Hydrogen interaction with carbon nanostructures: current situation and future prospects☆

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Abstract

Recent research on hydrogen in various carbon nanostructures is reviewed. Based on these research activities, we focus on a defect mediated hydrogen sorption in carbon nanostructures. Mechanically prepared nanostructured graphite has been reported to exhibit a specific interaction with hydrogen, probably due to the partial formation of the defect mediated hydrogen sorption. Current situations and future prospects of carbon nanostructures providing hydrogen storage functions are critically, but still positively, described in this paper.
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1. Introduction

Hydrogen trapping states on/in carbon-related materials [1] originate either from van der Waals interaction (physisorption, binding energy with ~0.1 eV), or from covalent C–H interaction (chemisorption, binding energy more than 2–3 eV). The recent research activities on hydrogen storage functions mainly focus on the physisorbed state on curved graphene sheets with an increased van der Waals interaction around liquid nitrogen temperature, compared to that on flat graphene sheets [2]. On the other hand, the chemisorbed state of dissociated hydrogen is not regarded suitable for hydrogen storage functions due to its high stability.

An intermediate binding energy between the physi- and chemisorption would exhibit suitable hydrogen storage functions [1]. This intermediate state, denoted here as 'defect mediated hydrogen sorption', has not been experimentally clarified yet, but some of the theoretical

reports have just recently mentioned *reduced* C–H binding energies that originate from the reconstruction and/or defect-formation in graphite [3,4].

In this review paper, we first briefly summarize the conventional physi- and chemisorbed states of hydrogen in various carbon nanostructures both from theoretical and experimental approaches, and then propose the possibility of the defect mediated hydrogen sorption in carbon nanostructures.

2. Physisorption state of molecular hydrogen

2.1. Theoretical approaches

Recent research activities regarding physisorption mainly focus on curved graphene sheets, especially on carbon nanotubes with round-shaped sheets. For example, the physisorption potential was estimated by Stan and Cole [2] to be about 0.09 eV for hydrogen inside the zigzag (13,0) single-wall carbon nanotube (SWNT) with a diameter of 1.018 nm at 50 K. This potential was more than 50% higher than the flat graphene sheets, but the ratio of physisorbed hydrogen in the SWNT to that on the flat graphene sheets was reduced drastically with increasing

temperature, i.e. 10 000 at 50 K, and 100 at 77 K. Rzepka et al. [5] reported that the hydrogen amounts for both a slit pore and a tubular geometry depended on the surface area, and that the maximum hydrogen amount was 0.7 mass% (P_{H2}=6 MPa, T=300 K). The hydrogen amount in the finite-diameter SWNT was calculated by Williams and Eklund [6] to increase with decreasing temperature from 1.4 mass% (P_{H2}=10 MPa, T=300 K) to 9.6 mass% (P_{H2}=10 MPa, T=77 K).

2.2. Experimental approaches

The hydrogen physisorption isotherm (T=80 K) on the purified SWNT (285 m^2 g^{-1} in BET surface area) was determined by Ye et al. [7]. The hydrogen amounts were 0.3 mass% for the SWNT and 2.3 mass% for the high surface area (1600 m^2 g^{-1}) saran-carbon (P_{H2}=0.32 MPa, T=80 K). At higher hydrogen pressures (P_{H2}=7 MPa, T=80 K), the hydrogen to carbon ratio for the SWNT reached 7.7 mass% (CH$_1$) in the initial absorption. A large variety of carbon samples, ranging from 100 up to 3300 m^2 g^{-1}, was investigated by Ströbel et al. [8]. Also Nijkamp et al. [9] reported that the hydrogen amount correlates well with the surface area of the samples. It is remarkable that the measurements in gas-phase reactions at 77 K exhibit the same quantities as those in electrochemical reactions at room temperature [10–13].

3. Chemisorption state of dissociated hydrogen

3.1. Theoretical approaches

The calculations by Lee and Lee on the hydrogen amount in the (5,5) SWNT at 0 K [14], indicated that there were two energetically favored chemisorption states with 7.7 mass%; firstly the arch-type with chemisorbed hydrogen outside the tube (binding energy with 2.65 eV), and secondly the zigzag-type with chemisorbed hydrogen alternatively outside and inside the tube (3.21 eV). The carbon atoms were radially reconstructed in the latter case, and this reconstruction might lead to the sp^3-like C–H coordination. (Reconstruction assisted hydrogen chemisorption was also reported by Jeloaica and Sidis [3] for the surface of graphite, at which hydrogen is exclusively trapped on top of a carbon atom.) The calculations by Tada et al. [15] indicated that the chemisorbed hydrogen was stable outside the nanotube, but not stable inside the tube, also that the C–H binding energy increased with decreasing tube diameter, due to the partial formation of sp^3-like C–H coordination.

3.2. Experimental approaches

There are some experimental reports about chemisorbed hydrogen in carbon nanostructures. The chemisorption processes in some graphite intercalation compounds (GICs) were systematically reviewed by Enoki et al. [16]. The alkali-metal–GICs, like C$_8$K with 'stage-1 structure', react with hydrogen above room temperature, and then dissociated hydrogen atoms enter the inlayer space between the alkali-metals to form triple atomic layer sandwiches, for example K$^+$–H$^-$–K$^+$. The maximum hydrogen amount was 0.5 mass% (C$_8$KH$_{0.67}$) at ambient pressure, and the hydrogen storage function was reported to be reversible.

The chemisorption processes were also reported in fullerenes. Brosha et al. [17] synthesized C$_{60}$H$_{18.7}$ (2.5 mass%) by means of direct reaction of fullerenes with hydrogen gas. This hydride was found to be stable up to 700 K, and they claimed that the hydrogen storage functions were not reversible due to transformations from the fullerenes into graphite-like species at elevated temperatures. Loutfy and Wexler [18] also reported on C$_{60}$H$_{46.8}$ (6.1 mass%) synthesized by gas-phase hydrogenation (P_{H2}=3 MPa, T=720 K).

4. Possibility of 'defect mediated hydrogen sorption'

The hydrogen desorption properties of the pre-treated SWNT reported by Dillon et al. [19–21] strongly indicated that there was non-physisorbed hydrogen desorbing around 600 K, though part of the hydrogen clearly comes not from carbon nanostructures but from metallic impurities contaminated during sonication, as was reported by Hirscher et al. [22,23]. Some controversial results on the origins of the hydrogen desorption properties of the pre-treated SWNT have been recently discussed by Zandonella [24].

Dillon et al. [21] claimed that desorbed hydrogen around 600 K was an intermediate state between physi- and chemisorption. The point for producing the non-physisorbed hydrogen in carbon nanostructures would be, we believe, the formation of defective structures [1]. The pre-treatment prior to hydrogenation seems not only to open the cap of the nanotubes but also to increase the number of defects like carbon dangling bonds, even in side-walls of the nanotubes [25]. (Besides the nanotubes, graphite nanofibers [26,27], i.e. stacking of small platelet graphite, have a large number of defects at the geometrical edge area of platelets.)

5. Hydrogen in the mechanically prepared nanostructured graphite

The hydrogen amount in mechanically prepared nanostructured graphite reaches up to 7.4 mass% [28,29], as shown in Fig. 1. Also, two desorption peaks of deuterium, starting at about 600 and 950 K, respectively, were observed from the deuterided nanostructured graphite (Fig. 2) [30]. The radial distribution function, RDF(r) spectrum,
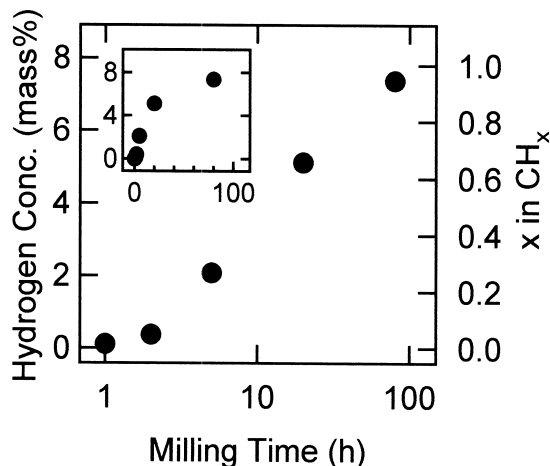
Fig. 1. Total hydrogen concentration in the mechanically prepared nanostructured graphite, as a function of milling time under an initial hydrogen pressure of 1.0 MPa at room temperature [28,29]. The inset shows the linear time scale.

clearly indicated that there were two types of C–D coordinations with the C–D distances about 0.11 (0.22) nm and 0.18 nm, respectively (Fig. 3) [28,31,32]. The former coordination with higher binding energy corresponds well to the conventional covalent C–D (or C–H) interaction, while the latter one with lower binding energy might indicate the formation of the defect mediated hydrogen sorption in carbon nanostructures [30,33]. Two types of hydrogen coordinations and their diffusion processes are also observed in the proton NMR spectra [34].

Cracknell [35] proposed a weak chemical potential for the C–H interaction on graphite, and estimated the hydrogen amount to be nearly 6 mass% ($P_{H2}=1$ MPa, $T=298$ K). This value agrees quite well with the experimental results in mechanically prepared nanostructured graphite [30].
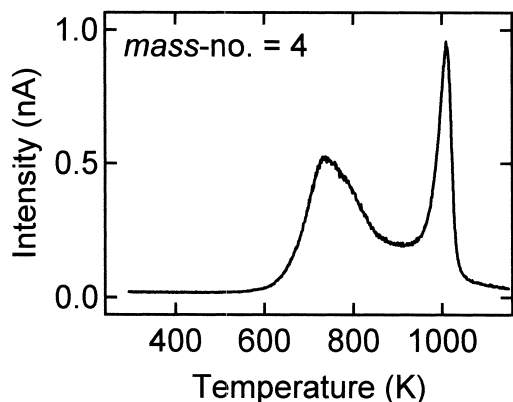

Fig. 2. Thermal desorption mass-spectroscopy of the mechanically prepared nanostructured graphite $CD_{\sim 0.9}$ [30]. The sample was first mechanically milled under an initial deuterium pressure of 1 MPa for 80 h, and then heated under purified argon atmosphere with heating rate of 10 K min^{-1}.
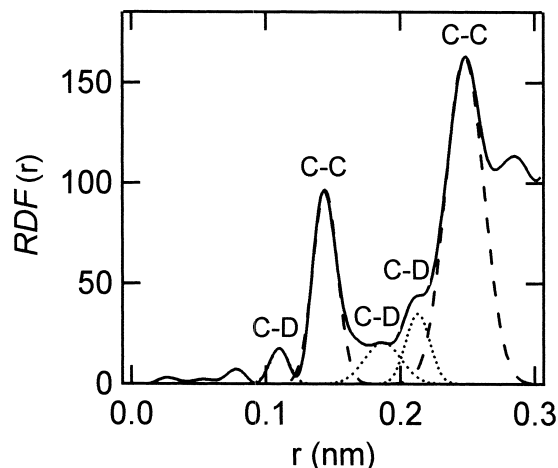

Fig. 3. Radial distribution function, RDF(r) spectrum, of the mechanically prepared nanostructured graphite $CD_{\sim 0.3}$ [28,31,32]. Two kinds of C–C coordination drawn with dashed line correspond to the first- (ca. 0.14 nm) and second-nearest (ca. 0.25 nm) neighbors in the graphite *in*-layer. The C–D coordinations are discussed in the text.

6. Concluding remarks

Judging from the experimental reports, the amount of physisorbed hydrogen is proportional to the BET surface area even for the carbon nanostructures. The value was estimated to be 1.5 mass%/1000 m^2 g^{-1}. Together with the maximum surface area of the nanotube (1315 m^2 g^{-1}), the maximum amount is estimated to be ~2 mass% at room temperature. The intermediate state between physi- and chemisorption, that is, 'defect mediated hydrogen sorption', would surely be important for hydrogen storage functions of carbon nanostructures.

Acknowledgements

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