

# Desorption property of hydrogen chemisorbed on the surface of activated carbon

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## Introduction

Hydrogen storage on carbon materials has been attracting attention recently because of the importance of hydrogen as an ideal substitute for fossil fuels. The high hydrogen-storage capacities of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) at ambient temperature have been demonstrated experimentally [1,2]. However, other reports have claimed that the maximum storage capacity of CNTs and CNFs is less than 0.7 wt% at ambient temperature and high pressure (10MPa) [3,4]. This discrepancy is believed to be due to the difficulty of evaluating the storage capacity and purity of the samples. In addition, the mechanism of hydrogen storage is not adequately understood. In a previous study, we accurately measured the hydrogen adsorption and desorption isotherms of several kinds of activated carbon fibers (ACFs), single-walled carbon nanotubes, and zeolites at 303 K by using a high-pressure adsorption apparatus [5]. Hydrogen molecules were physisorbed into micropores in the samples, but the capacity was less than 0.3 wt% at 303 K and 3.1 MPa. Rzepka et al. also reported that the physisorption alone is not sufficient to reach high capacity at ambient temperature [6].

In this study, we evaluated the hydrogen adsorption and desorption properties of modified ACF samples by means of temperature programmed desorption (TPD) measurements, and discussed the presence of hydrogen reversibly chemisorbed on the carbon surface with an intermediate binding energy larger than that of physisorption but smaller than that of a C-H covalent bond.

## Experimental

An ACF sample was oxidized with a 1M solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  at ambient temperature for 3 h. After oxidation, the sample was washed with pure water, and the oxidized ACF sample (Ox-ACF) was obtained. Two kinds of Pt-ACF samples were prepared from the Ox-ACF sample by an ion-exchange method with an aqueous  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  solution at 343 K for 4 h. The reduction treatment was carried out in a hydrogen flow at 473 K or 673 K for 1 h. After the samples were washed with pure water to remove the retained chloride, they were reduced again under the same conditions for 1 h.

The pore structures of the ACF samples were estimated from the nitrogen adsorption isotherms at 77K by using the  $\alpha_s$ -plot. The Pt content in the Pt-ACF sample was determined by X-ray fluorescence analysis. The average diameter of Pt particles was estimated from the 111 peak of the XRD profile by means of Scherrer's equation. The porosity parameters, Pt content, and average diameter of Pt particles are shown in **Table 1**.

Prior to TPD measurement, the sample was heated in an argon flow at 673 K for 0.5 h in the apparatus, and the evolved amounts of CO and CO<sub>2</sub> were analyzed with a quadrupole mass spectrometer (QMS). The flow gas was changed to deuterium, and the sample was then heated at 673 K for 0.5 h. After deuterium adsorption, the flow gas was changed back to argon, and the temperature was then maintained at 373 K for 0.5 h to remove the deuterium physisorbed on the sample. Finally, the TPD measurement was carried out by heating the sample up to 673 K at a heating rate of 5 K/min and maintaining the temperature at 673 K for 0.5 h in an argon flow. The amounts of desorbed D<sub>2</sub>, HD, and H<sub>2</sub> were recorded with the QMS as a function of temperature.

**Table 1** Characteristics of ACF samples used in this study.

Sample	Reduction temperature (K)	$S_{\text{micro}}^a$ (m <sup>2</sup> /g)	$V_{\text{micro}}^b$ (cm <sup>3</sup> /g)	$W_{\text{ave}}^c$ (nm)	Pt content (wt%)	$D_{\text{XRD}}^d$ (nm)
Ox-ACF	-	1540	0.58	0.75	-	-
Pt-ACF-473	473	1490	0.56	0.75	8.7	2.8
Pt-ACF-673	673	1560	0.60	0.76	8.9	3.1

<sup>a</sup> Specific surface area of micropore. <sup>b</sup> Micropore volume.

<sup>c</sup> Average micropore width. <sup>d</sup> Average diameter of metal particle determined by XRD.

## Results and Discussion

**Figure 1** shows D<sub>2</sub> desorption profiles of Pt-ACF-473 and Pt-black. Two peaks were observed, at 450 K and 673 K, in the D<sub>2</sub> profile of Pt-ACF-473 (first). The peak at 450 K coincided with the peak in the profile of Pt-black and could therefore be assigned to the desorption of deuterium chemisorbed on the Pt surface. Since the average surface area of Pt-black, 5.9 m<sup>2</sup>/g-sample, is close to that of Pt-ACF-473, 7.9 m<sup>2</sup>/g-sample, the D<sub>2</sub> amount can be quantitatively compared in **Figure 1**. On the other hand, the peak at 673 K is considered to be attributable to the desorption of deuterium from the carbon surface. The amounts of desorbed D<sub>2</sub> determined from the peak at 673 K are shown in **Table 2**. The desorption of HD and H<sub>2</sub> was negligible. This fact indicates that the hydrogen existed in the ACF sample originally is not desorbed up to 673 K. After TPD

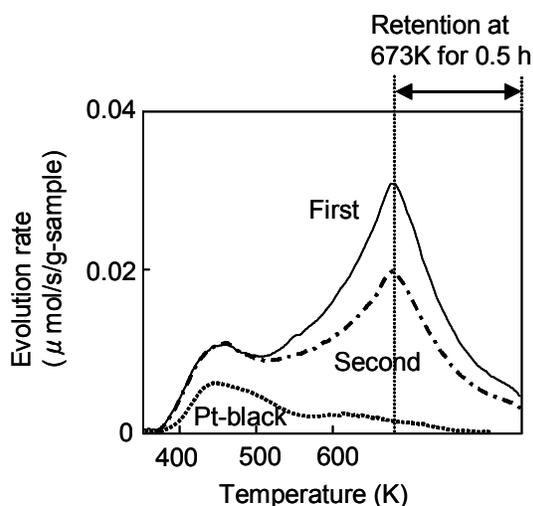
measurement up to 673 K, Pt-ACF-473 was maintained in a deuterium flow at 673 K for 0.5 h again, and the D<sub>2</sub> desorption profile (**Figure 1**, second) was then measured. The appearance of the peak at 673 K in the second profile indicates the reversible adsorption/desorption of deuterium on the carbon surface.

**Figure 2** shows D<sub>2</sub> desorption profiles of Ox-ACF and Pt-ACF-673. In the profile of Ox-ACF, the peak at 673 K was also observed, however, the amount of desorbed deuterium, 10.9 μmol/g, was much smaller than that desorbed from the Pt-ACF sample. Thus, the Pt loading remarkably enhanced the amount of adsorbed and desorbed deuterium. The amount of deuterium desorbed from Pt-ACF-673 was smaller than the amount of Pt-ACF-473. **Table 2** also shows the amounts of evolved CO and CO<sub>2</sub> during pretreatment in an argon flow at 673 K before deuterium adsorption. The smaller amounts of evolved CO and CO<sub>2</sub> from Pt-ACF-673 than Pt-ACF-473 suggest that the sites formed by the release of CO and CO<sub>2</sub> play an important role as the sites for the deuterium adsorption. To clarify the state of adsorbed hydrogen, a 1:1 mixed gas of D<sub>2</sub> and H<sub>2</sub> was adsorbed at 673 K, and the TPD measurement was carried out in the same manner. The ratio of the amount of desorbed gas was approximately 1:2:1 for D<sub>2</sub>:HD:H<sub>2</sub> even in the case of Ox-ACF without Pt. Thus, the deuterium was adsorbed as atoms not as molecules on the carbon surface. That is to say, the peak at 673 K cannot be explained by the physisorption of hydrogen molecules.

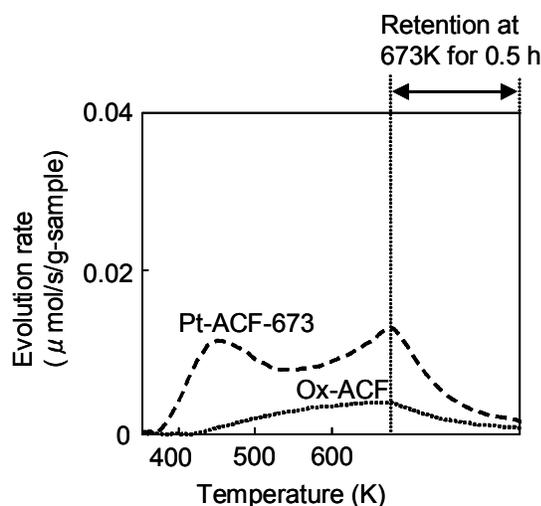
**Table 2** Amounts of D<sub>2</sub>, CO and CO<sub>2</sub> evolved.

sample	D <sub>2</sub> (μ mol/g)	CO <sup>a</sup> (mmol/g)	CO <sub>2</sub> <sup>a</sup> (mmol/g)
Ox-ACF	10.9	0.42	0.82
Pt-ACF-473	64.4	0.34	0.45
Pt-ACF-673	33.1	0.09	0.08

<sup>a</sup> during pretreatment.



**Figure 1** D<sub>2</sub> desorption profiles of Pt-ACF-473 and Pt-black.



**Figure 2** D<sub>2</sub> desorption profiles of Ox-ACF and Pt-ACF-673.

The present results led us to conclude that deuterium was reversibly adsorbed on the carbon surface as atoms and that the amount of deuterium was remarkably enhanced by Pt loading. Orimo et al. previously reported the high hydrogen-storage ability of nanostructured graphite prepared by the mechanical milling of graphite under a hydrogen pressure of 1 MPa [7]. The high capacity, 6 wt%, after milling for 80 h was obtained from the peak at 700 K in the hydrogen desorption profile; however, the adsorption was irreversible. They and other groups proposed that hydrogen atoms were adsorbed on or bonded to the defective sites formed by mechanical milling and estimated the desorption activation energy to be 124 kJ/mol, which is larger than that of physisorbed hydrogen (19 kJ/mol) but smaller than that of a C-H covalent bond (429 kJ/mol) [7-9]. Although the amount of deuterium adsorbed on the Pt-ACF sample was much smaller than that on the nanostructured graphite, the present study showed the reversible hydrogen chemisorption on the carbon surface for the first time. The amount of hydrogen adsorbed on carbon surface should be enhanced by improvement of the sample (e.g., increase in the number of active sites) and adsorption conditions (e.g., high pressure).

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