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HYDROGEN ADSORPTION ON ULTRA-FINE METAL-CARBON COMPOSITE PARTICLES

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This is an investigation on the storage of hydrogen at 288 ~ 308 K on ultra-fine particles. We studied the pore structure by nitrogen adsorption at 77 K on thermal-treated ultra-fine particles with CO_2 and pristine ultra-fine particles.

Keywords: hydrogen; adsorption; ultra-fine particle (UFP)

INTRODUCTION

Hydrogen is receiving considerable attention because of its potential as a clean fuel for mobile and stationary purpose in the future. Storage of hydrogen as well as safe and efficient methods for its retrieval is receiving high priority in research. Various methods of storing hydrogen have been investigated [1–10], including carbon nanotubes, carbon nanofibers, metallic hydrides, and metal alloys.

Recent advances in hydrogen-storage technology with the use of carbon nanotubes, both single-walled and multi-walled, have been undertaken since Dillon *et al.* first noted that there was significant hydrogen adsorption of as-prepared soot containing a trace amount of SWNT, 0.1 ~ 0.2 wt%, at 133 K [2]. Chen *et al.* reported an unusually high rate of hydrogen adsorption on an alkali-doped carbon nanotube, 14 ~ 20 wt% [11]. Most recently, an alkali-doped carbon nanotube was found to adsorb only 2 wt% dry hydrogen at room temperature [12]. Liu *et al.* also showed a high rate of hydrogen storage in a carbon nanotube containing 50 ~ 60% SWNT,

4.2 wt%, when the SWNT was treated by acid cleaning and subsequent vacuuming at 733 K [13]. In this study, we investigate hydrogen storage at 288 ~ 308 K using ultra-fine particles. We studied the pore structure by nitrogen adsorption at 77 K on thermal-treated ultra-fine particles with CO_2 and pristine ultra-fine particles.

EXPERIMENTAL

Ultra-fine particles of Fe, Ni, and C with a diameter of 5 ~ 20 nm were prepared by carbon arc-plasma. The metal content of the preparation of ultra-fine particles is summarized in Table 1. Ultra-fine particles were stable under the atmosphere because they were surrounded with graphite sheets and amorphous carbon.

Hydrogen adsorption studies were performed using a gravimetric method in which weight changes of samples with gas adsorption were measured using a balance. In this study, a magnetic suspension balance (Mettler AT 261, resolution 10 μg) was used. The samples were heated to 573 K with a vacuum to completely remove the adsorbed gas. Hydrogen adsorption/desorption was performed at 288 K ~ 308 K from 0.01 MPa to 10 MPa.

The thermal treatment temperature was increased to 1173 K at a rate of 20°C/min and maintained for 5 and 20 minutes in a CO_2 atmosphere. The flow rate of the CO_2 was fixed at 200 ml/min^{-1}. Prior to the thermal treatment, TGA analysis of the ultra-fine particles was carried out to determine the temperature range and time. The pristine and thermal-treated samples were characterized by N_2 adsorption at 77 K.

RESULTS AND DISCUSSION

The results of hydrogen adsorption on ultra-fine particles (UFPs) at 298 K are shown in Table 1. Under 10 MPa, C-B714 attained equilibrium, but metal-carbon composite particles did not. In addition, the Ni-carbon

TABLE 1 Adsorption Data for Ultra Fine Particles

Preparation No.	Metal content [wt %]			Adsorption [mg/g^{-1}]
		in graphite	in soot	
C-B714	graphite	0.0%	0.0%	1.1
Fe-C517	Fe_2O_3-kneading	3.0%	11.0%	1.1
Ni-C704	NiO-kneading	3.2%	10.1%	1.8
Ni-C823	NiO-kneading	3.2%	6.1%	2.2

TABLE 2 Pore Structure of Different UFPs Determined by SPE Method [14–16]

Preparation No.	Total S/A ($m^2\ g^{-1}$)	Micropore S/A ($m^2\ g^{-1}$)	External S/A ($m^2\ g^{-1}$)	Average pore width (nm)
C-B714	140	20	120	5.2
C-B714-CO_2	620	340	280	1.3
Ni-C823	250	60	190	3.2
Ni-C823-CO_2	590	240	350	1.3

composite particles showed a slight difference between adsorption and desorption. However, the UFPs showed poor hydrogen adsorption.

Therefore, we investigated the thermal treatment in an oxidizing CO_2 atmosphere. The thermal treatment temperature was determined with 1173 K at a rate of 293°K/min^{-1} and maintained for 5 and 20 minutes in a CO_2 atmosphere.

From results of the adsorption isotherms of N_2 on different UFPs at 77 K, the values of the micropore and external areas were obtained for different UFP samples (Table 2). The thermal treatment with CO_2 remarkably enlarged the total surface area and the micropore surface area due to the development of the micropore structure. In addition, the thermal treatment decreased the average pore width to about 1.3 nm.

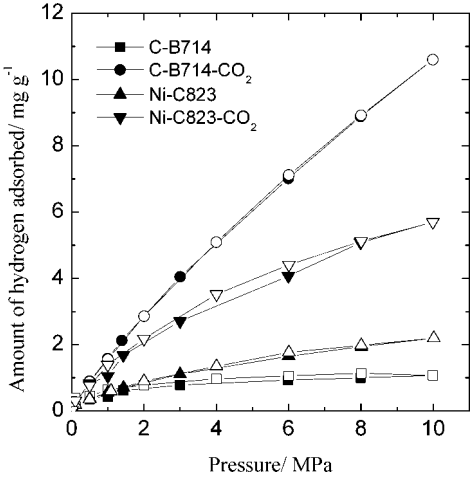

FIGURE 1 Hydrogen adsorption isotherms at 298 K on thermal-treated UFPs in CO_2. Solid symbols: Adsorption, Open symbols: Desorption.

TABLE 3 Monolayer Adsorption Capacity of Pristine and Thermal Treated UFPs

Preparation No.	Weight loss (%)	Q_m (mg g^{-1})
C-B714	–	1.2
C-B714-CO_2	29	25.9
Ni-C823	–	3.1
Ni-C823-CO_2	44	9.1

Figure 1 shows hydrogen adsorption isotherms at 298 K on thermal-treated UFPs with CO_2. Because many micropores are produced by thermal treatment in CO_2, the CO_2 treatment remarkably improves the hydrogen storage capacity of C-B714 (by about 10 times). Furthermore, there is no hysteresis on C-B714-CO_2. To obtain the monolayer adsorption capacity (Q_m), a Langmuir plot was used, and the Q_m values of pristine and thermal-treated UFPs are shown in Table 3. In the case of C-B714, the monolayer adsorption capacity of thermal-treated UFPs was about 22 times as large as that of pristine UFPs.

We investigated the properties of hydrogen adsorption with changes in temperature. Hydrogen adsorption isotherms on Ni-C823-CO_2 with changes in temperature are shown in Figure 2.

The amount of hydrogen adsorbed decreases with increasing the adsorption temperature. In addition, these isotherms show a slight difference between adsorption and desorption. Therefore, this process is a

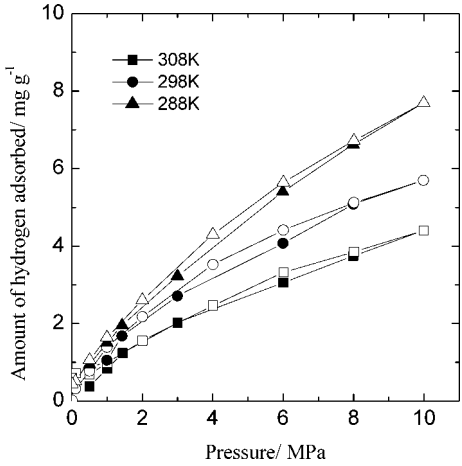

FIGURE 2 Hydrogen adsorption isotherms on Ni-C823-CO_2 with the change in temperature. Solid symbols: Adsorption, Open symbols: Desorption.

typically exothermic and reversible process. From these isotherm results, the low isosteric heat of adsorption is ($-30 \sim -19$ kJ/mole^{-1}).

CONCLUSION

In the present study of the adsorption of N_2 on thermal-treated UFPs, many micropores could be obtained. In addition, the monolayer capacity of C-B714-CO_2 was 22 times as large as that of the pristine UFPs. The adsorption of hydrogen on Ni-C823-CO_2 seemed to be a physical adsorption, considering the small difference between adsorption and desorption and the low isosteric heat of adsorption ($-30 \sim -19$ kJ/mole^{-1}). Because thermal-treated UFPs show reproducible and modestly high hydrogen adsorption at room temperature, they show promise as an effective hydrogen storage material.

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