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Phase transition of capillary condensed liquids in porous silica: effect of surface hydroxyl groups¹

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Abstract

Phase transition temperatures of capillary condensed organic liquids in porous silica were measured using a 1020/DSC system (Perkin-Elmer Ltd.). The amounts and types of hydroxyl groups on the sample surfaces were precisely controlled to discuss the surface effect on the phase transition temperature. The melting point of the solid phase of benzene in the pores decreased with increasing concentration of the surface hydroxyl groups. On the other hand, in the case of n-hexane, such an effect was not observed. From these results, it is assumed that the liquid structure of capillary condensed benzene in the pores changes with the amounts and types of surface hydroxyl groups. This consideration is confirmed from IR spectroscopy.

Keywords: Phase transition; Capillary condensed liquid; Silica; Surface hydroxyl group

1. Introduction

The physical properties and structure of capillary condensed liquid in a small pore are different from those of bulk liquid [1,2]. For example, the density [3] and heat capacity [4] of water confined in silica pores change as a function of pore size. It is suggested that the physical properties and structures of capillary condensed liquid in a pore are affected by surface forces of a solid. Thus, the degree of change in the physical properties and structures of capillary condensed liquid in a pore reflects the strength of the interaction between capillary condensed liquid and a solid surface.

Porous silica materials are generally used as an adsorbent. It is well known that adsorption properties of silica materials remarkably change with their surface structure [5–

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7]: pore size, pore shape and the amounts or types of functional groups. In the case of silica, the hydroxyl groups on the surface mainly dominate the adsorption properties. Therefore, the physical properties and structures of capillary condensed liquid in silica pores are expected to change with not only pore size but the amounts and types of surface hydroxyl groups. The physical properties and structures of capillary condensed liquids in pores gives useful information on adsorption or separation procedure and to clarify various surface phenomena. In many studies, the physical properties and structures of capillary condensed liquids in pores have been discussed in correlation with the pore size rather than the surface chemical properties of solids [1,2,8]. In this study, the surface hydroxyl groups of the samples were precisely controlled, and the phase transition temperature of capillary condensed organic liquids in these surface modified pores was measured using a DSC system. The effects of surface hydroxyl groups on the phase transition temperatures of capillary condensed organic liquids have been investigated.

2. Experimental

2.1. Sample preparation

Porous silica samples were prepared by pressing amorphous silica powders (Aerosil, A-200, Nippon Aerosil Ltd). Both the amounts and types of surface hydroxyl groups were controlled by heat treatment, rehydroxylation after the heat treatment and surface modification. Heat treatment of the samples was achieved by degassing at 773–1273 K for 2 h under reduced pressure. Under this process, hydrogen-bonded surface hydroxyl groups were eliminated and siloxanes were formed. Rehydroxylation of siloxanes was accomplished by exposing the samples to the atmosphere or high relative humidity (95% RH). Surface modification was carried out by reaction between hexamethyldisilazane (HMDS) molecules and surface hydroxyl groups. The hydroxyl groups were replaced with trimethylsilyl groups by refluxing the mixture of the silica sample and HMDS in *n*-hexane solvent for 72 h. Surface areas and pore size distributions of the samples were calculated from adsorption and desorption isotherms of nitrogen at 77 K using the Brunauer–Emmett–Teller [9] and the Cranston–Inkley methods [10], respectively. The concentration of surface hydroxyl groups was determined from the reaction of the Grignard reagent with surface hydroxyl groups (active hydrogen) on silica samples. Benzene and *n*-hexane were employed as adsorbates. These molecules are not chemisorbed on the silica surface in the present experimental condition and evolve heat large enough to be measured when the phase transition occurs. To avoid contamination by water molecules, the heat-treated samples were degassed at the corresponding heat-treated temperature, and the trimethylsilylated samples were degassed at 473 K, in a glass tube attached with a breakable seal and the organic liquids were directly introduced into the sample tube through the breakable seal.

2.2. Calorimetric measurement

The phase transitions of capillary condensed liquids were measured using a 1020/DSC system (Perkin-Elmer Ltd.) in the temperature range 213–303 K for benzene and 123–

Table 1
Surface properties of SiO₂ samples

| No. | Pretreatment temperature/K | Treatment | <i>N</i> / –OH nm ⁻² | Types of OH groups | Pore radius/ nm |
|-----|----------------------------|------------------------------|------------------------------------|-----------------------|--------------------|
| 1 | 473 | – | 2.3 | Free + H-bond | 8.4 |
| 2 | 673 | – | 1.4 | Free + H-bond | 8.4 |
| 3 | 1273 | – | 0.7 | Free | 7.8 |
| 4 | 1273 | Rehydroxylation | 2.6 | H-bond + free | 7.8 |
| 5 | 723 | Silylation + rehydroxylation | 1.3 | H-bond | 9.6 |
| 6 | 473 | Silylation | 1.6 | H-bond + free | 10.3 |
| 7 | 473 | Silylation | 2.2 | H-bond + free | 9.5 |

213 K for n-hexane. The cooling and heating rate were 5 K min⁻¹. The samples (ca. 5 mg) were sealed using aluminum pans and covers. The phase transition temperatures were determined by extrapolation of a peak curve of melting in the heating process.

2.3. IR spectral measurement

IR spectra were obtained using a Fourier transform spectrometer (Nicolet system-800). Self-supporting silica pellets were mounted in a glass cell which can be evacuated and heated.

3. Results and discussion

3.1. Characterization of samples

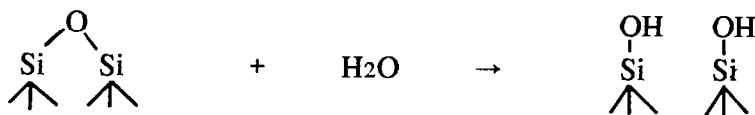
Characterization of samples prepared are summarized in Table 1. The amount of hydroxyl groups were controlled to be in the range from 2.6OH to 0.7OH nm⁻². The surface hydroxyl groups are mainly classified into two types: free (no hydrogen bonding) and hydrogen-bonded hydroxyl groups. These types are distinguishable from the IR spectra measurement of the OH stretching vibration. The IR spectra of samples 1, 3 and 5 are shown in Fig. 1. Sample 1 shows two peaks. A sharp band at 3747 cm⁻¹ is assigned to free hydroxyl groups and the other broad band near 3600 cm⁻¹ is attributed to hydrogen-bonded hydroxyl groups. These two types of hydroxyl groups can be controlled by the above three methods: heat-treatment, rehydroxylation and trimethylsilylation.

3.1.1. Heat treatment

The heat treatment preferentially eliminates the hydrogen-bonded hydroxyl groups and finally leaves the free type hydroxyl groups on the surface. Sample 3 whose surface has only free hydroxyl groups is obtained by this heating method.

3.1.2. Rehydroxylation

Siloxane surface prepared by heat treatment is rehydroxylated with water vapor as follows:



The resulting hydroxyl groups produced are adjacent to each other, so these groups can form hydrogen bonds.

3.1.3. Trimethylsilylation

It is known that the free hydroxyl groups react with HMDS reagent preferentially compared with hydrogen-bonded hydroxyl groups [11]. In the case of sample 5 which was obtained by treatment with HMDS, the broad band close to 3600 cm^{-1} was observed and the band at 3747 cm^{-1} disappeared. Absorption bands near 3000 cm^{-1} were assigned to the CH stretching vibration of trimethylsilyl groups introduced by surface modification. From these results the surface of sample 5 has only hydrogen-bonded hydroxyl groups without free type hydroxyl groups and trimethylsilyl groups.

Using the IR spectra method described above the types of surface hydroxyl groups on the samples used in this study are classified as follows: (1) samples 1 and 2 have both free hydroxyl groups and hydrogen-bonded hydroxyl groups; (2) sample 3 has only free hydroxyl groups; (3) sample 5 has only hydrogen-bonded hydroxyl groups, and (4) samples 4, 6 and 7 have mainly hydrogen-bonded hydroxyl groups.

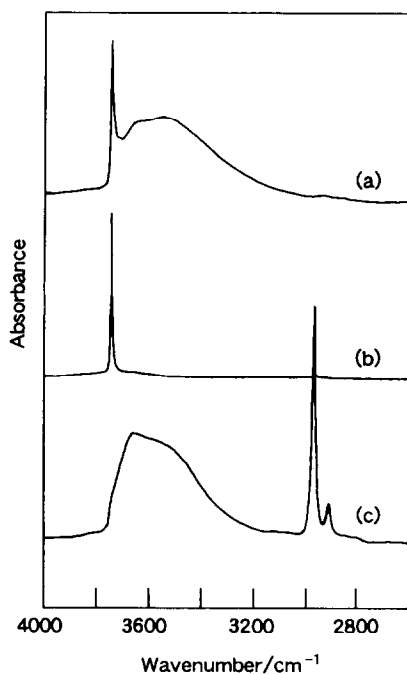


Fig. 1. The IR spectra of typical silica samples. (a) Evacuated at 473 K (sample 1). (b) Evacuated at 1273 K (sample 3). (c) Trimethylsilylation after evacuation at 723 K (sample 5).

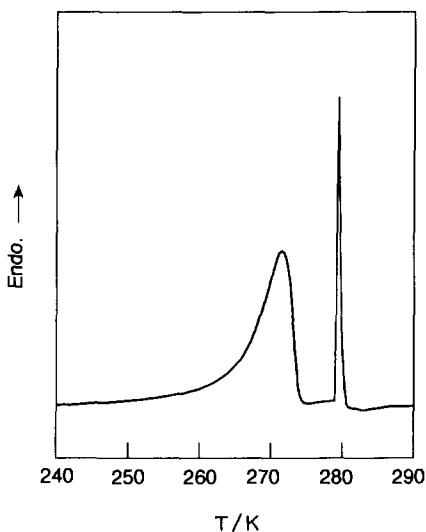


Fig. 2. A typical DSC curve of the phase transition of benzene in the silica pore.

The pore size distribution curves of all samples are monodispersed shapes and their peak values are summarized in Table 1. The pore radius values of the samples are slightly different from each other. It is thought that the pore size was varied by sintering at high temperature treatment by which the nature of the packing of silica powder was changed.

3.2. Phase transition of the solid phase in a pore

A typical DSC curve during the melting process is shown in Fig. 2. The phase transition is a change from solid to liquid state of benzene. Two peaks due to the phase transition (melting) were observed. The temperature of the peak observed in the high temperature region almost coincided with the melting point of the bulk solid, thus this peak is regarded as the melting of the solid formed on the outer surface of the sample. The other peak in the low temperature region is attributed to the melting of the solid formed in the pore. For all samples, the melting temperatures of the solid phase in the pores are lower than those of the bulk solid phase. The difference between the melting point of the solid phase in the pore and that of the bulk solid phase is defined as ΔT_{tr} . It is well known that the phase transition temperatures of capillary condensed liquids markedly depend on the pore size. A linear relationship between the phase transition temperature and the reciprocal of the pore radius has been reported [12]. The decrease in ΔT_{tr} of the freezing or melting point is theoretically presented in the following equation:

$$\Delta T_{tr} = -(2\gamma_{sl}V_m T_0 \cos \theta) / r\Delta H_m \quad (1)$$

where V_m is the molar volume of the liquid, T_0 is the phase transition temperature of bulk

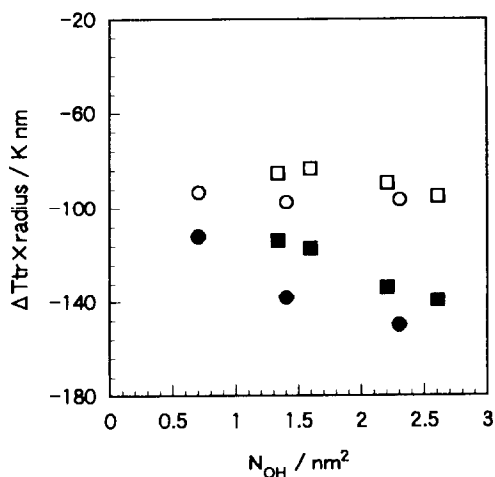


Fig. 3. The relationship between $\Delta T_{tr} \times r$ and the content of surface hydroxyl groups. □, n-hexane (mainly hydrogen-bonded hydroxyl groups); ○, n-hexane (mainly free hydroxyl groups); ■, benzene (mainly hydrogen-bonded hydroxyl groups); ●, benzene (mainly free hydroxyl groups).

liquid, r is the pore radius, ΔH_m is the mole enthalpy of melting, γ_{sl} is the liquid-freezing solid interfacial tension, and θ is the contact angle between the interfacial surface and the pore wall.

The product of $\Delta T_{tr} \times r$ shows a constant value, and it is concluded that the pore radius is a dominant factor to the phase transition temperature. In Fig. 3 $\Delta T_{tr} \times r$ is plotted as a function of the concentration of the surface hydroxyl groups on the samples. In the case of n-hexane, the values of $\Delta T_{tr} \times r$ are approximately constant. Therefore, ΔT_{tr} depends on the pore radius and is independent of the surface hydroxyl groups. On the other hand, as for benzene, the values of $\Delta T_{tr} \times r$ change with the concentration of the surface hydroxyl groups. The phase transition temperature of capillary condensed benzene decreases with increasing concentration of the surface hydroxyl groups. From this result, it is concluded that the surface hydroxyl groups affect the liquid properties of capillary condensed benzene in the pore. The difference in the interaction between adsorbed molecules and the surface hydroxyl groups is attributed to such differences in the phase transition described above. It is supposed that the interaction of benzene molecules with the surface hydroxyl groups is greater than that of n-hexane molecules. Furthermore ΔT_{tr} depends on not only the concentration of the surface hydroxyl groups but the types of surface hydroxyl groups (free and hydrogen-bonded). That is, the interaction of benzene molecules with the surface free hydroxyl groups is greater than that with the hydrogen-bonded hydroxyl groups.

3.3. Interaction of adsorbed molecules with surface hydroxyl groups

The interactions of adsorbed benzene and n-hexane molecules with surface hydroxyl groups were investigated measuring the IR spectra. Fig. 4 shows the IR spectra of benzene and n-hexane adsorption on a silica surface which has only free hydroxyl groups.

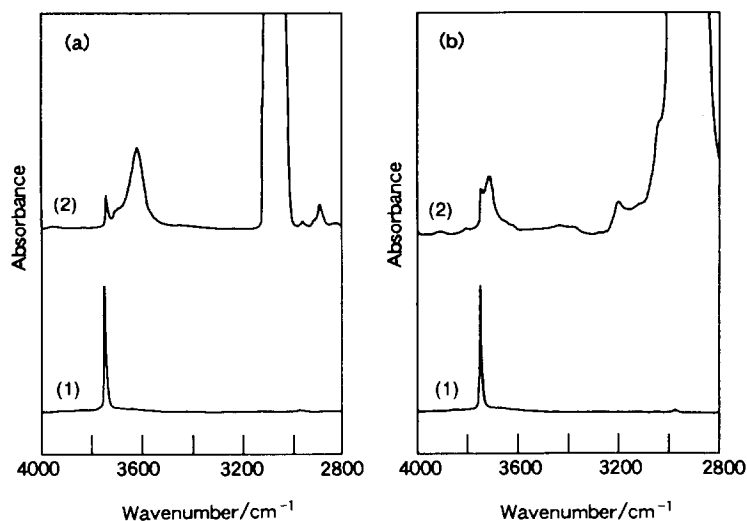


Fig. 4. The IR spectra of adsorptions of (a) benzene and (b) n-hexane on the silica surface containing only free hydroxyl groups; (1) before adsorption and (2) after adsorption.

The sharp band at 3747 cm^{-1} is attributed to the O–H stretching band of free hydroxyl groups. By adsorption of benzene molecules, this band largely decreased and new bands appeared. The lower band at 3620 cm^{-1} is attributed to perturbed hydroxyl stretching band and bands around 3000 cm^{-1} are assigned to C–H stretching bands of benzene molecules. In the case of n-hexane, the perturbed hydroxyl band appears at 3712 cm^{-1} . The shift amounts of the O–H stretching band of free hydroxyl groups, $\Delta\nu_{\text{OH}}$, are found to be 127 cm^{-1} for benzene adsorption and 35 cm^{-1} for n-hexane adsorption. The appearance of the perturbed hydroxyl bands by the adsorptions suggests the existence of interactions between hydroxyl groups and adsorbed molecules. Galkin et al. [13] reported that the heat of adsorption of benzene and several alkyl benzene derivatives on silica surface related to $\Delta\nu_{\text{OH}}$. The perturbed hydroxyl band shifts to lower wavenumbers with increasing interaction strength of adsorbed molecules with surface hydroxyl groups. Consequently, the magnitude of the interaction of benzene molecules with surface hydroxyl groups is greater than that of n-hexane molecules. Considering both n-hexane and benzene molecules do not possess a permanent dipole moment, the interactions of these molecules with surface hydroxyl groups are mainly a dispersion force. A small difference in polarizability between benzene ($1.032 \times 10^{-23}\text{ cm}^{-3}$) and the n-hexane molecule ($1.208 \times 10^{-23}\text{ cm}^{-3}$) cannot explain the large difference in the interaction of these molecules with surface hydroxyl groups. In the case of the benzene molecule, it is expected that π electrons of a benzene molecule interact with surface hydroxyl groups. Fig. 5 shows the IR spectra of benzene and n-hexane adsorption on a silica surface which has only hydrogen-bonded hydroxyl groups. The broad band near 3600 cm^{-1} is characteristic of hydrogen-bonded hydroxyl groups and the two bands close to 2900 cm^{-1} are attributed to the C–H stretching band of surface trimethylsilyl groups introduced by the modification. New bands near 3100 cm^{-1} produced by benzene adsorption are assigned to the C–

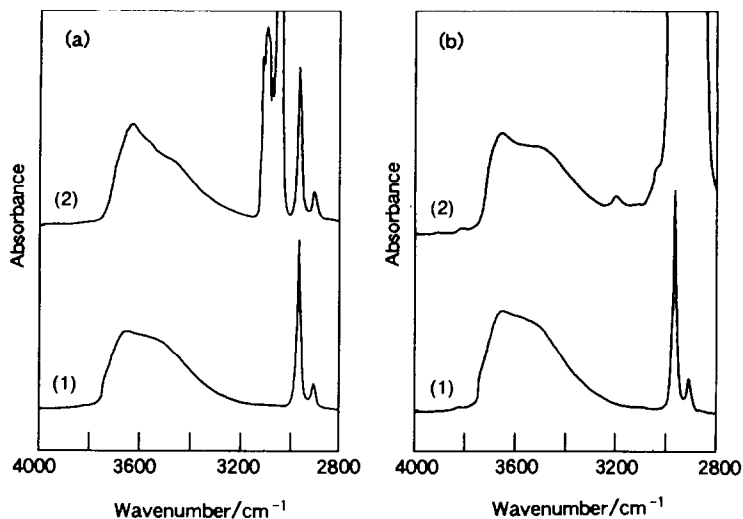


Fig. 5. The IR spectra of adsorptions of (a) benzene and (b) n-hexane on the silica surface containing only hydrogen-bonded hydroxyl groups: (1) before adsorption and (2) after adsorption.

H stretching bands of benzene molecules. Distinctly perturbed hydroxyl stretching bands are not recognized in both case. However, in the case of benzene adsorption, the peak value of the hydrogen-bonded hydroxyl band slightly shifted to the lower wavenumber region by about 30 cm^{-1} . Therefore, benzene molecules strongly interact with the free hydroxyl groups compared with the hydrogen-bonded hydroxyl groups. Since the C–H stretching bands close to 2900 cm^{-1} assigned to surface trimethylsilyl groups are not perturbed by benzene adsorption, the interaction of benzene molecules with trimethylsilyl groups is considered to be very weak.

3.4. Effect of surface hydroxyl groups on phase transition

As described above benzene molecules interact specifically with surface hydroxyl groups and the melting point of the solid phase of benzene in the silica pore decreases with the concentration of surface hydroxyls. The effect of surface hydroxyl groups on the phase transition of benzene in the silica pore is discussed by the change in the physical properties and structures of capillary condensed benzene. According to Eq. (1), the following values, γ_{sl} , V_m and θ , of capillary condensed benzene must change with the concentration of the surface hydroxyl groups. The contact angle between the interfacial surface and the pore wall will be regarded as zero, and the value is considered to be independent of the concentration of surface hydroxyl groups. Consequently γ_{sl} and V_m values of capillary condensed benzene in the silica pore are assumed to increase apparently with increasing concentration of surface hydroxyl groups. Molar volume (V_m) and interfacial tension (γ_{sl}) of a liquid are sensitive to the liquid structure. The increase in the value of the molar volume means a decrease in density. Therefore, it can be presumed that the

liquid structure of condensed benzene in the silica pore changes due to the interaction between π electrons and the hydroxyl groups. That is, benzene molecules in the vicinity of the silica surface are oriented to the surface and the degree of orientation depends largely on the concentration and the types of hydroxyl groups.

4. Conclusion

The phase transitions of capillary condensed liquids in silica pores were investigated using n-hexane and benzene. The melting point of the solid phase in silica pores was affected not only by the pore radius but also the surface chemical properties. In the case of benzene, the melting point decreased with increasing concentration of the surface hydroxyl groups. It is supposed that the specific interaction between π electrons of a benzene molecule and surface hydroxyl groups changes the liquid structure of capillary condensed benzene and causes the decrease in the melting point.

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