Hydrogen Adsorption/Desorption Property of Activated Carbon Loaded with Platinum

Hideyuki Takagi,* Hiroaki Hatori, and Yoshio Yamada†
National Institute of Advanced Industrial Science and Technology (AIST),
AIST Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569
†*Faculty of Engineering, Fukui University, 3-9-1 Bunkyou, Fukui 910-8507*

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The hydrogen adsorption isotherms of activated carbon fiber loaded with platinum (Pt–ACF) in the 303–673 K range indicated that a temperature above 573 K was required to give rise to an increase in the amount of adsorbed hydrogen due to the spillover phenomenon. Two peaks at 800 and 1200 K in the D_2 desorption profile of Pt–ACF clarified that two kinds of sites for adsorption or bonding of spiltover deuterium exist on the carbon surface.

Activated carbon loaded with Pt has been well used as a catalyst for hydrogenation under mild conditions. The activity of the catalyst is due to the fine Pt particles dispersed on the carbon surface owing to its high surface area. In addition, it has been reported that the hydrogen spillover phenomenon plays an important role in the catalytic property.[1] In the case of a solid acid catalyst loaded with metal, hydrogen molecules are dissociated on the metals, and the acid sites in the support act for accepting the hydrogen atoms diffused on the surface.[2] Although a number of studies have found evidence of hydrogen spillover on the carbon support, the detailed mechanism, that is, the interaction between the spiltover hydrogen and the carbon surface has not been adequately clarified.[1,3,4] Recently, some groups proposed that the hydrogen storage capacities of the carbon nanotube and nanofiber samples containing metal catalysts were enhanced by hydrogen spillover from the metals to the carbon surface.[5,6] Therefore, understanding the hydrogen spillover phenomenon on the carbon support will be beneficial not only for enhancing catalytic activity but also for developing hydrogen storage media with high capacity. In this study, we evaluated the hydrogen adsorption and desorption properties of Pt–ACF to discuss the state of spiltover hydrogen on the carbon surface.

The Pt–ACF sample was prepared from a commercially available ACF sample (Gunei Chemical Industry, The BET surface area is 1580 m^2/g.) by impregnation with an aqueous solution of H_2PtCl_6. Reduction treatment was carried out in a hydrogen flow at 673 K for 2 h. The Pt content of the Pt–ACF sample, which was determined by X-ray fluorescence analysis, was 10.6 wt %. The average diameter of the Pt particles was 5.7 nm, which was estimated from the 111 peak of the X-ray diffraction profile by means of Scherrer's equation. Hydrogen adsorption isotherms of the ACF samples in the 303–673 K range were measured with a volumetric apparatus (BELSORP 28SA, BEL Japan). Prior to measurement, the adsorption vessel was evacuated at 383 K for 12 h to degas the sample. After evacuation, hydrogen gas was introduced into the vessel, and a pressure of 0.05 MPa was maintained at 383 K for 0.5 h to reduce the Pt particles. Finally, the vessel was evacuated at the adsorption temperatures for 0.5 h, and the hydrogen adsorption isotherm was then measured.

Figure 1 shows the hydrogen adsorption isotherms of the Pt–ACF, ACF, and Pt black samples. The amount of H_2 adsorbed on Pt–ACF is expressed on the basis of the ACF sample weight, exclusive of Pt weight, in order to facilitate our discussion of the effect of Pt loading on hydrogen adsorption. At 303 K, the amount of H_2 adsorbed on the Pt–ACF sample was larger than that on the ACF sample. Since the average surface area of the Pt black sample, 5.7 m^2/g, was approximately equal to that of the Pt particles on the Pt–ACF sample, 5.4 m^2/g, the amount of adsorbed H_2 can be quantitatively compared in Figure 1. The adsorption isotherm of the Pt–ACF was in accord with the sum of the adsorption isotherms of the ACF and Pt black samples. Therefore, the increase in the amount of H_2 adsorbed on ACF at 303 K due to Pt loading can be explained by chemisorption on the surface of Pt particles. Thus, the increase in the adsorption capacity due to hydrogen spillover was not observed at room temperature in this study. For solid acid catalysts, a temperature above 423 K was reported to be necessary for hydrogen to spill over from the metal and diffuse over the surface of the support.[2,7] Therefore, we measured hydrogen adsorption isotherms at temperatures above 303 K.

The amounts of H_2 adsorbed on Pt–ACF at 373 and 573 K were smaller than that at 303 K. However, at 673 K, the amount of H_2 adsorbed on Pt–ACF was larger than the sum of the amounts of H_2 adsorbed on ACF and Pt black. Temperature-programmed desorption (TPD) measurements on both Pt–ACF and ACF samples under a hydrogen atmosphere indicated that CH_4 formation was negligible up to 673 K. The high amount of hydrogen adsorbed on Pt–ACF at 673 K can therefore be considered to be due to the spillover phenomenon; that is, hydrogen

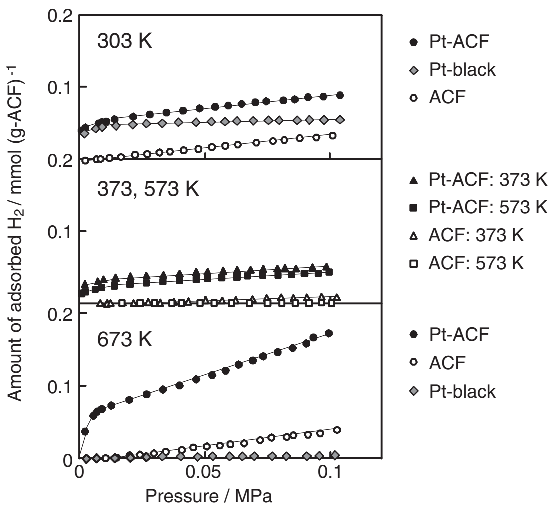

Figure 1. Hydrogen adsorption isotherms of the Pt–ACF, ACF, and Pt black samples at 303–673 K.

atoms dissociated on the Pt surface spill over and diffuse over the carbon surface, and then adsorb on or bond to the active sites.

To understand the state of the spiltover hydrogen on the carbon surface, we evaluated the deuterium desorption property after deuterium adsorption at 673 K by means of TPD measurements. Prior to measurement, the sample was heated in an argon flow at 673 K for 0.5 h. The flow gas was changed to deuterium, and the sample was heated at 673 K for 4 h under a deuterium pressure of 0.1 MPa. After deuterium adsorption, the gas was changed to argon again, and the temperature was then maintained at 373 K for 0.5 h to remove physisorbed deuterium. Finally, the TPD measurement was carried out by heating the sample to 1223 K at a heating rate of 5 K/min and maintaining the temperature at 1223 K for 0.5 h in an argon flow. The amounts of desorbed D_2, HD, and H_2 were recorded with a quadrupole mass spectrometer as a function of temperature.

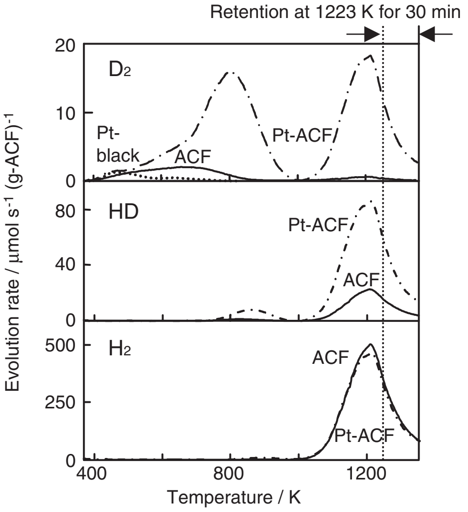

Figure 2. D_2, HD, and H_2 desorption profiles for the Pt–ACF, ACF, and Pt black samples after deuterium adsorption at 673 K.

The peaks were observed at 800 and 1200 K in the D_2 profile of the Pt–ACF sample (Figure 2). A shoulder peak at 450 K agreed with the peak in the profile of the Pt black sample and could therefore be assigned to the desorption of deuterium chemisorbed on the Pt surface. The peaks at 800 and 1200 K were attributed to the desorption of deuterium from the carbon surface. HD desorption was observed at temperatures above 750 K. The amounts of desorbed D_2 and HD were 0.058 and 0.255 mmol/g, respectively. The total amount of desorbed D_2, 0.186 mmol/g, which was estimated from the amounts of desorbed D_2 and HD, was approximately equal to the amount of adsorbed H_2 at 673 K and 0.1 MPa, 0.176 mmol/g ($H/Pt = 0.575$), estimated from the hydrogen adsorption isotherm. The desorption of D_2 and HD was also observed in the case of the ACF sample, but the desorbed amounts were much smaller than those for the Pt–ACF sample. The total amount of desorbed D_2, 0.039 mmol/g, was also equal to the amount of adsorbed H_2 at 673 K and 0.1 MPa, 0.040 mmol/g. Thus, the Pt on the carbon surface is required to give rise to a sufficient amount of spiltover hydrogen.

The present results led us to conclude that a temperature above 573 K is required to give rise to the increase in the amount of hydrogen adsorbed on the Pt–ACF sample due to the spillover phenomenon. The peaks at 800 and 1200 K in the D_2 desorption profile of Pt–ACF indicated that two kinds of sites for adsorption or bonding of the spiltover deuterium exist on the carbon surface. The peak at 1200 K corresponds to the desorption of deuterium covalently bonded on the edge structure of a hexagonal carbon layer.[8] Orimo et al. recently reported a peak at around 800 K in the hydrogen desorption profile of nanostructured graphite prepared by the mechanical milling of graphite under a hydrogen pressure of 1 MPa.[9] They and other groups proposed that hydrogen atoms were adsorbed on or bonded to defective sites formed by mechanical milling and estimated the desorption activation energy of the peak at 800 K to be 124 kJ/mol, which is smaller than that of the peak at 1200 K (244 kJ/mol).[9,10] We also evaluated the deuterium desorption property of Pt–ACF samples to which the functional groups were added by using an oxidation treatment. The amount of desorbed deuterium determined from the peak at 800 K was increased by the addition of functional groups, which suggests that functional groups play an important role as active sites for deuterium adsorption. The peak at 800 K was also observed in the D_2 desorption profile of the Pt–ACF sample, which was pretreated at 1223 K in an argon flow before deuterium adsorption to remove functional groups completely, although the amount of desorbed deuterium was smaller than that desorbed from the Pt–ACF sample without heat treatment. Therefore, the sites formed by the release of functional groups can be considered to act for accepting the spiltover deuterium as well.

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