

## **A study of the optimum temperature for hydrogen storage on Carbon Nanostructures**

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The energy of intermolecular interaction is used to probe into the optimum temperature for hydrogen storage by adsorption on carbon nanostructures. Thermodynamic analysis is undertaken based on the lattice theory to the adsorption data of hydrogen on Multi-walled Carbon Nanotubes (MWCNTs) over a temperature range of 123-310 K and pressure up to 12.5 MPa. Results show that the hydrogen-hydrogen interaction energy captures characteristics of physical adsorptions of supercritical gases; almost linearly increases with increases of adsorption temperatures and surface loadings. However, the result cannot reveal much information about the optimum temperature for hydrogen storage in the MWCNTs.

### INTRODUCTION

Recently a great number of reports of molecular hydrogen on a novel class of graphitic materials, carbon nanostructures, which include Carbon Nanofibers, Single-walled Carbon Nanotubes (SWCNTs) and Multi-walled Carbon Nanotubes (MWCNTs), have attracted a lot of attention by media and the automotive industry [1]. However, from the presented literatures, progresses achieved seem not so great as supposed to be, there still have such unclear points as the maximum adsorption capacity and the interaction mechanism of hydrogen molecules on these carbon nanostructures [2].

The work reported here is to study the temperature dependent state of hydrogen molecules on MWCNTs at a temperature range from 123-310 K. It was undertaken for several reasons. Firstly, as mentioned above [1-2], most of the hydrogen adsorption data in recent literatures needs reasonably theoretical explanations [3]. The second stimulus for us to do this work is still lack of hydrogen adsorption data on carbon nanostructures in continuous variations of temperature and pressure over a wide range. Thirdly, systematic analyses, which include the hydrogen-hydrogen interaction energy and the hydrogen-carbon interaction potential as well as the isosteric heat of adsorption, may much cogently evaluate the adsorption capacity of the adsorbent and clarify the state of adsorbed hydrogen molecules. Besides these, the research is also beneficial to locating the optimum storage temperature for hydrogen on the carbon nanostructure [3].

### EXPERIMENT

Isotherms of excess adsorption amount of hydrogen on the MWCNTs were volumetrically measured in

our lab, resulted isotherms are shown in Fig. 1; the pore size distribution (PSD) function  $f(r)$  of the MWCNTs determined by the adsorption isotherm of  $N_2$  on the MWCNTs at 77 K is shown in Fig. 2. The detailed information about the experiment can be referred to [3].

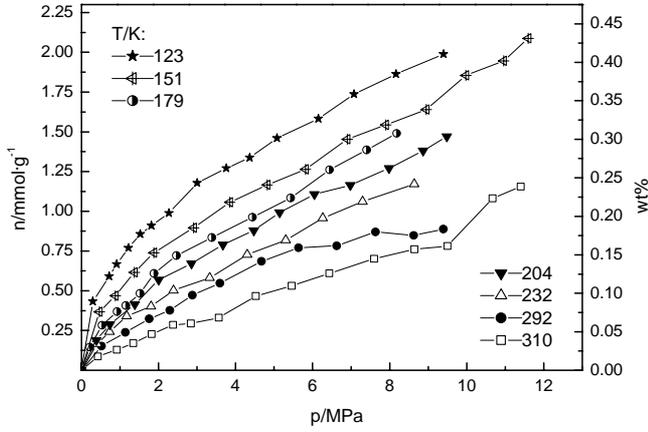


Figure 1 Isotherms of excess amount of hydrogen adsorption on the MWCNTs

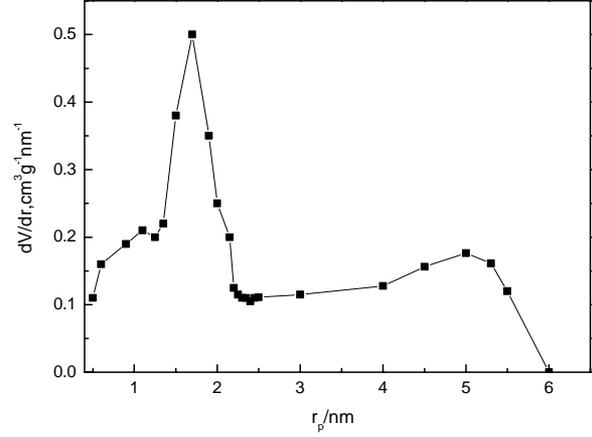


Figure 2 PSD of the MWCNTs determined by the analysis of nitrogen adsorption isotherm at 77 K

## ADSORPTION EQUILIBRIUM OF HYDROGEN ON MWCNTS

### Determination of the monolayer coverage

Based on the lattice theory [4], as discussed in the paper [5], if the adsorbate-adsorbate interaction energy and the adsorbate-adsorbent interaction potential are included and calculated by the Lennard-Jones potential function, one can get an approximate adsorption model as

$$kT \ln \frac{(\alpha_i/\alpha_m)(1-x_b)}{(1-\alpha_i/\alpha_m)x_b} + \Delta u(i) = 0, \quad \Delta u(i) = \varepsilon_{sf}(i) + \phi(i), \quad x_b = \alpha/\alpha_m, \quad x_i = \alpha_i/\alpha_m. \quad (1)$$

Here  $k$  is Boltzmann's constant;  $T$  the absolute temperature;  $\alpha$ ,  $\alpha_i$ ,  $\alpha_m$  respectively the number of adsorbate molecules per unit surface area in the bulk gas phase,  $i$ th adsorption layer and the maximum adsorption capacity state;  $\varepsilon_{sf}(i)$  and  $\phi(i)$  respectively the interaction potential from the adsorption wall and the molecular interaction to an adsorbed molecule in  $i$ th adsorption layer. From Eq. (1), one can obtain the excess amount of adsorbate molecules per unit surface area  $\Gamma_1$  in the first adsorption as [3]

$$\Gamma_1 = C \frac{x_b(1-x_b)\{1-\exp[\Delta u(1)/kT]\}}{x_b + (1-x_b)\exp[\Delta u(1)/kT]}. \quad (2)$$

Here  $\Delta u(1)$  is the change of the internal energy of adsorbate molecules in the first adsorption layer;  $C$  the correlating parameter. We can further get the following expression from Eq. (2)

$$\frac{\alpha}{\Gamma_1} = \frac{\alpha_m}{C\{1 - \exp[\Delta u(1)/kT]\}} \times \frac{\alpha}{\alpha_m - \alpha} + \frac{\alpha_m \times \exp[\Delta u(1)/kT]}{C\{1 - \exp[\Delta u(1)/kT]\}}. \quad (3)$$

Due to the prominent monolayer adsorption of supercritical hydrogen, under our experimental conditions,  $\alpha_m$  can be considered temperature dependent constants, a series of points  $\left( \frac{\alpha_{(j)}}{\alpha_m - \alpha_{(j)}}, \frac{\alpha_{(j)}}{\Gamma_{(j)}} \right)$  from the same measured isotherm will be in linear relationship [3]. Thereby, by the optimization, we obtain  $\alpha_m$  and the correlating parameter  $C$  (see Table 1). In Table 1, it shows that  $\alpha_m$  decreases with the temperature increasing and the value is smaller than that of liquid hydrogen upon the surface of the MWCNTs ( $26.864 \text{ nm}^{-2}$ ) [3], adsorbed hydrogen molecules are therefore likely in a compressed gas state.

Table 1 Determined values of hydrogen adsorption on MWCNTs

$T[\text{K}]$	$B_{2s} [\text{m}^3/\text{g}]$	$q_{st}^0 [\text{J/mol}]$	$\alpha_m [\text{nm}^{-2}]$	$C[\text{nm}^{-2}]$
123	8.245E-7	2135.932	14.233	9.944
151	6.223E-7	2368.724	13.269	9.262
179	6.559E-7	2601.516	12.429	8.853
204	5.587E-7	2809.366	11.851	8.276
232	5.987E-7	3042.158	11.338	7.872
292	4.789E-7	3540.998	10.655	6.434
310	3.486E-7	3690.650	10.457	5.661

#### Determination of the interaction potential of hydrogen-MWCNTs

We firstly used adsorption data in very low surface concentration region and got the second virial adsorption coefficient  $B_{2s}$  (Table 1). Then, by plotting the  $\ln(B_{2s}/\sigma_{ff} S_{BET})$  versus  $1/T$  ( $\sigma_{ff}$  and  $S_{BET}$  are respectively the collision diameter of a hydrogen molecule and the specific surface area of the MWCNTs) [3], we got the interaction potential  $\varepsilon_{sf}(r) = -505.86 \text{ K} \cdot k$  and the isosteric heat of adsorption in low limit surface concentration  $q_{st}^0$  (Table 1). From Table 1, we can find that  $q_{st}^0$  are smaller than  $5596.68 \text{ J/mol}$  of hydrogen on the graphitized carbon black [6].

#### Determination of the interaction energy of hydrogen-hydrogen

By algebraic manipulations and introducing the common expression presented by Do [7], we obtained following expressions from Eq. (3) for calculating the hydrogen-hydrogen interaction energy  $u$  in the first adsorption layer

$$\phi(1) = -\Delta u(1) - \varepsilon_{sf}(1) = kT \ln \frac{C \times \alpha \times (\alpha_m - \alpha) - \Gamma \times \alpha \times \alpha_m}{(\Gamma \times \alpha_m + C \times \alpha)(\alpha_m - \alpha)} - \varepsilon_{sf}(r), \quad (4)$$

$$u = -\phi(1) \cdot \frac{M}{n^2 N}, \quad \alpha_m = M, \quad n = \frac{\alpha_m}{\alpha_1}. \quad (5)$$

Here  $M$  is the number of independent active sites upon the adsorbent surface;  $n$  the number of active sites occupied by an adsorbed molecule [7]. Results calculated by Eqs. (4)-(5) are shown in Figs. 3-4.

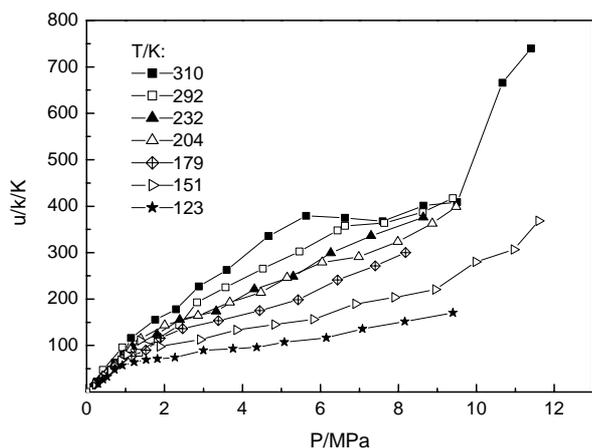


Figure 3 Variation of the hydrogen-hydrogen interaction energy with adsorption pressures at different temperatures on the MWCNTs

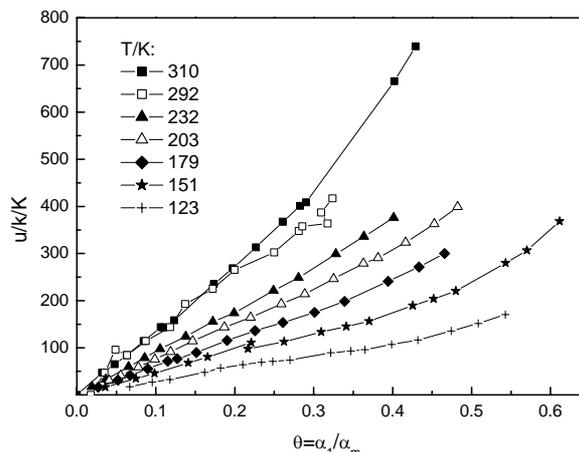


Figure 4 Temperature dependence of the hydrogen-hydrogen interaction energy at different surface loading on the MWCNTs

## CONCLUSIONS

Adsorbed hydrogen molecules on the MWCNTs are likely in a compressed gas state. The isosteric heat of hydrogen adsorption in low limit of the surface concentration on the MWCNTs is smaller than that on the graphitized carbon black. The hydrogen-hydrogen interaction energy shows characteristics of physical adsorptions of supercritical gases, the optimum adsorption temperature has not been revealed by the determined results and should still be in researching.

## ACKNOWLEDGEMENTS

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