

DIRECT OBSERVATION OF HYDROGEN ABSORBED ON CARBONACEOUS MATERIALS

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Abstract

Characteristics of the hydrogen absorbed on carbonaceous materials were evaluated in terms of molecular mobility obtained from pulse $^1\text{H-NMR}$. Investigations were performed on activated carbon fibers, ACF, A-7 ($870\text{m}^2/\text{g}$), A-20 ($2050\text{m}^2/\text{g}$) and zeolite 5A, 13X. Spin-spin relaxation time, T_2 , was employed to evaluate the mobility of hydrogen adsorbed on the samples. The CPMG pulse sequence was used to generate $^1\text{H-NMR}$ transverse relaxation signals. The CPMG signals obtained from hydrogen introduced into ACFs and zeolites consist of two components, namely L1 component arisen from gaseous hydrogen exists in a gap of samples and L2 component arisen from hydrogen adsorbed on samples. The amount of absorbed hydrogen calculated from the intensity of L2 components are larger than that obtained from conventional volumetric methods. For pulse NMR, hydrogen is classified with molecular mobility, that is, T_2 value. Therefore, the difference of the amounts of absorbed hydrogen indicate that the L2 components are not arisen from surface excess hydrogen which is obtained from volumetric methods, but from absolute adsorbed hydrogen.

Introduction

Interactions between hydrogen and carbonaceous materials have attracted much interest motivated by practical possibility for energy storage materials. In order to develop the materials of practical significance for hydrogen storage, it is important to understand the relationships between the characteristics of materials and hydrogen storage capacities. However, the effects of surface characteristics on the hydrogen adsorption capacities are not fully evaluated. Adsorption studies were typically carried out with conventional methods such as volumetric and gravimetric measurements. On the other hands, pulse $^1\text{H-NMR}$ is a technique for evaluating the motion and mobility of molecules in terms of the relaxation behaviour of protons and applicable to materials which have protons regardless of the phase state of the materials. In this study, characteristics of hydrogen adsorption on the activated carbon fiber samples are evaluated in terms of molecular mobility obtained with pulse $^1\text{H-NMR}$.

Experiment

Materials

Two activated carbon fiber (ACF) A-20 ($2050\text{m}^2/\text{g}$) and A-7 ($870\text{m}^2/\text{g}$), and Zeolite 5A and 13X was used in this study. The sample was placed into quartz high pressure NMR sample tube which was connected to a gas line and stop valve. The sample in the quartz tube was then pre-treated at 673K under vacuum ($<10^{-5}$ torr) for 24hrs.

Pulse $^1\text{H-NMR}$ Measurements

After the pre-treatment, the sample in the NMR tube was moved into $^1\text{H-NMR}$ probe, then hydrogen gas of 0.5MPa - 3.5MPa was introduced into the tube. The temperature of the sample was maintained with a flow of nitrogen from 133K to 303K. Spin-spin relaxation time, T_2 , measurements were conducted using a Tecmag Apollo Pulse NMR spectrometer operated at 38MHz for ^1H nuclei. The CPMG pulse sequence was employed to generate $^1\text{H-NMR}$ transverse relaxation signals. Change in the CPMG signal intensity, I_t , with decay time, t , is defined by Equation 1.

$$I_t = I_0 \exp[-(t/T_2)^{m_i}] \quad m_i = 1 \text{ for exponential, } m_i = 2 \text{ for Gaussian} \quad (1)$$

where I_0 is the intensity of the signal at decay time $t = 0$ corresponding to the number of protons in the specimen, and T_2 is the spin-spin relaxation time reflecting the mobility of molecules. When the specimen consists of several components, the obtained signal can be deconvoluted on the basis of the

relaxation characteristics, and the signal can be described as a sum of each of the components.

$$I_{\text{Total}} = \sum I_i \quad (2)$$

where I_i is signal intensity for component i described in Equation 1 and I_{Total} is the sum of the components corresponding to the observed signal. The spin-spin relaxation time and the fractional intensity of each component were calculated according to Equation 1.

Results and Discussion

Magnetic relaxation phenomenon of gaseous hydrogen

First, we discussed pressure dependence of the magnetic relaxation phenomenon of gaseous hydrogen using empty NMR sample tube. The CPMG signal of hydrogen gas consists of an Exponential component. The spin-spin relaxation time for hydrogen gas, $T_{2\text{LGas}}$, determined from curve deconvolution of CPMG signals increased with increase in pressure and with decrease in temperature. The variation in $T_{2\text{LGas}}$ with the density of hydrogen gas calculated using the Virial Equation is shown in Figure 1. An approximately linear relationship exists between $T_{2\text{LGas}}$ and the density. It has already known that the magnetic relaxation of hydrogen molecules in lower density range (0.05 - 2.0 atm, 77.5K) is governed mainly with spin rotation interaction result in a decrease in T_2 value with increase in the density (Abragam, 1961 and Hardy, 1966). The linear relationship observed in Figure 1 indicates that the magnetic relaxation of hydrogen gas in this density region is also governed mainly with spin rotation interaction. As shown in Figure 2, the initial intensity, I_0 , of CPMG signals for hydrogen gas increased with increase in the amount of hydrogen exist in the NMR sample tube. Thus, the quantitative evaluation of hydrogen is feasible from the intensity of CPMG signal obtained by pulse ^1H -NMR.

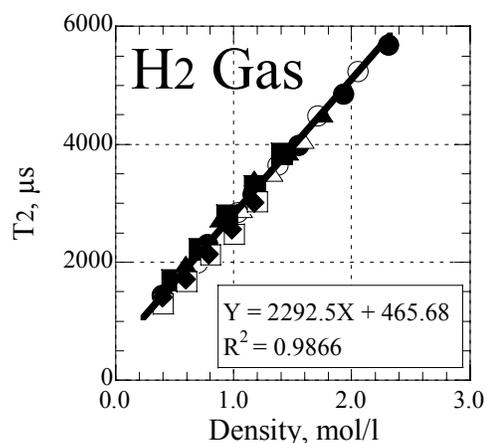


Figure 1. Variation in $T_{2\text{LGas}}$ with the density of hydrogen gas.

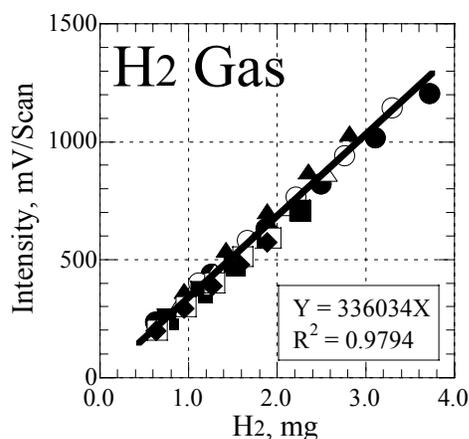


Figure 2. Relationship between the intensities of CPMG signals and the amounts of hydrogen

Characteristics of hydrogen adsorbed on porous materials

CPMG signals were obtained for the hydrogen introduced into the NMR sample tube which contained ACFs and Zeolites samples. The CPMG signals consist of two Exponential components, that is, relatively rapidly decaying component, L1, and slowly decaying component, L2. The T_2 for L1 component, $T_{2\text{L1}}$, shows almost the same value for the hydrogen gas observed in the same measurement condition. The T_2 value for L2 component, $T_{2\text{L2}}$, is about two times that of L1 components. The variation of $T_{2\text{L1}}$ imply that the L1 component arise from the gaseous hydrogen existing in a gap of samples. And the value of $T_{2\text{L2}}$ which is about two times higher that that of $T_{2\text{L1}}$ reflects lower

mobility of hydrogen molecules than that for gaseous hydrogen. This might be indicating that the hydrogen in L2 component exists in a dense or restrained condition result from adsorption of hydrogen on to the surface and /or pore of samples.

Assuming that the spin rotation interaction mainly affects the magnetic relaxation of the components in a same manner as hydrogen gas, the density and the amount of hydrogen adsorbed on the samples were calculated by the relations shown in Figure 1 and 2. Changes in the amount of adsorbed hydrogen on Zeolite 5A and ACF A20 are shown in Figure 3 and 4 with those obtained by conventional volumetric method. For both Zeolite 5A and ACF A20, the amount of adsorbed hydrogen obtained by pulse $^1\text{H-NMR}$ shows higher value than volumetric method. In case of pulse $^1\text{H-NMR}$, hydrogen is classified with mobility of hydrogen molecules, T_2 , in other words the density of hydrogen. Thus, the adsorbed hydrogen evaluated by pulse $^1\text{H-NMR}$, that is L2 components, refers to the hydrogen in similar density regardless of the presence of interaction with surface of adsorbents. It is reasonable to consider that the adsorbed hydrogen evaluated by pulse $^1\text{H-NMR}$ is arisen from absolute adsorbed hydrogen, and the amount of the hydrogen is larger than that of surface excess hydrogen obtained from volumetric method. Figure 5 and 6 depicts the change in the densities of hydrogen adsorbed on Zeolite 5A and ACF A20. The densities were calculated from both T_2 values and pore volumes obtained by nitrogen adsorption method. As we would expect, the densities calculated from T_2 values are much smaller than that from pore volumes. These results indicate that the hydrogen on the surface or pore of adsorbents exist in more sparse condition than that considered from pore volumes.

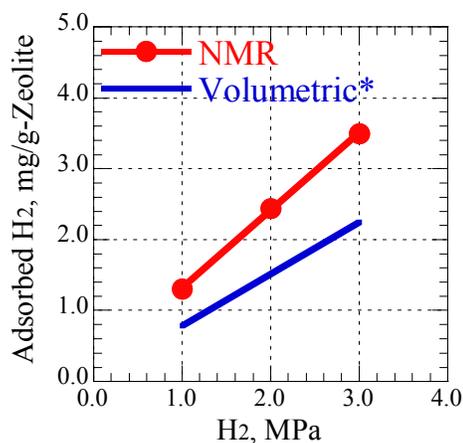


Figure 3. Changes in the amount of adsorbed hydrogen on Zeolite 5A.

* S.B.Kayiran et. al., 2002, Surf. Interface Anal, 34, 100-104.

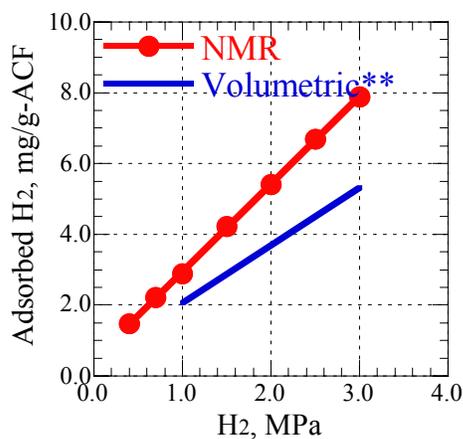


Figure 4. Changes in the amount of adsorbed hydrogen on ACF A20.

** Matsumoto et. al., 2005, Prep. of Carbon Soc. of Japan Ann. Meeting, 80-81.

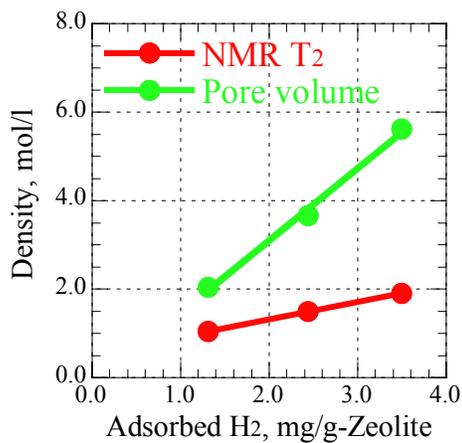


Figure 5. Changes in the density of adsorbed hydrogen on Zeolite 5A calculated from T₂ and pore volume.

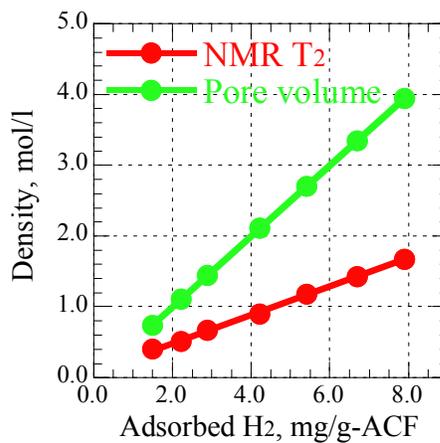


Figure 6. Changes in the density of adsorbed hydrogen on ACF A20 calculated from T₂ and pore volume.

Summary

The results obtained in this study are summarized as follows;

1. Pulse ¹H-NMR is an effective tool for hydrogen adsorption study.
2. It can be considered that the hydrogen adsorbed on the adsorbent evaluated by pulse ¹H-NMR is arisen from absolute adsorbed hydrogen.
3. The densities of adsorbed hydrogen calculated from T₂ values are much smaller than that from pore volumes.

References

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