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^{129}Xe NMR of Xenon Trapped in Fully Dehydrated Mesoporous Silica

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Abstract

^{129}Xe NMR spectra of natural abundant xenon gas trapped in fully dehydrated mesoporous materials with pore sizes smaller than 2 nm in diameter were observed under atmospheric pressure in the temperature range between 168 and 373 K. The average pore diameters of the materials studied in this paper were 0.5, 1 and about 2 nm for molecular sieves 5A and 13X and synthesized mesoporous silica, respectively. The samples were fully dehydrated using an ultra-high vacuum (UHV) system and xenon gas was introduced with the sample pre-cooled to 168 K just above the boiling point of xenon. The ^{129}Xe NMR spectra were observed as a function of increasing temperature and the ^{129}Xe shift were observed at each temperature for the three samples under atmospheric pressure. The behaviors of xenon atoms in small pores observed in equilibrium states can provide important information on relationships between the pore structure and ^{129}Xe chemical shift.

Keywords

^{129}Xe NMR, mesoporous silica, molecular sieves, low-dielectric constant materials

1. Introduction

^{129}Xe Nuclear Magnetic Resonance (NMR) is one of the important methods to measure the pore diameters and interactions between trapped species and the innerwall of the pores [1]. This technique has been applied to probe porosity of mesoporous silica and the pore size is known to relate with the chemical shift [2]. Since the Van der Waals radius of Xe is known to be 0.216 nm, the possible pore size to adsorb xenon should be larger than 0.4 nm in diameter. Then the mean pore diameters ranging from 0.4 to 300 nm are the possible target to show the relationship experimentally. We have tried to apply it to a self-assembled porous silica sample (Lowk1), which is known as a candidate of low-dielectric constant materials for interconnects in future ultra-large scale integrated circuits (ULSIs)[3]. The development of porous silica suitable for this purpose is to obtain a low-dielectric constant and a high mechanical strength.

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2. Method and Materials

The self-assembled porous silica sample was prepared from acidic silica sol mixed with the cationic template of cetyltrimethylammonium chloride [3]. Metal impurities in the sample were minimized by using the electronic-grade silica sol. The sample was fine powder and the amount of the fully degassed sample was ~ 0.27 g. Molecular sieves of 5A and 13X were purchased from Nacalai Tesque, Inc. as pellet and the fully degassed sample of 0.39 and 0.30 g of 5A and 13X were used, respectively. Fully dehydrated samples were prepared as follows. The sample was put in a 10-mm NMR sample tube and connected to a vacuum line, gradually evacuated and then the temperature was increased to 200 °C and kept over 1 week until the pressure became below 5 x 10^{-6} Pa by an ultra-high vacuum system (UHV) on a Varian V70 turbo molecular pump.

The sample temperature was set below 168 K before the introduction of the xenon gas under vacuum. The room-temperature xenon gas was introduced into evacuated samples of the porous silica, the thermally polarized ^{129}Xe NMR signal was then observed after placing in the sample in a high field magnet. The temperature was gradually increased without further addition of xenon gas. The ^{129}Xe NMR spectra were measured by a Tecmag Apollo equipped by a wide-bore 6.3 T SCM at the frequency of 74.7 MHz. The 90° pulse width was 30 μs. The spin-lattice relaxation time T_1 was found to be short for the 5A and 13X. Each spectrum was observed with 64 accumulations at 90° pulse with 2 s repetition time. Since the longest T_1 of ^{129}Xe in 5A and 13X was ~ 0.35 s, the magnetization was fully recovered at each scan. The tuning of the probe was adjusted at every temperature because of the wide temperature range observation. Before measuring at each temperature, the sample was kept at least 30 m. Since the T_1 of Lowk1 is much longer compared with 5A and 13X, the measuring conditions were varied to obtain reasonable S/N spectra as following; at 173 K, 45° pulse, repetition time 10 s, 40 accumulations, at 213 K, 45° pulse, repetition time 12 s, 40 accumulations, at 273 K, 60° pulse, repetition time 20 s, 80 accumulations, and at 333 K, 60° pulse, repetition time 120 s and 320 accumulations.

3. Results and Discussion

The measurements of ^{129}Xe NMR spectra were started from 173 K and the number of xenon atoms decreased as the temperature increased. The ^{129}Xe NMR spectra for Lowk1 are shown in Figures 1. The observed changes were continuous in the spectra for 5A owing to the temperature increase; these changes were decreases in signal intensity and line width, and an increase in field shift. On the other hand, the ^{129}Xe spectral patterns for 13X varied in a different manner. The signal intensity and position of 13X changed similarly to those of 5A until 223 K, and then the signal became narrower between 233 and 263 K, and the signal intensity decreased above 323 K. The ^{129}Xe spectrum of Lowk1 at 173 K showed an intense signal and was observed by one scan until 213 K, as shown in Figure 1, yielding quantitative peak areas. As the temperature increased, the signal became broader and the accumulations were necessary to obtain a reasonable signal-to-noise ratio. The ^{129}Xe peaks moved to high fields as the temperature increased and temperature dependences of the ^{129}Xe shift referred to as the gas signal are shown in Figure 2.

As shown in Figure 2, the ^{129}Xe NMR shift of 291 ppm for xenon confined in 5A at 168 K in the present study is very close to that for liquid xenon in free space. As the temperature increased, the ratio of xenon confined in pores of 5A decreases relative to the gas in free space decreased owing to adsorbed and gas phase equilibrium. The ^{129}Xe shift moved to a higher field because of the larger contribution of xenon in free space or the decrease in the residence time and/or number of xenon atoms inside the pore. The xenon atoms trapped in the 5A pores at 173 K gradually moved to free space as the temperature increased. The residence time and number of xenon atoms in the pores decreased exponentially, and also the ^{129}Xe shift

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moved to the higher field side exponentially. The ^{129}Xe shift can be assumed to be proportional to the number of resident xenon atoms in the 5A pores under atmospheric pressure.

The pore diameter of 13X is designed to be larger than that of 5A and is about 1 nm. The possible number of xenon atoms that enter a 13X pore is two. At 168 K the 13X can trap two xenon atoms in a pore and with the temperature increase, a xenon atom moved to free space. The xenon gas in the 13X pore can move more freely in a wider space than that in the 5A pore. The temperature-dependent shift of ^{129}Xe NMR for the molecular sieves 5A and 13X under atmospheric pressure can be interpreted consistently by adsorbed and gas phase equilibrium.

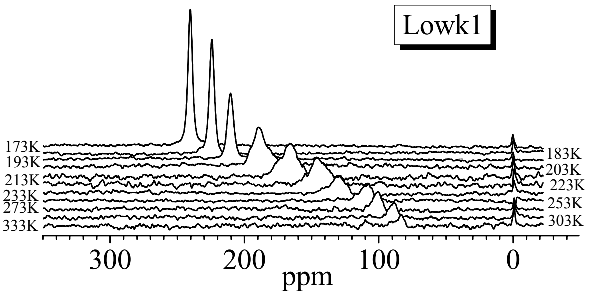

Fig. 1. ^{129}Xe NMR spectra of Lowk1.

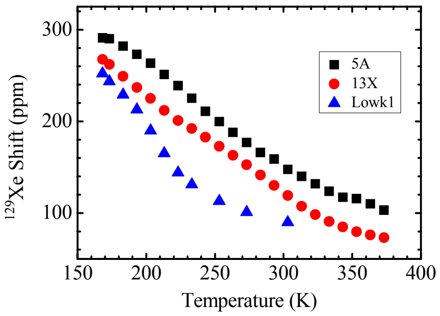

Fig. 2: ^{129}Xe shifts of 5A, 13X and Lowk1.

Different from the molecular sieves, (1) Lowk1 contains no high-concentration paramagnetic metal impurities and (2) its pores are two-dimensional hexagonally ordered cylindrical and about 2 nm in diameter. The ^{129}Xe shift of Lowk1 at 168 K showed a field (15 ppm) slightly higher than that of 13X, and the differences increased as the temperature increased (about 60 ppm between 233 and 283 K) and again decreased. Above 353 K, the ^{129}Xe shifts of 13X and Lowk1 were coincident. Since the pore diameters of Lowk1 is larger than that of 13X, the number of xenon atoms absorbed in the Lowk1 pores should decrease faster as the temperature increases. The steeper decrease in ^{129}Xe shift (higher field shift) with the temperature corresponds to the quicker decrease in the number of resident xenon atoms in the Lowk1 pores between 183 and 253 K. The number of resident xenon atoms decreased gradually as the temperature increased above 260 K.

4. Conclusions

A ^{129}Xe NMR study on mesoporous materials under atmospheric pressure has been carried out. The combined use of UHV treatment and ^{129}Xe NMR techniques at atmospheric pressure enables the estimation of the size and distribution of pores by chemical shift measurement. The present method proposed for the evaluation of nanoparticles, permselective membranes and mesoporous materials for achieving low-dielectric constant is efficient in determining the overall pore structures of whole samples in addition to the local structures.

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