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Hydrogen sorption by porous materials composed of one to three elements selected from boron, carbon and nitrogen and metal modification to enhance the sorption



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ABSTRACT

In order to develop novel hydrogen storage materials with high hydrogen capacity, layered compounds with high specific surface areas and large pore volumes, referred to as BN's, CN's and C's, were synthesized from B-, C- and/or N-containing substances through specified wet processing and optimized calcinations. Hydrogen contents at 77 K under 0.8 MPa of hydrogen increased as specific surface areas increased independently of the formulations of the samples, and almost all of them exceeded the predicted values for two dimensional condensation of hydrogen, that is, 2.34 mass% per 1000 m² g⁻¹. While modification with Pd did not increase the hydrogen capacity, Pt-modification brought about substantially higher hydrogen capacity at 77 K. Ni-modification also imparted higher hydrogen capacity to C's prepared by calcination of electrospun polyacrylonitrile fibers, but formation of mesopores on destroying micropores through excessive modification would reduce the hydrogen capacity.

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1. Introduction

Nanocarbons have been expected to be applicable as hydrogen storage media. One of the authors, N.N., published a work on single-walled carbon nanotubes, where the hydrogen capacity was about 1 mass% at room temperature and 2.5 mass% at liquid nitrogen temperature (77 K) under 100 kPa of hydrogen [1]. Since the specific surface area of the employed sample was about $500 \text{ m}^2 \text{ g}^{-1}$, it was thought that some novel materials with high specific surface area of a few thousand m² g⁻¹ were to be utilized for practical hydrogen storage, hopefully at room temperature. However, nanocarbons are now regarded as inferior to metalorganic frameworks (MOFs) in respect of hydrogen capacity both per volume and per weight, and sorption under cryogenic conditions is believed as a matter of course [2]. The superiority of MOFs was clarified on the basis of hydrogen uptake-specific surface area relation [3]. It was claimed that the hydrogen capacity at 77 K simply increased with the specific surface area independently of what the tested materials were [4]. If such a relation is generally valid, hydrogen molecules would occupy a certain area irrespectively of states of matrices. Trials to enhance the hydrogen capacity by designing novel matrices would be thus of no sense and only the

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attempts to enlarge the surface area would make sense for higher hydrogen capacity. Narrowing the range of the search for novel matrices would not inspire the development of hydrogen storage materials based on some new concepts. As a matter of fact, the independence of hydrogen capacity of sorts of materials has not yet been precisely evidenced. The first objective of the present study is thus to test the predicted independence using analogous materials comprising B, C and/or N. Another objective is concerning with the effects of metal-modification. It was pointed out that purified single-walled carbon nanotubes containing no metals did not adsorb hydrogen [5], and since then the effects of metalmodification on hydrogen sorption has been widely studied [6-10]. There would presumably exist specific metal-matrix combinations of high hydrogen capacity. The second objective is thus to search for novel metal-modification effects. Hydrogen capacity will be hereinafter discussed at 77 K, since the one at room temperature is too small (less than 0.1 mass%) to be practically applicable.

2. Experimental

Melamine diborate was prepared from melamine and boric acid in an aqueous mixture with a boric acid/melamine molar ratio of 3.0 (excessive in boric acid), was filtered and dried, and was calcined at 723 K in air for 1.8 h and at 1173 K in N₂ for 1 h to obtain BN. Both melamine and boric acid were purchased from Kanto Chemical Co., Inc. and employed without purification. The preparative method was essentially the same as described in the literature [11]. The product was already identified and reported as $B_4N_3O_2H$. This compound is referred to as BN in the present work. When Pd-modification was intended, an acetone solution of palladium





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acetate was mixed with melamine diborate so as to distribute 1 Pd atom per 1 nm² of melamine diborate. Palladium acetate was purchased from Sigma–Aldrich Co. and employed without purification.

CN's were prepared by calcination of melamine in the presence of NH₄Cl, purchased from Kanto Chemical Co., Inc., in air at 723 K for 1 h and successively at 973 K for 1 h. The mass ratio of NH₄Cl to melamine was 0.33 and the both ingredients were tightly mixed using formaldehyde, purchased from Kanto Chemical Co., Inc. Here the condition of calcination was the same as described in the literature [12]. When Pd- or Pt-modification was intended, an aqueous solution of palladium acetate or dinitrodiammineplatinum (II) was respectively mixed with melamine so as to distribute 1 metal atom per 50 nm² of predicted product. Dinitrodiammineplatinum (II) was purchased from Sigma–Aldrich Co. and employed without purification.

C's were prepared by calcination of electrospun polyacrylonitrile (PAN) fibers with diameters of 0.5–1 μm at 1073 K in Ar-10% H₂ for 2 h. Nanofiber Electrospinning Unit manufactured by Kato Tech Co. Ltd. was used with dimethylformamide solutions of PAN supplied. When Ni-modification was intended, 0.045–0.9 g of Ni (II) acetylacetonate was added to 20 mL of 5.0 mass% PAN solutions. PAN was purchased from Sigma–Aldrich Co., and dimethylformamide and Ni (II) acetylacetonate from Kanto Chemical Co., Inc.

Characterization of the prepared samples was performed by using Topcon SM-300 scanning electron microscope (SEM), Micromeritics ASAP 2010 nitrogen adsorption apparatus, Rigaku MultiFlex Cu K α X-ray diffractometer (XRD), Shimadzu FTIR-8400S Fourier transform infrared spectrometer (FT-IR) and Shimadzu ESCA-850 X-ray photoelectron spectrometer (XPS), and hydrogen sorption characteristics were assessed by a typical volumetric method at 77 K and at room temperature using Suzuki Shokan PCT-2ST hydrogen sorption apparatus.

3. Results and discussion

3.1. BN compounds

Melamine diborate was precipitated in pillar forms as shown in Fig. 1a, and calcined BN particles were also in similar appearances as shown in Fig. 1b. While the thickness of the latter was reduced to a few to several tenth of the one of the former, the specific surface area significantly increased from $0.7 \text{ m}^2 \text{ g}^{-1}$ for melamine diborate in Fig. 1a to $340 \text{ m}^2 \text{ g}^{-1}$ for BN in Fig. 1b. This suggested that the calcined BN sample had some porous structures. When melamine diborate with higher specific surface area as large as $3 \text{ m}^2 \text{ g}^{-1}$ was calcined, BN with higher specific surface area was obtained as shown in Fig. 1c. The sizes of pillars were smaller than those in Fig. 1b and the specific surface area was enlarged to 714 m² g⁻¹. The specific surface area of the BN compound was thus controllable by changing the starting specific surface area of melamine diborate. Typical XRD peaks at around $2\theta = 26.5^{\circ}$ for the (002) reflection and at around $2\theta = 43^{\circ}$ for the (10) turbostratic

reflection were similarly observed as described in the literature [11]. FT-IR bands at 800 and 1400 cm⁻¹ for BN, 1620 cm⁻¹ for NH and 3500 cm⁻¹ for OH were similarly found as illustrated in the literature.

Hydrogen sorption isotherms at 77 K showed substantially reversible nature as shown in Fig. 2. Each isotherm for the first hydriding-dehydriding cycle in Fig. 2 coincided with the one for the respective second cycle. The hydrogen contents increased as specific surface areas increased. The variation of the former with the latter is illustrated in Fig. 3, where other data points for CN's and C's are also included. Hydrogen contents of BN depicted by open circles exceeded the predicted values for two dimensional condensation of hydrogen, that is, 2.34 mass% per 1000 m² g⁻¹. Here the stripped domain phase with a density enhancing factor ρ of 1.126 [13] was assumed. If hydrogen commensurately condenses, 1 g of a sorbent with 1000 $m^2 g^{-1}$ of specific surface area would adsorb 6.35×10^{21} hydrogen molecules with 0.1575 nm² of occupying area to reach 2.08 mass% of hydrogen content. This value is enhanced to 2.34 mass% through formation of the stripped domain phase. The reason why the hydrogen concentrations of the BN compounds exceeded the predicted values has not been clarified. Existence of more crowded phases, multilayered adsorption and exotic sorption in micropores are plausible. It is to be noted that the upward deviations of the hydrogen contents were observed where hydrogen sorption was not yet saturated.

Pd-modification did not bring about higher hydrogen capacity as shown by filled circles in Fig. 3. For example, a typical Pdmodified sample of 814 m² g⁻¹ had a little bit smaller hydrogen capacity, 1.762 mass%, than a pristine sample with less specific surface area of 714 m² g⁻¹, 1.868 mass%. The SEM appearances of both the samples were similar as shown in Fig. 1c and d, and pore volumes determined by nitrogen adsorption were also similar. The micropore volume of the Pd-modified sample of 814 m² g⁻¹ was $0.38 \text{ cm}^3 \text{g}^{-1}$ as estimated by a Dubinin-Radushkevich plot, and the mesopore volume was $0.06 \text{ cm}^3 \text{ g}^{-1}$ as calculated from the step width of the hysteresis. The corresponding values for the pristine sample were 0.36 cm³ g⁻¹ and 0.07 cm³ g⁻¹, respectively. Neither the presence of Pd nor the slightly larger micropore volume enhanced hydrogen sorption. The chemical state of the loaded Pd would be metallic. The $3p_{3/2}$ binding energy as determined by XPS was 533 eV for as-prepared samples and was not altered through several hydriding-dehydriding cycles at 623 K under



Fig. 1. SEM secondary electron images of (a) melamine diborate, 0.7 m² g⁻¹, (b) BN, 340 m² g⁻¹, (c) BN, 714 m² g⁻¹ and (d) Pd-modified BN, 814 m² g⁻¹.



Fig. 2. Hydrogen sorption isotherms at 77 K for BN's with different specific surface areas.



Fig. 3. Variation of hydrogen content at 77 K under 0.8 MPa of hydrogen with specific surface area for BN, Pd-modified BN, CN, Pd- or Pt-modified CN, C and Nimodified C. The straight line denotes a predicted one assuming 2.34 mass% per $1000 \text{ m}^2 \text{ g}^{-1}$.

0.8 MPa of hydrogen and vacuum. Since the Pd-modification was adjusted to distribute 1 Pd atom per 1 nm² of melamine diborate, the final abundance of Pd would be 1 Pd atom per 60–80 nm² of the BN compound, and the mass% of Pd would be about 0.2%. This estimation is based on the fact that the yield of B₄N₃O₂H from melamine diborate was 48% and that the typical specific surface area around 600-800 m² g⁻¹ had been enhanced 180-210 fold on the calcination. For further discussions, intended variation of the Pd loading would be necessary. Since the relative ratio of the mesopore volume to the micropore volume was found to increase through intended formation of BCN compounds on calcination of melamine diborate in the presence of magnesium, respective roles of mesopores and micropores for hydrogen sorption would be separately discussed. The BCN compounds herein represent B-C-N ternary compounds with layered structures that contain 10-17 mass% of C depending on the Mg/B molar ratio of 0.3-2.0 during the calcination.

3.2. CN compounds

The C/N mass ratios of synthesized CN compounds determined by elemental analyses were around 1.4, which was much higher than the expected value, 0.64, for C_3N_4 . As a matter of fact, a C/N mass ratio of 0.64 could be reached when formaldehyde was not used for tight mixing of melamine and NH₄Cl prior to calcinations. During the search for the optimum conditions to obtain the highest specific surface area, the C/N ratio deviated to the carbon-rich side. The dependence of the specific surface area on the portion of formaldehyde was not monotonous. The expected XRD reflection for the (002) spacing of g-C₃N₄ appeared at $2\theta = 27.5-25.9^{\circ}$, and the specific surface area increased as 2θ decreased. CN stretching band was always observed by FT-IR. While the prepared CN compounds



Fig. 4. Nitrogen adsorption isotherms at 77 K for electrospun C and Ni-modified C. Open: adsorption, filled: desorption.

had micropores correspondingly to their specific surface areas, none of them had mesopores.

From reversible isotherms similar as those in Fig. 2, the data points represented by triangles in Fig. 3 were obtained. Hydrogen storage capacity at 77 K increased with specific surface area, and almost all triangles deviated to the higher hydrogen capacity side compared with the prediction line based on the two dimensional condensation of hydrogen with the stripped domain phase, but the Pd-modification did not bring about higher hydrogen capacity as shown by a filled triangle. Also in the case of Pt-modification illustrated by half filled triangles, higher hydrogen capacity was not attained compared with pristine CN's plotted by open triangles in a specific surface area range between 200 and 400 m² g⁻¹. On the other hand, significant enhancement of the hydrogen capacity was observed in a lower specific surface area range below $100 \text{ m}^2 \text{ g}^{-1}$. This would be a symptom for high activity of Pt at 77 K. The chemical states of Pd and Pt in the modified samples were not known since XPS spectra were not accurately recorded. The intended modification of 1 metal atom per 50 nm² of CN would bring about too small abundance of the metals for the XPS measurement.

3.3. Electrospun fiber derived nanocarbons

An open square in Fig. 3 corresponds to a nanocarbon sample derived from electrospun fibers and those samples modified with Ni by adding 0.045 g and 0.90 g of the Ni complex correspond to filled squares. In addition, nitrogen adsorption isotherms are shown in Fig. 4. The specific surface area of the unmodified sample was $210 \text{ m}^2 \text{ g}^{-1}$, the micropore volume $0.10 \text{ cm}^3 \text{ g}^{-1}$, and the hydrogen content 0.78 mass% at 77 K. The corresponding values for Ni-modified sample with 0.045 g of the complex were quite well as $458 \text{ m}^2 \text{ g}^{-1}$, $0.23 \text{ cm}^3 \text{ g}^{-1}$ and 1.40 mass%, but those with 0.90 g of the complex were $244 \text{ m}^2 \text{ g}^{-1}$, $0.10 \text{ cm}^3 \text{ g}^{-1}$ and 0.66 mass%, and $0.04 \text{ cm}^3 \text{ g}^{-1}$ of mesopores were formed instead. Formation of mesopores on destroying micropores through an excessive Ni-modification would somehow reduce the hydrogen capacity.

4. Conclusion

Hydrogen storage capacity at 77 K increased with specific surface area for BN's, CN's and C's, irrespectively of the elemental composition, and essentially exceeded the prediction based on the assumption of the reported two dimensional condensation of hydrogen with the stripped domain phase, that is, 2.34 mass% per $1000 \text{ m}^2 \text{ g}^{-1}$. This empirical theorem was not valid prematurely at 0.8 MPa, where saturation of hydrogen sorption was not attained, and was not to be applied to estimate the upper limit of the hydrogen capacity of high specific surface area materials. While modification with Pd did not increase the hydrogen capacity of BN's and CN's, Pt-modification brought about substantially higher hydrogen capacity for CN's particularly in the lower specific surface area region. It is unclear whether micropores favor hydrogen sorption at 77 K rather than mesopores, but formation of mesopores on destroying micropores reduced the hydrogen capacity of Ni-modified C's.

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