

HYDROGEN ADSORPTION BEHAVIORS OF POROUS GRAPHITE NANOFIBERS

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Introduction

Graphite nanofibers appear to be novel and unique catalyst supports. The ideal materials for hydrogen storage should have the following characteristics: have a high specific surface area, and also have well-developed micropores in the structures. However, as-synthesized GNFs have a relatively low specific surface area of around 200-300 m²/g, compared to other porous materials, such as activated carbons (~1000 m²/g) and activated carbon fibers (~2000 m²/g), and which is one of main reasons for the limitation of their applications.

The purpose of this work is the preparation of porous GNFs which have well-developed pore structures in order to prepare materials with high specific surface area for the high hydrogen adsorption capacity.

Experimental

As-synthesized GNFs used in this study were a straight type which have 95~98 vol.% of purity. Prior to use as-synthesized GNFs, the metal catalysts used in the synthesis and amorphous carbons were removed by two steps purification: exposing at 500°C in oxygen stream for 90 min and soaking in 5 M HNO₃ for 3 h. These purified GNFs were named virgin GNFs (VGNF). The preparation of porous GNFs was performed by a physical activation method. About 5 g of VGNF were placed in a tubular furnace. An ultra-pure N₂ gas (50 cc/min) was fed into the furnace until target activation temperature and then an ultra-pure CO₂ gas (100 cc/min) was fed for 2 h. The samples were prepared by various activation temperatures from 800 to 1050°C, and named as P800, P900, P950, P1000, and P1050. N₂ and H₂ adsorption isotherms were measured using an ASAP 2010 (Micromeritics) at 77K in order to get textural properties and hydrogen adsorption capacity of the porous GNFs, respectively.

Results and discussion

Figure 1 shows the N₂/77K adsorption isotherms of porous GNFs prepared as a function of activation temperature. All GNFs showed a rapid increase at low relative pressure, and then increased proportionally to the relative pressure. These type of isotherms indicates that porous GNFs have well-developed micro- and mesopores in the structure. For understanding pore structures in details, several methods (BET, D-R, and etc) were used, and the results were listed in Table 1.

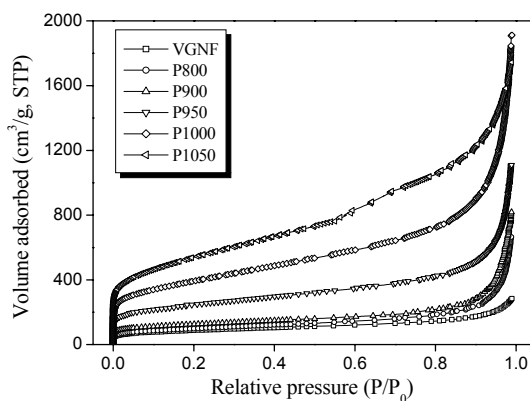


FIGURE 1: N₂/77K isotherm curves of the GNFs prepared as a function of activation temperature.

The specific surface area and total pore volume of VGNF were 317 m²/g and 0.439 cm³/g, respectively. As mentioned above, the specific surface area of commercial porous carbons is over 1000 m²/g. So, those of a VGNF are quite low, compared to those of others. In Table 1, it was found that specific surface areas of the samples increase with increasing activation temperature. As verified in Figure 1, the increase in the specific surface area became active after 950°C. Meanwhile, the P1000 sample has enough large surface area, and the P1050 sample has much higher surface area than those of commercial ones.

Meanwhile, the fraction of micropores in porous GNFs was smaller than that of the VGNF but increase proportionally to the activation temperature. It is valuable to note that the activation condition is not optimal, and that in VGNF there can be residual metal catalysts that are not removed in the purification step because those catalysts might be located in the inner area of the as-synthesized GNFs. If the amount of residue is around 10 wt% of VGNF, it can be expected that over 2500~3000 m²/g of specific surface area can be obtained under optimal activation conditions.

For evaluating hydrogen adsorption capacity of the porous GNFs, like N₂ adsorption, H₂/77K adsorption was used, and it was found that the hydrogen adsorption capacity was proportion to the specific surface area of the carbons.

TABLE 1. Textural Properties of the Porous GNFs as a Function of Activation Temperature.

	S _{BET} ^a	V _T ^b	V _{mc} ^c	V _{ms} ^d
VGNF	317	0.439	0.125	0.314
P800	353	1.029	0.131	0.898
P900	456	1.266	0.175	1.091
P950	852	1.715	0.331	1.384
P1000	1432	2.125	0.511	1.614
P1050	2011	2.697	0.725	1.972

^a Specific surface area (m²/g), ^b Total pore volume (cm³/g), ^c Micropore volume (cm³/g), ^d Mesopore volume (cm³/g)

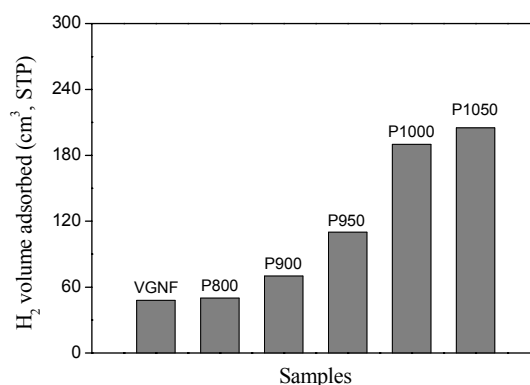


FIGURE2: H₂/77K isotherm curves of the GNFs prepared as a function of activation temperature.

Conclusions

In conclusion, the pore structure of porous GNFs is enhanced by increasing the activation temperature in a CO₂ activation process, and the specific surface area of the GNFs increases over 2000 m²/g. This indicates that the GNFs prepared in this study can be a promising material for the hydrogen storage.

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