STUDY OF ISOTOPIC EFFECT FOR HYDROGEN AND DEUTERIUM ADSORPTION ON NANOPOROUS CARBON (NPC) AT 67-78 K

Bondarenko S.D., Alekseev I.A.*
Petersburg Nuclear Physics Institute,
188300, Gatchina, Leningrad dist., Russia
* *Fax +7 (81371) 31985, E-mail: aleksiv@pnpi.spb.ru*

Introduction

The significant amount of publications is devoted to study of hydrogen sorption on nanoporous carbon materials. High-temperature sorption, which is routinely activated process and results in a chemisorbed state of the bound hydrogen, was studied in [1, 2]. Liu *et al.* [3] and Dillon *et al.* [4] adduced data on physical adsorption of hydrogen of natural isotopic composition at room and cryogenic temperatures.

Theoretical and simulations studies predict that adsorption of hydrogen isotopes in nanotubes at cryogenic temperatures may result in extraordinary large selectivity (up to 100000 for T_2 over H_2 at 20 K) [5, 6]. But there is no experimental information about adsorption isotherms and separation factors of the hydrogen isotopic modifications on nanoporous materials at cryogenic temperatures, and its obtaining has doubtless interest.

Samples of the nanoporous carbon (NPC) synthesized by heat treatment of carbide silicon and carbide titanium in chlorine have been studied in the present work. NPC used in this work is produced as a body of cylinder shape with a sufficient mechanical strength. The samples of materials are characterized by the advanced structure of pores, which contains two types of pores: macropores (with the sizes in a few micron) and nanopores with sizes about 0.8 nm. Surface area and volume of pores NPC with matrix from SiC are 900 cm^3/g and 0.44 m^2/g, from TiC are 1200 cm^3/g and 0.39 m^2/g [7].

Results and discussions

Pure natural isotopic composition hydrogen (protium), deuterium (atomic concentration of deuterium 99.9%) and their mixture were used as adsorbate in the experiments.

Analysis of the hydrogen isotopic composition and impurity content was carried out by a method of gas chromatography. Impurity content did not exceed $3{\cdot}10^{-4}$ %. Absolute error of definition of deuterium atomic concentration in gas for the region of high deuterium concentrations (> 98 %) is 0.05 %, for wide region of concentrations - up to 0.5 %.

Samples of nanoporous carbon were preliminarily crushed till the sizes of 1-5 mm and placed in an adsorption cell. The adsorbents were previously reactivated for 4 hours at the temperature of 680 K and at the pressure of 1 Pa. Before each cycle of measurements the samples of NPC were made a regeneration within two hours with heating of adsorbent, and vacuum degassing of all volume of installation up to residual pressure ~0.1 Pa. Background (residual) pressure in system at cooling adsorbent up to boiling point of liquid nitrogen (without delivering adsorbate) did not exceed $8{\cdot}10^{-3}$ Pa.

The equilibrium adsorption isotherms of protium and deuterium have been measured volumetrically at temperatures within 67-78 K in the pressure range from 10 Pa to 0.2 MPa. The adsorption cell was cooled in liquid nitrogen boiling under vacuum. The error of determination of adsorption capacity is not above ±2 cm^3.

The separation factors of H_2, HD and D_2 molecules at adsorption on samples of NPC have been determined by method of equilibration of gaseous and adsorption phases. The isotope composition of the gaseous phase and the adsorption phase was determined using gas chromatograph. The composition of adsorption phase was measured after removing of gas phase and desorption of gas out of NPC. The separation factor between components 1 and 2 was calculated by formula:

$$\alpha_{1\text{-}2} = A_1G_2/A_2G_1 \qquad (1)$$

where A_i, G_i are concentrations of i-component in adsorption and gas phase.

Several series of measurements of NPC adsorption capacity have been carried out. Their results agree well with themselves.

It was established that the temperature of regeneration of NPC within the limits of 473-673 K does not influence on adsorption capacity of NPC with respect to protium and deuterium. Hydrogen and deuterium are completely desorbed from the sample of NPC at temperature 470-480 K. Adsorption capacity of NPC samples is 10-15 cm^3 hydrogen on 1g adsorbent at room temperature and under atmosphere pressure.

Adsorption isotherms of protium and deuterium on the samples of nanoporous carbon adsorbent at temperature 67-78 K are shown in Fig. 1 and Fig. 2. The adsorption capacity of nanoporous carbon adsorbent on deuterium exceeds capacity on protium over all the investigated pressure range. The difference between adsorption value of deuterium and hydrogen is increased with rising of pressure.

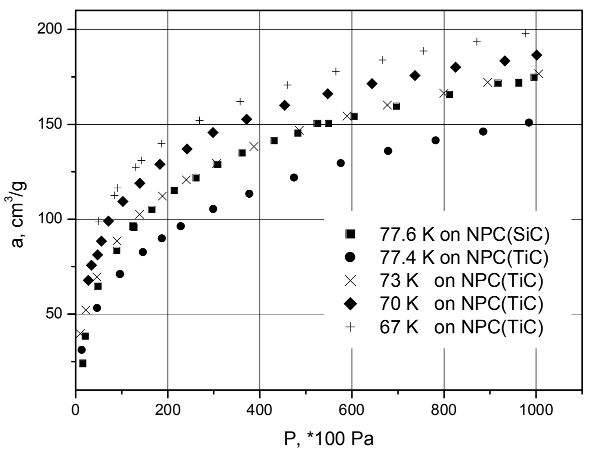

Fig. 1. Adsorption isotherms of protium on NPC

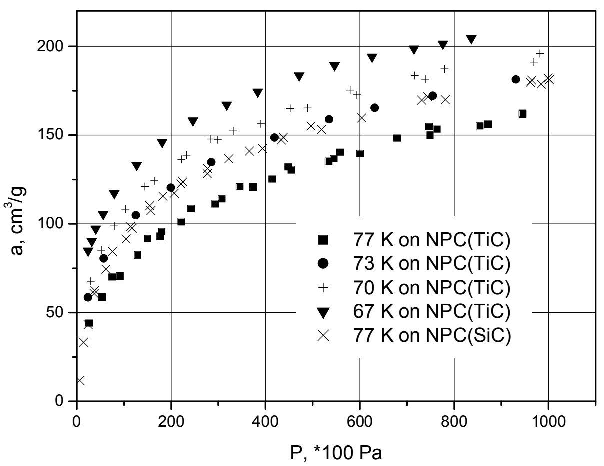

Fig. 2. Adsorption isotherms of deuterium on NPC

In the present work the separation factors of H_2, HD, and D2 molecules on the samples of NPC have been measured at 68 K and 78 K and pressure about 100 kPa for the first time. Average results of several measurement series are presented in the table.

Separation factors of hydrogen isotopes on NPC

NPC	T, K	D_2-H_2	D_2-HD	HD-D_2
SiC	78	1.35±0.25		
TiC	78	1.32±0.03	1.15±0.04	1.14±0.04
	68	1.43±0.02	1.18±0.02	1.21±0.02

The separation factor of hydrogen isotopes on NPC is a bit larger than one is on common activated carbon at the same temperature, but smaller than on zeolites.

Conclusion

Adsorption isotherms of pure hydrogen and deuterium on samples of nanoporous carbon (NPC) have been determined at range of temperature 67-78 K. Adsorption capacity of NPC samples relative to deuterium is larger than one to hydrogen, and both values are considerably larger than values of hydrogen isotopes adsorption capacity on common sorbents such as zeolites and active carbons.

Separation factors of hydrogen (H_2), hydride of deuterium (HD) and deuterium (D_2) have been determined for adsorption of hydrogen isotopes mixtures on the samples NPC at temperatures 68 K and 78 K. The values don't extremely large. They are close to ones of active carbons.

Acknowledgements

Authors are grateful to Prof. S.K. Gordeev for samples of NPC given for this research.

The present work has been supported by Russian federal program "Integracia", grant I0656/2141.

References

1. Tarasov B.P., Hydrogenation mechanism of fullerit-metall composites, J. Common Chem., 1998, 68(8): 1245-1248. (In Russian)
2. Evard E.A., Gabis I.E., Gordeev S.K., Investigate of hydrogen sorption by nanoporous carbon, In: Fullerens and similar fulleren structures. Collected articles, Minsk, BGU, 2000, p. 34-40. (In Russian)
3. Liu C., Fan Y.Y., Liu M. et al., Hydrogen storage in single-walled carbon nanotubes at room temperature, Science, 1999, 286 (5): 1127-1129.
4. Dillon A.C., Jones K.M., Bekkedahl T.A. et al., Storage of hydrogen in single-walled carbon nanotubes, Nature, 1997, 386 (27): 377-379.
5. Wang Q., Challa S. R., Sholl D. S., Johnson J. K., Quantum Sieving in Carbon Nanotubes and Zeolites, Physical Review Letters, 1999, 82 (5): 956-959.
6. Challa S.R., Sholl D.S., Johnson J.K., Adsorption and separation of hydrogen isotopes in carbon nanotubes: Multicomponent grand canonical Monte Carlo simulations, J. Chem. Physics, 2002, 116 (2): 814-824.
7. Gordeev S.K. Nanoporous and nanofragmental carbon composite materials. In G. Benedek et al. (eds.) Nanostructured carbon for advanced applications, Kluwer Academic Publishers, 2001, p. 71-88.