NMR studies on supercritical fluids in nanoporous materials*  

Yusuke Hiejima, Mitsuhiro Kanakubo,† Kimitaka Minami, Taka-fumi Aizawa, Hiroshi Nanjo, and Yutaka Ikushima  
Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan.  
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d_{c} = 5.84 \text{MPa} and 
T_{c} = 289.7 \text{K}, P_{c} = 5.84 \text{MPa} and 
d_{c} = 1.10 \text{g cm}^{-3} \text{[5]. The critical point is close to that of \carbon dioxide, and the supercritical condition is experimentally accessible. Moreover,} \text{129}^{_{\text{Xe}}} \text{NMR spectroscopy has advantages of relatively high sensitivity and wide variation of the chemical shift. Then, confined Xe could be for a model system for micro- and nanofluidics, where supercritical carbon dioxide might be utilized instead of the conventional organic solvents.  
In this work,} \text{129}^{_{\text{Xe}}} \text{NMR spectroscopy is applied to investigation of fluid Xe confined in porous glasses. The chemical shift of confined Xe is obtained in a wide range of density from the gas phase to the liquid phase including the supercritical region. By varying the pore diameter and the surface functional groups of the matrices, the size and the surface effects on confined Xe are discussed.}

II. EXPERIMENTAL

A Controlled-Pore Glass (CPG), which is a porous silica glass, was used as the matrix. The CPG provided as 80-120 mesh powder was purchased from Sigma Aldrich Co. Ltd. The physical properties of the CPG were listed in Table I. The CPG and the surface-modified CPG (CPG-Me) were treated as follows. The CPG was washed in nitric acid and rinsed by distilled water for several times, and then, dried at 423 K for one hour. The surface of the purified CPG was modified by the silylation procedure with hexamethyldisilazane [6], where the surface hydroxyl groups were converted to trimethylsilyl groups. Note that the silylation procedure does not significantly affect the pore size distribution [6, 7]. Each matrix (CPG or CPG-Me) was filled in a capillary tube, where one end of the tube was sealed and the other end was open and capped by filling pure quartz wool. The matrices filled in capillary tubes were dried again at 423 K for one hour, and three capillary tubes were installed in the sample cell. The chemical shifts are simultaneously obtained for Xe confined in three different matrices, as well as for bulk Xe.

129\text{Xe} \text{NMR spectra were obtained with a spectrometer Varian Inova 500. A high-pressure NMR sample cell [8] was made of a poly(etherether ketone) tube of 10 mm diameter and a titanium cap. The sample cell was connected to a syringe pump (ISCO260D), which was used for compression of pure Xe (99.995%, Japan Fine Products Corp.). The pressure was monitored by a digital pressure indicator (Druck DPI 145), where the uncertainty was less than \pm 0.1 \text{MPa}. The NMR measurements were carried out along the isotherm of 300 K up to 15 \text{MPa}. The sample temperature was determined in advance with a calibrated thermometer (Takara D641) with a precision of \pm 0.1 \text{K.}
TABLE I: Physical parameters for the Controlled-Pore Glasses (Provided from the manufacturer).

| CPG   | Mean pore size / nm a | Pore volume / cm³ g⁻¹ | Surface area / m² g⁻¹ |
|-------|-----------------------|------------------------|-----------------------|
| CPG75 | 7.5 (±6.0)            | 0.47                   | 140                   |
| CPG120| 11.5 (±7.3)           | 0.49                   | 119.5                 |
| CPG240| 22.6 (±6.2)           | 0.85                   | 94                    |

aThe numbers in parentheses denote the pore distribution in %.

FIG. 1: Density dependence of the observed chemical shifts at 300 K. The chemical shifts of Xe confined in the CPGs with various pore sizes are denoted by closed symbols. The open symbols denote the chemical shifts of bulk Xe, which agree well with the reported values at 298 K [9] represented by the solid line. The critical density is also depicted by the arrow.

FIG. 2: Density dependence of the chemical shift, δ_conf, of confinement for the CPG (open symbols) and the CPG-Me (closed symbols) at 300 K.

III. RESULTS AND DISCUSSION

In Figure 1, the chemical shifts of bulk and confined Xe are plotted as a function of density. Here we set the chemical shift of bulk Xe at the dilute limit to zero. The error bars estimated from the spectral widths are also shown. The observed chemical shift, δ_obs, of bulk Xe is approximately linear to density, and the density dependence agrees well with the reported one [9]. The observed chemical shift, δ_conf, of Xe confined in the CPG is appreciably larger than that of δ_obs. In the gas phase, δ_conf shows significant upward deviation from δ_obs. Above the critical density, the upward deviation becomes smaller, and approaches zero at the high density limit. These behaviors of δ_conf may be explained by the interactions of Xe, that is, the intermolecular interaction (fluid-fluid interaction) and the interaction to the wall (fluid-wall interaction). In the gas phase, where the fluid-wall interaction is more important, the chemical shift is much enhanced for the CPG than the CPG-Me, because the surface hydroxyl groups interact with Xe molecules more strongly than the trimethylsilyl groups. Above the critical density, where the fluid-fluid interaction is more important, the surface effect becomes very small, while the size effect persists even in the liquid state. The maximum of δ_conf is located at ~0.2 g cm⁻³ for the CPG, and at ~0.5 g cm⁻³ for the CPG-Me. This apparent shift of the maximum due to the surface modification is a consequence of the change in the fluid-wall interaction.

To discuss the effect of confinement, we define the chemical shift, δ_conf, of confinement by

\[ \delta_{\text{conf}} = \delta_{\text{obs}} - \delta_{\text{bulk}}. \]

In Figure 2, δ_conf for the CPG and the CPG-Me is shown as a function of density. In the dilute gas region, δ_conf increases with density, and has a maximum below d_c. At high densities, δ_conf gradually decreases with increasing density, and approaches zero at the high density limit. These behaviors of δ_conf may be explained by the interactions of Xe, that is, the intermolecular interaction (fluid-fluid interaction) and the interaction to the wall (fluid-wall interaction). In the gas phase, where the fluid-wall interaction is more important, the chemical shift is much enhanced for the CPG than the CPG-Me, because the surface hydroxyl groups interact with Xe molecules more strongly than the trimethylsilyl groups. Above the critical density, where the fluid-fluid interaction is more important, the surface effect becomes very small, while the size effect persists even in the liquid state. The maximum of δ_conf is located at ~0.2 g cm⁻³ for the CPG, and at ~0.5 g cm⁻³ for the CPG-Me. This apparent shift of the maximum due to the surface modification is a consequence of the change in the fluid-wall interaction.

The fluid-fluid interaction is also affected by confinement, because the local density of Xe is somewhat different from the bulk density. For gaseous Xe in various zeolites, the chemical shift of confined Xe, which is also significantly larger than that of bulk Xe, is a linear function of the amount of adsorption [1]. Even at high densities near the supercritical region, chemical shift of Xe confined in zeolites is described in terms of the Langmuir’s
In Figure 3, $\delta_0$ is plotted against the pore diameter in a double logarithmic plot together with those for the FSM-16 [10] and the Vycor glass [13]. Although the porous structures are different between porous glasses and mesoporous silica, a single curve is obtained for these silica materials. These results are consistent with the correlation for Xe at $\sim$0.1 MPa confined in various silica materials [14]. In Figure 3, the dotted line represents $\delta_0$ for zeolite with a shape of cylinder of infinite length, which is estimated from the empirical relation [15]. Although the line does not coincide with that for the silica materials, the gradient of the curve below 3 nm is similar.

By replacing the surface hydroxyl groups by the trimethylsilyl groups, $\delta_0$ decreases by $\sim$10, which depends little on the pore size. One might think that the pore size of the CPG-Me is smaller than the CPG, however, such reduction of the pore diameter should increase the chemical shift. Then, the lower shift of $\delta_0$ is explained by the surface effect. For the Vycor glass [13], which has strongly adsorptive surface, $\delta_0$ is larger by $\sim$25 than other mesoporous silica materials. Note that we have also found that $\delta_0$ for the Vycor glass before the activation process, by which adsorbed substances are removed, is smaller by $\sim$30% than that for the Vycor glass. Then, $\delta_0$ is a measure of the surface condition of the porous materials, as well as the pore diameter.

**IV. CONCLUSION**

$^{129}$Xe NMR spectroscopy is applied to investigation of Xe confined in the Controlled-Pore Glass (CPG) and the surface-modified CPG. The chemical shifts of bulk and confined Xe are obtained simultaneously up to the supercritical region. The density dependence of the chemical shift for confined Xe is affected by the matrix. Below the critical density the both of the size and surface effects are observed, while the surface effect becomes minor and the size effect persists above the critical density. The chemical shift of confined Xe at the dilute limit depends on the surface potential of the matrix, as well as the pore size.