

Direct Measurements of Adsorption Heats of Hydrogen on Nanoporous Carbons

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Since a exciting report of hydrogen storage in single-walled carbon nanotubes by Dillon and his colleagues [1], nanoporous carbon materials, such as carbon nanotubes, carbon nanohorns and microporous activated carbon, have attracted considerable attention as hydrogen storage materials. Adsorption plays a predominating role in the hydrogen storage process on solid surfaces. The adsorption is a spontaneous process, which is caused by interaction between gas molecules and surface, hence, it is always exothermic process and observed as adsorption heats. For this reason, direct measurement of the adsorption heats by adsorption microcalorimetry would provide quantitative information on the strength of adsorption interaction and the adsorption mechanism. However, the adsorption amounts of hydrogen on carbon materials are far less than those of condensable vapors near room temperature due to low critical temperature of hydrogen (33.2 K), therefore, the adsorption heats can not be determined accurately at conventional measurement conditions near room temperature and the atmospheric pressure. This contribution reports the calorimetric characterization of hydrogen adsorption on nanoporous carbon materials at low temperature and high-pressure conditions.

The high-pressure adsorption apparatus consists of a volumetric adsorption line connected to a twin-conduction type microcalorimeter. Activated carbon fibers (ACF, Ad'all Co.) of different micropore sizes (Table 1) were used as model adsorbents. Each ACF has slit-shaped micropores of uniform size [2]. The adsorption isotherms and differential heats of adsorption at high-pressure region from 0 to 10 MPa were simultaneously measured at isothermal condition from 203 to 298 K. The adsorption isotherms on ACF were of Henry type regardless of adsorption temperature and pore width; the uptakes increased linearly with equilibrium pressure. The adsorption isotherm at lower sorption temperature tended to show higher sorptivity. The adsorption amounts at ca.10 MPa were 0.5 – 0.8 mass %, as exemplified in Figure 1 for A7, but the uptake per unit area for A7 is higher than that of A20, suggesting higher sorptivity on ACF of narrower pore size. In the case of adsorption in narrower micropores of A7, overlapping of the force fields of faced pore walls enhances the potential field in the micropore, and the enhancement is 1.75-fold [2-4]. This potential enhancement would bring about higher sorptivity of hydrogen. Differential heats of adsorption on A7 were shown in Figure 2. The adsorption heats were 4 to 6 kJ/mol regardless of adsorption temperature, which agrees with calculated value based upon dispersion interaction (van der Waals interaction). Isotheric heats of adsorption were estimated from the adsorption isotherms by the Clausius-Clapeyron equation and they agreed well with the experimental results. These results suggest that hydrogen adsorption takes place even over critical temperature by dispersion interaction, and the pore width would play an important role in the sorptivity.

[1] A. C. Dillon et al., *Nature*, **386**, 377, 1997.

[2] D.H. Everett and J.C. Powl, *J. Chem. Soc., Faraday Trans. 1*, **72**, 619, 1976.

[3] K. Kaneko, R.F. Cracknell, D. Nicholson, *Langmuir*, **10**, 4606, 1994

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Table 1 Characteristics of activated carbon fiber used in this study

Sample	Surface area [m ² g ⁻¹]	Pore volume [mLg ⁻¹]	Pore diameter [nm]
A7	780	0.3	0.7
A20	2,180	1.0	1.1

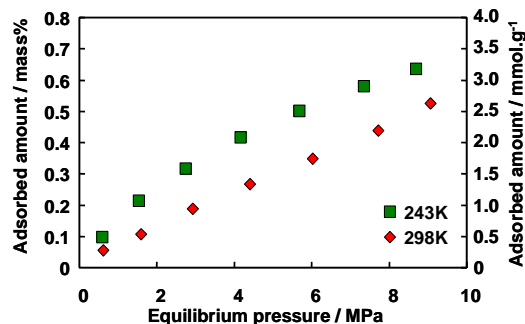


Figure 1 Adsorption isotherm of hydrogen on ACFs.

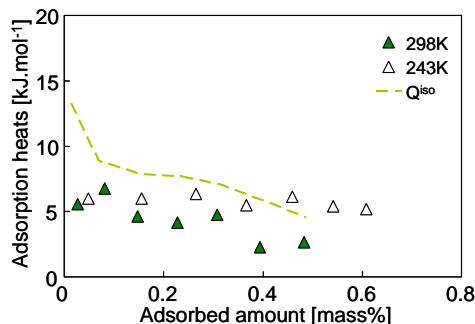


Figure 2 Differential heats of hydrogen adsorption on ACFs. Broken line indicates isotheric heats of adsorption, Q^{iso} .