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Journal of Alloys and Compounds 446–447 (2007) 380–384

Journal of ALLOYS AND COMPOUNDS

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Comparison of hydrogen adsorption on nanoporous materials

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Received 1 November 2006; received in revised form 28 November 2006; accepted 29 November 2006
Available online 2 January 2007

Abstract

Carbon-based microporous materials such as nanoporous activated carbons (AC), single-walled carbon nanotubes (SWNTs) and metal-organic frameworks (MOFs) have been proposed as storage materials for hydrogen. In this paper we discuss and compare various physisorption materials as storage medium for hydrogen. Promising utilizations remain limited to certain niche applications, such as bulk transportation of hydrogen. Meeting the ambitious US Department of Energy (DOE) target will require going beyond structural optimization, and qualitatively change the interactions involved in the sorption process, by investigating the effects of dopants, catalysts and substitution.
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Keywords: Hydrogen absorbing materials; Fullerenes; Thermodynamic modeling

1. Introduction

In order to develop and demonstrate viable hydrogen storage technologies, a set of gravimetric and volumetric system targets have been proposed by the US Department of Energy (DOE), based on achieving a driving range of 500 km for a hydrogen powered vehicle. The gravimetric R&D systems targets [1] are 6 wt% by 2010 and 9 wt% by 2015, whereas the volumetric targets are 1.5 kWh/l, by 2010 and 2.7 kWh/l by 2015. Current compression storage technologies fall short of the 2010 targets and there is little hope that they will meet the 2015 targets. Storage of hydrogen by physisorption on the surface of solids has been the object of intense scrutiny over the last few years. The most promising and widely investigated adsorbents are carbon-based microporous materials such as nanoporous activated carbons (AC), single-walled carbon nanotubes (SWNTs) and metal-organic frameworks (MOFs). These materials have a high specific surface that can be optimized for hydrogen storage through various physical and chemical treatments. Finding the best adsorbents for hydrogen storage basically involves optimizing three parameters. First, the characteristic binding energy of the hydrogen molecule with the material determines the operating temperature of a sorption-based storage system and its residual density in passive operation. Second, the specific surface specifies the maximum storage density (at high pressure). Third, the density of the substrate is a determining factor in the size and weight of the storage unit.

The study of porous materials for hydrogen storage involves, on the experimental side, the development of reliable sorption measurement techniques and synthesis processes. Early experiments on SWNTs and carbon nanofibers reported inconsistent results ranging from 0 to 10 wt% under comparable conditions. This spread was mainly due to sample preparation and the small mass of adsorbent available for sorption measurements, which require highly sensitive systems. These issues have now been generally addressed. Four independent measurements of the adsorbed density of hydrogen on the same IRH-3 carbon showed variations of less than 10%, within the accuracy range of the measurement systems. Theoretical studies of hydrogen sorption on porous materials aim to determine the specific nature of hydrogen–carbon interactions and to reliably predict the adsorption isotherms of hydrogen. Finally, engineering analyses seek to study the effect of key transport and equilibrium sorption parameters on performance of physisorption-based storage systems, to address cyclability and durability issues, to design optimal systems and address safety issues.

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doi:10.1016/j.jallcom.2006.11.192

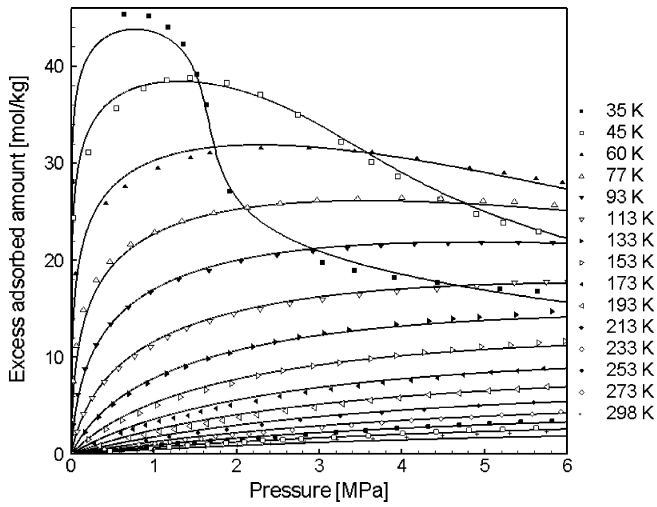

Fig. 1. Adsorption isotherms of hydrogen on AX-21 powder over the temperature and pressure ranges of interest to storage applications, obtained using a volumetric system. The points represent the experimental data, the continuous lines represent the fit to the Ono–Kondo isotherm.

2. Physisorption of hydrogen on carbon structures

Activated carbon has been successfully demonstrated as a storage medium for natural gas at ambient temperature and low pressures. For hydrogen, reasonable storage densities (about 40% that of LH_2 at 20 K) require cryogenic operation (77 K) and a carbon with a high surface area and a high bulk density. Fig. 1 shows the excess adsorption isotherms of hydrogen on activated carbon over the supercritical range (35–300 K). The carbon used in this experiment was granular AX-21, with a specific surface of 2800 m^2/g and a density of 0.3 g/cc. The isotherms are fully reversible and present no hysteresis. They also show that hydrogen adsorbed densities of practical interest to storage applications only occur at low temperatures (≅77 K). The presence in the isotherms of a maximum at high pressure and low temperatures is a typical feature of excess adsorption isotherms. It occurs when the density of the bulk gas increases faster than that of the adsorbed phase as a function of pressure. The excess adsorbed density is defined as the difference between the amount of hydrogen stored in the pores of an adsorbent at a certain temperature and pressure, and the amount that would be present under the same conditions in the absence of surface–gas interactions. The total storage density is the sum of the two parts.

The experimental data can be fitted over the temperature and pressure range of interest using a five parameter fit of a modified supercritical Dubinin isotherm [2]. This model has the advantage of being relatively simple to use for engineering applications. However, it does not have a proper low-pressure limit. The Ono–Kondo adsorption isotherm, based on self-consistent equations adapted by Aranovitch et al. to supercritical adsorption on carbon slit-pores has the advantage of having a proper Henry's law regime and of being expressed in terms of constants that have simple physical meaning [3,4]. In this approach, the coverage (or molecular fraction per adsorption site) on the ith layer $x_i = \rho_i/\rho_s$ (where ρ_s is the molar density of a completely filled adsorption layer) can be calculated from

$$\ln\left(\frac{x_i(1-x_b)}{x_b(1-x_i)}\right)+\frac{z_0E}{kT}(x_i-x_b)+\frac{z_2E}{kT}(x_{i+1}-2x_i+x_{i-1})=0$$

with

$$x_1 = x_N$$

and

$$\ln\left(\frac{x_1(1-x_b)}{x_b(1-x_1)}\right)+\frac{E}{kT}(z_1x_1+z_2x_2+z_0x_b)+\frac{E_a}{kT}=0$$

and where the excess adsorption isotherm is defined as:

$$\Gamma = A\sum_{i=1}^{N}x_i - V_b\rho_b$$

which is a slight variation of those presented in references [3,4]. The same self-consistent equations are used, but the excess adsorption is defined according to the standard definition of excess adsorption. A fit over the whole range of temperature and pressure investigated experimentally yields the following parameterization: $E_a = -3.871$ kJ/mol (adsorbate/adsorbent interaction), $E = 0.519$ kJ/mol (average intermolecular interactions inside the pores), and $\rho_s = 74.0$ mol/l (saturation density of a layer). The saturation constant A, however, has to be temperature dependent to represent the full range of the experimental data, but can be fitted to the simple function:

$$A(T) = A_0 - A_1\ \exp(-B/T)$$

with $A_0 = 30.426$ mol/l, $A_1 = 12.623$ mol/l and $B = 71.042$ K.

This approach has a well-defined low-pressure limit (Henry's law) and can yield the virial coefficients of the adsorbate–adsorbent system. It cannot, however, describe in details the porous structure of the carbon. These effects are assumed small and are incorporated into the fitting parameters of the model.

Physisorption of hydrogen on an adsorbent raises thermal management issues in the design of sorption-based systems, due to the exothermic nature of adsorption and the endothermic nature of desorption. These thermal effects can be characterized by the isosteric heat of adsorption.

The high pressure, low temperature adsorbed density of hydrogen on activated carbon and nanostructures generally correlates linearly with the pore volume or the specific surface of the adsorbent [5]. The adsorption isotherms of hydrogen on activated carbons with similar pore structure can thus be modeled using the isotherm described above provided that it is multiplied by the ratio of the specific surface of the adsorbent to the specific surface of AX-21.

A study of micropore filling of activated carbons shows that at these temperatures, the density of hydrogen in the pore approaches that of liquid hydrogen [5]. Further increasing the storage density of hydrogen by physisorption would entail storing hydrogen in the porous structures at densities beyond that of liquid hydrogen. Experimental results suggest that little improvement in the storage capacity can be expected using pure activated carbons. Simulated adsorption isotherms of hydrogen

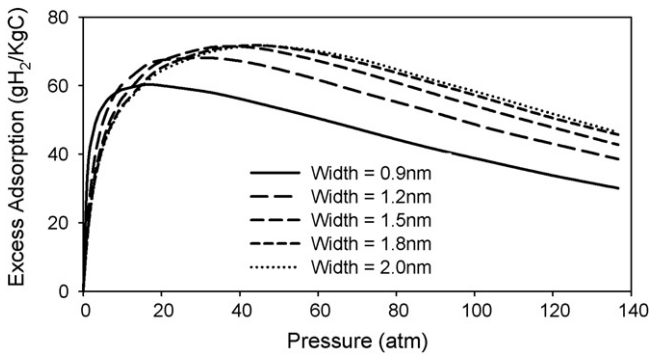

Fig. 2. Hydrogen adsorption isotherms on carbon slit pore at 77 K as a function of spacing between graphene layers, obtained using Grand Canonical Simulations. The excess adsorption is defined in this context as the difference between the number of hydrogen molecules in the simulation cell in the presence of the adsorbent and without the adsorbent.

on slit pores show that a maximum of about 8 wt% excess hydrogen at 77 K and 40 bars (Fig. 2). Larger values could be obtained at the cost of lowering the operating temperature of the storage system (see Fig. 1).

Although activated carbon can store important amounts of hydrogen at 77 K, the thermal management issues associated with the operation of a cryogenic storage system has prompted work on other carbon structures that could adsorb hydrogen in significant quantity at higher temperatures. Carbon nanofibers appeared promising initially but detailed reproducible studies of adsorption of hydrogen on various carbon nanofibers showed that from 0.1 to 105 bars and 77 to 295 K, the maximum excess adsorbed density obtained was 0.7 wt% at 105 bars [6–8]. Due to their narrow pores, SWNTs have also been proposed as adsorbents for hydrogen. Their cylindrical geometry can lead to favorable internal sorption sites. A calculation using a cylindrical Lennard–Jones potential show that the potential well inside a SWNT could be as deep as 12.3 kJ/mol, compared to 3–5 kJ/mol for activated carbons. When bundled, their interstitial sites can be even more favourable, but the very small pore volume associated with these sites makes their overall contribution small. Moreover, they are difficult to access because of the small size of the pores. The adsorption isotherms of hydrogen on SWNTs are type 1 reversible isotherms similar to activated carbon. Under ambient conditions, the amount of hydrogen adsorbed in SWNTs appears to be small (<1 wt%) [9] whereas at 77 K and 1 atmosphere, values ranging from 1 to 2.5 wt% have been reported depending on sample preparation [10–13]. At higher pressures, values of 6 wt% at 77 K and 2 atm [14] and of 8 wt% at 40 atm and 80 K have been obtained [15]. An average adsorption enthalpy of 4.3 to 4.5 kJ/mol has been reported, typical of carbon adsorbents.

Table 1 shows the effect of acid treatment and consecutive exposures to heat of SWNTs on the hydrogen intake (at 77 K and 1 bar) and on the specific surface. The maximum excess adsorbed density (4.6 wt%) was obtained after treatment with HF and heat at 600 °C, corresponding to the highest specific surface obtained [16]. Table 1 shows that the adsorption properties are very sensitive to sample activation and that the structural parameters of SWNTs can be controlled to optimize sorption properties. A more detailed discussion of these results can be found in reference [16].

There are little indications that substantial improvement of the adsorbed density can be expected. Grand Canonical Monte Carlo simulations of hydrogen sorption on SWNTs bundles (using standard Lennard-Jones interactions) show that for a hexagonal arrangement, a maximum of about 3 wt% can be achieved at 77 K and 1 bar for nanotube diameters ranging from 12 to 14 Å, with a spacing of 6 Å between the walls of adjacent tubes [17]. The excess density is defined in the simulations as the difference between the number of hydrogen molecules in the simulation volume in the presence of the adsorbent and in its absence at a given pressure and temperature. The volume of the adsorbent is not excluded. The simulation values are thus, lower by an additive factor equal to the density of the bulk gas divided by the density of the adsorbent. A simulation value of 3 wt% would thus, correspond to about 4–5 wt% if the volume of the adsorbent is excluded. The maximum value that can be expected is about 6 wt% at 40 bars [17]. Quantum effects can only lower this value [18].

Other carbon structures have recently been proposed for hydrogen adsorption. High surface area carbide derived carbons, obtained from thermo-chemical etching of titanium carbide, exhibit a hydrogen storage capacity of 3 wt% at 77 K and 1 atmosphere. These structures are basically a disordered arrangement of bent graphene layers with a narrow size distribution [19].

MOFs are nanostructures of transition metals bridged by carbon ligands that have recently been proposed as sorbents for hydrogen storage. The main interest in these materials lie in their very large specific surfaces (1000–6000 m^2/g) [20] and the fact that they may be customized to specific storage applications by varying ligands, transition metals and doping them with metals. Experiments show that at room temperature (295 K), reversible hydrogen uptakes of less than 1 wt% have been obtained [13,21]. At 77 K, maximum excess adsorption densities of 2–7.3 wt% at 50–80 bars have been obtained [21,22].

Table 1
Effect of sample preparation on the excess storage density of hydrogen on SWNTs at 77 K and 1 bar and on the specific surface of the adsorbent

Acid	Acid treated		First heat treatment (600 °C)		Second heat treatment (800 °C)	
	S_{spec} (m^2/g)	H_2 (ads wt%)	S_{spec} (m^2/g)	H_2 (ads wt%)	S_{spec} (m^2/g)	H_2 (ads wt%)
HF	635	1.07	1555	4.6	806	1.73
HCl	878	1.55	1047	3.15	829	2.11
H_2SO_4	690	1.93	1084	1.38	430	1.12
HNO_3	40	1.04	375	0.98	193	1.22

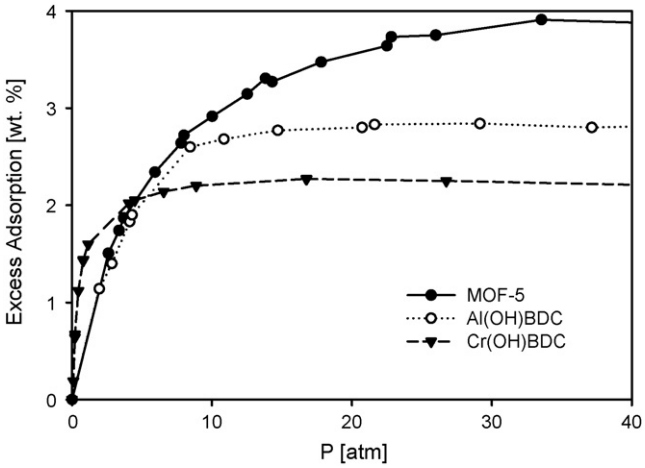

Fig. 3. From top to bottom: hydrogen uptake on MOF5, MIL-53 (Al) and MIL-53 (Cr). The BET specific surfaces are 3560, 1800 and 950 m^2/g, respectively.

The adsorption enthalpy for activated carbon, SWNTs and MOFs obtained using a Dubinin analysis differs in the low coverage region. The enthalpy of adsorption is largest for SWNTs and smallest for MOFs, suggesting stronger adsorbent–adsorbate interactions for SWNTs. At high coverage the values converge, and the enthalpies remain below 5 kJ/mol, which is consistent with physisorption [13]. For both activated carbons and MOFs, the specific surface and the maximum gravimetric excess adsorbed densities correlate linearly. A grand canonical Monte Carlo study of hydrogen adsorption on graphitic fragments shows a linear correlation between adsorbed density and specific surface at 35 bars and 77 K [17]. These simulations also show that the low-pressure gravimetric uptake of hydrogen increases with the density of the carbon nanostructure, due to narrower pores and increased surface–hydrogen interactions, whereas at high pressure, where the specific surface available for adsorption becomes the determining factor, the trend is reversed. This behavior, observed in carbon nanostructures when hydrogen adsorption isotherms on SWNTs and activated carbon are compared, was also recently observed in hydrogen sorption experiments on MOFs and related structures (Fig. 3) [21,23].

The excess density of hydrogen stored on carbon and MOF nanostructures has been limited so far to about 6–7.5 wt% at 77 K and 30–40 bars. Enhancing the storage capacity of carbon nanostructures will require fundamentally altering the sorption process. This could be achieved by doping them with certain metals [24]. Calculations predict room temperature reversible storage densities of 1.7 wt% for hydrogen on $C_{54}Be$, and of 7–8 wt% on titanium-doped SWNTs under ambient conditions [25,26]. However, recent calculations show that titanium will agglomerate on the surface of carbon nanostructures, leading to a significantly lower value than initially predicted (about 2 wt%) [27]. These effects have not yet been observed experimentally. Spillover has also been proposed as a mechanism to enhance the storage density of carbon-based and MOF nanostructures. This approach relies on the use of a metallic catalyst to dissociate molecular hydrogen, using surface diffusion through a bridge to store atomic hydrogen in a receptor. This approach has been realized experimentally. An increase of a factor of 2.9 for the activated carbon AX-21 and 1.6 for SWNTs at 298 K and 1 bar was obtained using a Pd/carbon catalyst [28].

3. Conclusion

Physisorption of hydrogen on undoped carbon nanostructures and metal organic frameworks is a fully reversible and cyclable storage option for hydrogen that has the advantage of fast kinetics and low storage pressure. However, it is strongly temperature-dependent and requires cryogenic operation to obtain storage densities of interest to hydrogen energy applications. Current nanocarbon adsorbents fall short of the DOE targets for the use of hydrogen as a transportation fuel. Promising utilizations remain limited to certain niche applications, such as bulk transportation of hydrogen. Carbon nanostructures can be optimized for storage applications through structural optimization. However meeting the ambitious DOE targets will require qualitatively changing the nature of the interactions by doping metals, although this remains to be demonstrated experimentally.

Acknowledgements

We wish to thank NSERC, Natural Resources Canada, the Auto 21 Network of Centres of Excellence and Hydrogenics for their support.

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