CAs is more pronounced with the material carbonized at 800°C showing ~10% enhancement in the saturation value (2.3 wt% vs 2.0 wt%) over the material carbonized at 1050°C sample despite having a lower BET surface area (970 m^2/g vs 1100 m^2/g). This observation may be attributable to H_2 interaction with

accessible Ni particles, consistent with behavior previously described as metal-assisted cold-storage.[11] We cannot, however, discount the possibility that the metal dopants influence the textural properties of the CA during carbonization. For instance, the Ni may be altering the CA structure during pyrolysis, making available pores that are not adequately measured by N_2 BET measurements, but that are accessible to H_2.

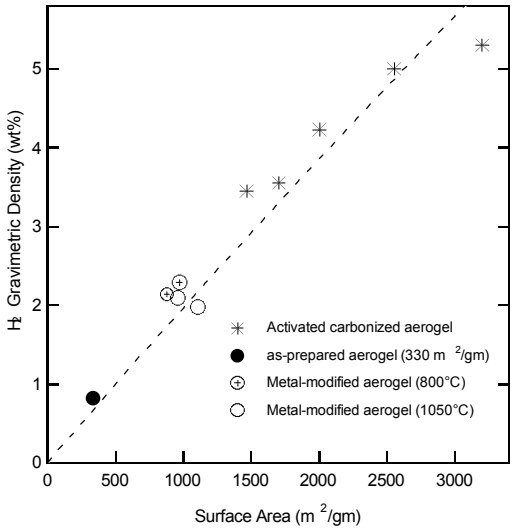

Figure 2. Excess gravimetric density (H_2 wt.%) saturation value at 77K as a function of BET surface area. The line is 1 mass% sorption per 500 m^2/g, converted to wt%.

Previous studies have noted the linear dependence of hydrogen sorption at 77 K and 35 bar pressure versus surface area in activated carbons.[2,3] When the sorption amount is expressed in mass% (mg hydrogen)/(g aerogel), the sorption dependence scales as 1% hydrogen sorbed for every 500 m^2/g of surface area. In Figure 2, we plot the saturation value, i.e. the maximum amount of hydrogen sorbed in the surface excess isotherm trace versus the BET surface area. We note that this approach varies somewhat from the original analyses of Chahine, as the maximum surface excess quantity of sorbed hydrogen can occur at pressures other than 35 bar. In our aerogels, saturation occurs typically at ~30 bar for higher surface area materials. We also note that we express the saturation value in wt%, which yields a slightly lower quantity than values expressed in mg of sorbed hydrogen per gm of sorbent. At 77 K, hydrogen surface excess sorption of CAs scales with BET surface area up to 2550 m^2/g, yielding up to 5 wt% gravimetric density. The surface area dependence for the aerogel with a surface area of 3200 m^2/g is somewhat weaker with a gravimetric density of 5.3 wt%. The absolute value of 5.3 wt% is comparable to the highest value we have measured in an activated carbon,[12] however, aspects of the structure of the aerogel with a surface area of 3200 m^2/g might promote H_2-H_2 gas interactions that would weaken the surface area dependence. We are presently investigating this behavior.

While adiabatic calorimetry provides the most direct measure of thermodynamic behavior during hydrogen uptake, we can rely on other approaches in order to evaluate sorption enthalpies. The easiest means is to evaluate the differential enthalpy of adsorption at zero coverage from the isotherm, as defined by an analysis of the Henry's law region (low pressure, linear regime slope). This approach has the benefit of gauging hydrogen-surface interactions while minimizing interactions between adsorbed hydrogen molecules. To this end, high-resolution isotherm measurements at low pressure (in the range 0-2.5 bars) have been performed. The analysis of Cole[13,14] enables us to use a region of the isotherm beyond the linear portion in order to obtain the relevant enthalpies, as summarized in Table 1.

Table 1. Differential enthalpy of adsorption at zero coverage and saturation values at 77 K for activated and metal-doped CAs.

CA Material	ΔH (kJ/mol)	H_2 (wt%)
ACA (1460 m^2/g)	6.7	3.5
ACA (1700 m^2/g)	6.5	3.6
ACA (2000 m^2/g)	6.4	4.2
ACA (2550 m^2/g)	6.4	5.0
ACA (3200 m^2/g)	6.2	5.3
Co-CA-800ºC (1050ºC)	7.5 (7.2)	2.1 (2.1)
Ni-CA-800ºC (1050ºC)	7.0 (7.1)	2.3 (2.0)

In this communication, we have presented hydrogen sorption properties of ACAs with surface areas up to 3200 m^2/g. As with values reported in the literature for activated carbons, we find a linear dependence of H_2 surface excess saturation value with the surface area. In addition, we note an increase in the H_2 excess gravimetric density for a CA that has been doped with Ni nanoparticles. The differential enthalpy of adsorption at zero coverage for the metal modified materials was measured to be >7kJ/mole, slightly higher than for unmodified aerogels. Further work will be necessary in order to decouple effects of carbonization temperature from that of the metal dopants in establishing the mechanism of enhanced sorption in metal-modified aerogels. Given the flexibility of CA synthesis, and the ability to control surface area, pore volume, and substituent/dopant levels, CAs offer engineering viability for hydrogen sorption applications where both gravimetric and volumetric density are important parameters.

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SUPPORTING INFORMATION. Figure 1S: adsorption isotherms at 77 K for the Ni- and Co-modified carbon aerogels.

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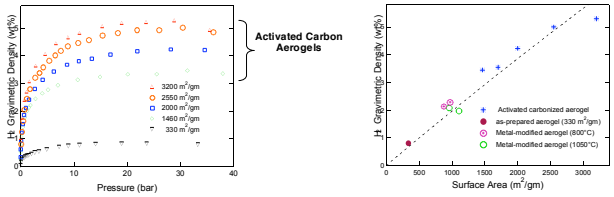

ABSTRACT FOR WEB PUBLICATION (Word Style “BD_Abstract”). Authors are required to submit a concise, self-contained, one-paragraph abstract for Web publication.

We report the hydrogen surface excess sorption saturation value of 5.3 wt% at 30 bar pressure at 77 K, from an activated carbon aerogel with a surface area of 3200 m^2/g as measured by Brunauer-Emmett-Teller (BET) analysis. This sorption value is one of the highest we have measured in a material of this type, comparable to values obtained in high surface area activated carbons. We also report, for the first time, the surface area dependence of hydrogen surface excess sorption isotherms of carbon aerogels at 77 K. Activated carbon aerogels with surface areas ranging from 1460 to 3200 m^2/g are evaluated and we find a linear dependence of the saturation of the gravimetric density with BET surface area for carbon aerogels up to 2550 m^2/g, in agreement with data from other types of carbons reported in the literature. Our measurements show these materials to have a differential enthalpy of adsorption at zero coverage of ~5 to 7 kJ/mole. We also show that the introduction of metal nanoparticles of nickel improves the sorption capacity while cobalt additions have no effect.