Hydrogen States in the Graphite Ball-milled under Hydrogen Atmosphere

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It is reported that nanostructured graphite, ball-milled under hydrogen atmosphere, desorbs 7.4mass% of hydrogen gas (H_2) during the temperature programmed desorption (TPD). Two remarkable peaks are observed in TPD spectrum at around 750K (peak1) and around 1000K (peak2). The mechanism how such a significant amount of hydrogen is contained in graphite is not known. We have observed that iron particles, which are introduced as impurity during ball-milling, played a significant role in the formation of hydrogenated graphite. The feature of hydrogen desorption at peak2 is similar to that of iron phthalocyanine. Key words: graphite, ball mill, hydrogen, temperature programmed desorption

1. INTRODUCTION

Much attention has recently been directed towards the carbon-related materials for hydrogen storage so as to realize the society mediated by hydrogen since some astonishing results were reported. According to Dillon et al., certain single wall nanotubes absorbs and desorbs 5~10 wt.% of hydrogen gas at ambient temperature and moderate pressure[1]. Chambers et al. claimed that carbon nanofibers retains 67 wt.% of hydrogen at room temperature and 12 atm in 1998 [2]. Contrary to these amazing results, however, several negative results are also reported [3]-[5]. Meanwhile Orimo et al. reported that graphite, ball-milled for 80 hours under hydrogen atmosphere, contained 7.4 wt.% of hydrogen which amounts be atomic to ration C:H=1:0.95[6]-[9]. By means of temperature programmed desorption (TPD), thus ball-milled graphite desorbs contained hydrogen with showing two characteristic desorption peaks at around 750 K and 1000 K. Generally, C-H covalent bond cleaves at much higher temperatures. How such a significant amount of hydrogen desorbs from milled graphite at such as 750 K is not yet clear. Recently, it has been pointed out that metal impurities, which were introduced into the sample by wearing out of mortar walls during the milling, might be playing a significant role in the hydrogenation and hydrogen desorption processes of this material[10]. Other researchers also consider that influence of the metallic impurities on hydrogenation of graphite[11].

We have two purposes in this paper. The first is to confirm the result of Orimo et al. The second is to investigate the influence of metallic impurities in the formation process of hydrogenated graphite.

2. EXPERIMENTAL

2.1. Sample preparation

We used graphite powder (99.997% purity, GoodFellow, $\sim 200 \ \mu m$) as a starting sample. About 1 g of graphite powder was subjected to the ball milling with using a planetary ball mill apparatus (Fritsch, pulverisette-6). The materials of which the mortars and balls are made are stainless steel (Fe-85.3%, Cr-12%, C-2.1%, Cu-1.65%, Si-0.3%, Mn-0.3%) and zirconia (ZrO₂-97%, CaO, MgO, Al₂O₃, Fe₂O₃, TiO₂, SiO₂-3%). Balls of 10 mm in diameter were placed in the mortar of 80 cm³ inner volume. The rotation speed was set to 400rpm. Each mortar has valves so as to evacuate the air and introduce hydrogen up to 0.6 MPa. Hydrogen gas is recharged to the mortar during the pause of ball-milling so as to supply the hydrogen gas absorbed by the material during the ball-milling. The total milling time was 80 hours through the repetition of 30-minute milling and 15-minute pause. After milling, all samples were handled under Ar atmosphere in a glove box, which is equipped with an Ar purification system, to avoid oxidation and water adsorption.

2.2. Investigation of the influence of metal particles

For some experimental runs, to see the influence of the constituent of the stainless steel mortar, steel powder (Fe/Cr18/Ni, GoodFellow, ~45 μ m) or iron powder were intentionally added into graphite during the milling in ZrO₂ mortar. We compared the thermal decomposition and hydrogen desorption of iron phthalocyanine C₃₂H₁₆FeN₈ (Fe-Pc, Kishida Chemical Co., Ltd.), which we consider as a representative of iron-containing hydrocarbon.



Fig. 1 Comparison of TPD spectra of graphite sample mechanically ground under hydrogen atmosphere in stainless steel mortar and in ZrO_2 mortar with that of crude sample.

2.3. Sample characterization

The samples were examined by means of TPD (Bel Japan Inc., TPD-43) in vacuo and X-ray powder diffractometer (XRD, Rigaku RINT 2000, Cu-K α radiation). In order to determine the amount of desorbed we calibrated the TPD with using TiH₂ (99% over purity, Kojundo Chemical Lab. Co., Ltd.). TiH₂ is one of the stable hydrides under ambient conditions and desorbs hydrogen at around 800 K.

3. RESULTS AND DISCUSSIONS

3.1. Influence of metallic impurities on hydrogenation of graphite

Results of TPD measurement of the milled sample with using mortars under hydrogen atmosphere are shown in Fig. 1. As shown in Fig. 1, the crude graphite barely desorbs hydrogen in the measured temperature range. In the case of steel mortar, two remarkable peaks that are similar to the result of Orimo et al. appears in the spectrum; these peaks are at 800 K and 1000 K, respectively. We consider that the



Fig. 2 XRD profiles of samples; (a) crude sample, (b) graphite milled in ZrO_2 mortar and (c) graphite milled in stainless steel mortar.

result obtained by Orimo et al.[6] was essentially confirmed as we observed about 3 wt.% of hydrogen desorption from this sample. TiH₂ was used to calibrate the peak area of TPD spectrum to determine the amount of desorbed hydrogen. On the other hand, when graphite powder milled in the ZrO₂ mortar, trace amount of hydrogen were detected without showing any characteristic peaks. Powder XRD profiles (Fig. 2) show that, in both cases of steel and ZrO₂ mortars, the graphite is in amorphous state as is indicated in the disappearance of graphitic [002] peak. In the case of ZrO₂ mortar the signal from ZrO₂ crystal, which must be introduced into the sample from the worn-out mortar wall during the ball milling. Interestingly, in the case of steel mortar, a tiny feature in the XRD profile at $2\theta = 40$ to 46 seems to be attributed as an iron carbide, not as metallic iron. This observation suggests that the graphite undergoes a certain chemical reaction with the walls of steel mortar during the ball milling, with consequently forming the particles of iron carbide. The above-mentioned amount of desorbed hydrogen, 3 wt.%, was calculated by subtracting the mass of contaminant as follows: The ball-milled sample was calcined at 1500 K. The amount of contaminant was calculated by assuming the entire ash residue after calcination is to be Fe_2O_3 . We found that in some cases that the percentage of thus calculated amount of contaminant reaches to several tens wt.%. To get more information about the influence of metallic impurities, we added intentionally metal impurities, steel powder and iron powder. Each metal added sample was milled in the ZrO₂ mortar. As shown in Fig. 3, two characteristic peaks in TPD are observed in case of steel powder addition. The dehydrogenation properties of graphite added metallic impurity are clearly different from crude sample. These results indicate that metallic impurity plays a role in hydrogenation of graphite during the ball milling under hydrogen atmosphere via certain chemical



Fig. 3 Comparison of milled graphite samples which include metallic impurities.

reaction. This process of hydrogenation can be seen as a reverse phenomenon of catalytic graphitization of carbon.[14]-[16] Catalytic graphitization is the process that amorphous carbon becomes well structured graphite through the catalytic reaction under the presence of metallic particulates.

The Peak2 appears at the similar temperatures for all the samples with showing a narrow peak width. This implies that the hydrogen desorbing at this temperature is situated in a single environment in the carbon matrix. The similar sharp hydrogen desorption peak at 950 K from the thermal decomposition of Fe-Pc in Fig. 3 renders us to infer that this hydrogen is bonded covalently to the dangling bond of the carbon whose cleavage is aided catalytically by the presence of iron. On the other hand, the Peak1 has a broad feature and does not appear in the case of the decomposition of Fe-Pc. We can infer that the hydrogen, desorbing at this temperature, is bonded to less stable site than to the dangling bond, and that the broadness of the peak reflects the amorphous nature of this site. Examination based on energetics is under way in our group.

References

- A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Behtune, and M. J. Heben, *Nature* 386, 377-379 (1997).
- [2] A. Chambers, C. Park, R. T. K. Baker, and N. M. Rodrigues, J. Phys. Chem. B102, 4253-4256 (1998).
- [3] R. T. Yang, Carbon, 38, 623-641 (2000).
- [4] C. C. Ahn, Y. Ye, B. V. Ratnakumar, C. Witham, R. C. Bowman, Jr. and B. Fultz, *Appl. Phys. Lett.* 73, 3378-3380 (1998).
- [5] Y. Chen, D. T. Shaw, X. D. Bai, E. G. Wang, C. Lund, W. M. Lu and D. D. Chung, *Appl. Phys. Lett.* 78, 2128-2130 (2001).
- [6] S. Orimo, G. Majer, T. Fukunaga, A. Zuttel, L. Schlapbach, and H. Fujii, *Appl. Phys. Lett.* 75, 3093-3095 (1999).
- [7] S. Orimo and T. Matsushima, H. Fujii, T. Fukunaga, and G. Majer, J. Appl. Phys. 90, 1545-1549 (2001).
- [8] G. Majer, U. Eberle, et al, *Physica B*, **328**, 81-89 (2003).
- [9] G. Majer, E. Stanik, et al., J. Alloys Compd. 356-357, 617-621 (2003); Corrigendum, *ibid.*, 377, 316 (2004).
- [10] T. Kiyobayashi, K. Komiyama, N. Takeichi, H. Tanaka, H. Senoh, H. T. Takeshita, N. Kuriyama, *Mater. Sci. Eng.*, B108, 134-137 (2004).
- [11] T. Ichikawa, S. Isobe, E. Gomibuchi, H. Fujii, D. M. Chen, *Mater. Sci. Eng.*, B108, 138-142 (2004).
- [12] H. E. Kissinger, J. Res. Natl. Bur. Std., 57, 217-221 (1956).
- [13] H. E. Kissinger, Anal. Chem., 29, 1702-1707 (1957).
- [14] M. Inagaki, Cabon 79s, 73-79 (1979).
- [15] A. Oya and S. Otani, Carbon 17, 131-137 (1979).
- [16] A. Otani, Carbon 102, 118-131 (1980).

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