

QUANTUM EFFECTS IN ADSORPTION OF HYDROGEN ISOTOPES ON SINGLE-WALL CARBON NANOHORN ASSEMBLY

Hideki Tanaka¹, Masako Yudasaka², Sumio Iijima^{2,3}, Hirofumi Kanoh⁴, Katsumi Kaneko⁴

¹ *Diversity and Fractal Science, Graduate School of Science and Technology, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan*

² *JST/SORST, NEC Corporation, Miyukigaoka, Tsukuba 305-8501, Japan*

³ *Department of Physics, Meijo University, Shiogamaguchi, Tenpaku, Nagoya 468-8502, Japan*

⁴ *Materials Science, Graduate School of Science and Technology, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan*

Corresponding author e-mail address: Kaneko@pchem2.s.chiba-u.ac.jp

Introduction

The study on hydrogen storage with single-walled carbon nanotubes (SWNTs) stimulated the fundamental aspect in physical adsorption of hydrogen. The simulation study with path-integral Monte Carlo (PIMC) carried out by Johnson et al. [1] showed that quantum effects should be explicitly taken into account to understand the adsorption of hydrogen isotopes inside SWNTs and interstitial channels of the SWNT bundles at 20 K. Since then systematic experimental studies with the aid of simulation are intensively requested to confirm the quantum effects in adsorption of light molecules on SWNT related materials. In experimentally confirming the quantum effects on hydrogen isotopes adsorption, single-wall carbon nanohorn (SWNH) is one of useful materials because of no metallic impurities. SWNHs can be produced by a CO₂ laser ablation of pure graphite in an atmospheric pressure of argon gas. SWNH has a typical tube diameter of about 3 nm with length in the range of 30-50 nm, and a cone cap at the one end of the tube. SWNHs are associated each other to form a *dahlia* flower-like aggregate structure (diameter ~ 80 nm), providing nano-porosity in the assembly structure.

Experimental

The adsorption isotherms of hydrogen isotopes (hydrogen and deuterium) on SWNHs in the temperature range of 40 – 77 K were measured with laboratory-designed volumetric adsorption equipment [2,3]. The apparatus consists of a gas handling system and a cryostat with a He closed-cycle refrigerator. All samples were outgassed under a vacuum better than 0.1 mPa at 423 K for 2 h. The temperature was kept within ± 0.05 K during adsorption measurement.

Simulation

Grand canonical Monte Carlo (GCMC) simulations based on Feynman-Hibbs (FH) effective potential were performed at above 40 K to compare with experimental results. In simulating the adsorption isotherms of hydrogen and deuterium, Close-packed SWNT bundle models (tube diameter: $d = 3.2$ nm) were used. The FH effective potential was adapted to introduce quantum corrections to the statistical properties generated by a classical Lennard-Jones (LJ) potential [4]. A quantum particle is represented by Gaussian wave packet in the FH treatment. Gaussian Feynman-Hibbs (GFH) effective potential can be given by a convolution integral of Gaussian distribution of a particle position to the classical interaction potential over whole space. The GFH effective potential is expanded to second order, thus the quadratic Feynman-Hibbs (QFH) potential is obtained. The QFH potential is of great advantage to simulate quantum fluid systems because interaction potential calculations are not time-consuming compared with PIMC simulation. In this study, SWNT-quantum LJ molecule interactions were calculated by integrating QFH effective potential over an infinitely long cylindrical tube with a hypothetical continuum distribution of the carbon atoms.

Results and Discussion

Figure 1 shows hydrogen and deuterium adsorption isotherms on the SWNH assembly at 50 K and 77 K. The deuterium uptakes on the SWNH assembly in the whole temperature range 40 to 77 K were invariably larger than those for hydrogen. This indicates that deuterium can be preferably adsorbed on the SWNH assembly compared with hydrogen due to smaller quantum effects, and thus the SWNH assembly has a selectivity of deuterium over hydrogen for hydrogen-deuterium mixture gas adsorption.

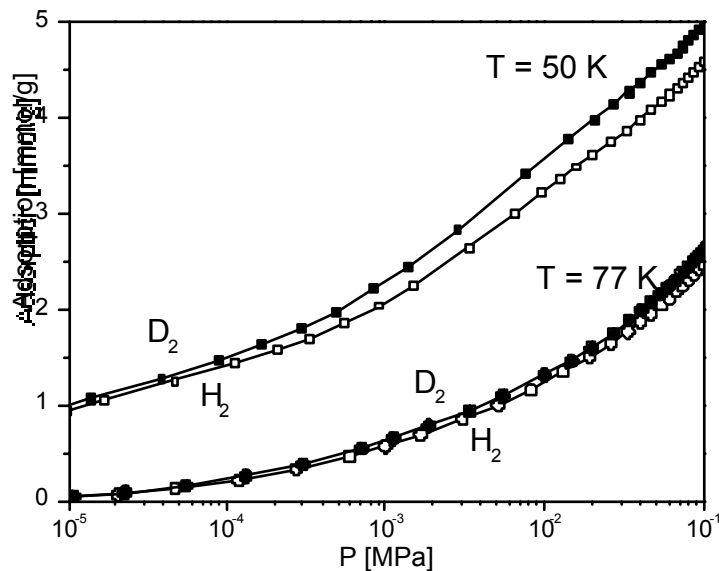


Figure 1. Hydrogen and deuterium adsorption isotherms on the SWNH assembly at 50 and 77 K

The quantum effective solid-fluid and fluid-fluid interaction potentials calculated by QFH potential shows a smearing of the classical potentials depending on the system temperature and the molecular mass, that is, potential well depths for SWNH-H₂ and H₂-H₂ interactions are always shallower than those for deuterium. Simulated hydrogen adsorption isotherms for the SWNT bundle models showed smaller adsorption than deuterium in the temperature range 40-77 K. Figure 2 shows the comparison between experimental hydrogen isotopes adsorption isotherms for the SWNH assembly and simulated ones for the SWNT bundle model at 77 K. The experimental isotherms are not quantitatively in good agreement with the simulated isotherms. This suggests that the interstitial channel between nanohorns has a size distribution due to the tube diameter and arrangement distributions. However, the difference in the adsorption amount between hydrogen and deuterium from the simulations is in good agreement with that from the experimental results. Therefore, this indicates that the GCMC simulations based on the Feynman-Hibbs formalism can represent the difference in adsorption behaviors between hydrogen isotopes induced by quantum effects.

References

- [1] Wang, Q., Challa, S. R., Sholl, D. S., Johnson, J. K., Quantum sieving in carbon nanotubes and zeolites. *Phys. Rev. Lett.*: 1999; 82, 956-959.
- [2] Tanaka, H., El-Merraoui, M., Kodaira, T., Kaneko, K., Possibility of quantum effect in micropore filling of Ne on AlPO₄-5, *Chem. Phys. Lett.*: 2002; 351, 417-423.

[3] Tanaka, H., El-Merraoui, M., Kanoh, H., Steele, W. A., Yudasaka, M., Iijima, S., Kaneko, K., Quantum effects in hydrogen adsorption in internal tube space of single-wall carbon nanohorns. J. Phys. Chem.: to be submitted.

[4] Sesé, L. M., Study of the Feynman-Hibbs effective potential against the path-integral formalism for Monte Carlo simulations of quantum many-body Lennard-Jones systems. Mol. Phys.: 1994; 81, 1297-1312.

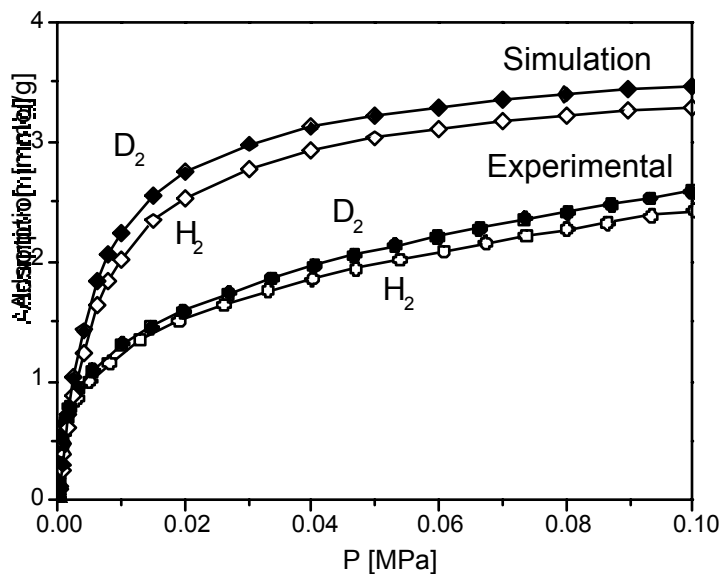


Figure 2. Comparison between simulation (the SWNT bundle model) and experimental (the SWNH assembly) isotherms for hydrogen isotopes at 77 K.