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Heat of immersion of amorphous and crystalline silicas in water: effect of crystallinity[1]

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Abstract

The origin of the difference in the heat of immersion in water between amorphous and crystalline silicas has been studied. We have investigated the effect of crystallinity of silicas on the heat of immersion. The degree of crystallinity was controlled by heating a amorphous silica with sodium chloride appropriate time. The heat of immersion closely depended on the crystallinity. The IR spectra of surface hydroxyl groups revealed that the increase in the heat of immersion with the crystallinity was attributed to the increase in hydrogen-bounded hydroxyl groups. It is concluded that a regular arrangement of the hydrogen-bounded hydroxyl groups on the crystalline silica surfaces stabilizes adsorbed water layer extensively and causes the increase in the heat of immersion compared to that of amorphous silicas. © 1998 Elsevier Science B.V.

1. Introduction

The interaction between water molecules and silica surfaces has been studied by numerous researchers using calorimetry [1], infrared spectroscopy [2], dielectric measurement [3], nuclear magnetic resonance [4], neutron scattering [5] and quantum mechanical calculations [6]. The heat of immersion of silicas in water is one of useful physical properties which represents strength of the interaction between water molecules and silica surfaces. A large number of the heats of immersion of various silicas in water have been reported [7–9]. The effects of surface hydroxyls [10,12] and particle size [12,13] of silicas on the heat of immersion have been also discussed. Though the difference in the heats of immersion of amorphous and crystalline silicas in water has been pointed out [7,10,14], the origin of the difference is not clear yet. Crystalline silica powders generally have a low surface areas, so these powders are not worthy as adsorbents, and there is little information on the surface of crystalline silicas. Recently the difference in surface properties of amorphous and crystalline silicas was studied by measurement of water adsorption enthalpy and quantum mechanical calculations [15]. Most of crystalline silica powders are prepared by grinding, so the existence of amorphous layer and some defects produced at surface cause a difficulty in systematic studies of crystalline silica surface. In this study crystalline silicas were prepared by crystallization of amorphous silica without grinding and the effect of crystallinity of silicas on the heat of immersion in water has been investigated.

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2. Experimental

The silica sample used for this study was amorphous silica powder (Tatsumori, SO-C2) which was prepared by oxidation of silicon powder and had a low surface area (7.1 m^2/g). Crystallization of the amorphous silica powder was performed by heating with 5 wt% sodium chloride at 1093 K. Control of the crystallinity was achieved by regulation of heating time. The crystallized silicas were washed with distilled water and immersed in 10%HClaq. After then, the powders were washed with distilled water and dried at 383 K. No sodium and chlorine ions at the surface of the powders were identified by X-ray photoelectron spectroscopy. Quartz powder (Tatsumori, 5X) commercially available crystalline silica, was used as a crystalline sample. Before experimental use the samples were outgassed at 473 K for 2 h under a pressure of 10^{-3} Pa. Crystallization of amorphous silica was confirmed by X-ray diffraction and degree of crystallinity was estimated from the heat of α-β transition of crystalline silicas measured by a Perkin-Elmer DSC-7 differential scanning calorimeter. The number of surface hydroxyl groups was determined by their chemical reactions with the Grignard reagent, and types of hydroxyl groups were identified by a Nicolet System 800 FTIR spectrometer using a diffuse reflectance method. Adsorption isotherms of water on the samples were measured at 293 K with a volumetric method. Surface areas of the samples were estimated by the BET method using the nitrogen adsorption at 77 K. The heats of immersion of the samples in water were measured by a Tokyo Riko MMC-5111 conduction-type microcalorimeter at 298 K.

3. Results and discussion

3.1. Relationship between heat of immersion and crystallinity

The characteristics of the heats of immersion of the samples in water are shown in Table 1. The phase of the crystallized silicas was identified as a cristobalite phase and crystallinity depended on heating time with sodium chloride. Crystallization caused a decrease in specific surface area which was due to sintering. The concentration (3.4 OH/nm^2) of the surface hydroxyl groups on the amorphous silica sample was smaller than the average value (4.9 OH/nm^2) on amorphous silicas which was reported by Zhuravlev [16]. Such small concentration of the sample is due to high temperature treatment during preparation of the sample. On the other hand, the crystallization procedure conversely enriched surface hydroxyl groups on account of the following reasons. The heating with sodium chloride enhances bond rupture of Si–O–Si network structure, so number of hydroxyl groups will be considered to increase with this bond rupture. Moreover, as the density of cristobalite (2.33 g/cm^3) is slightly greater than that of the amorphous silica (2.2 g/cm^3), the increase in the surface atom density with progress of crystallization gives rise to the increase in surface hydroxyl groups. The concentration of the surface hydroxyl groups on the crystallized silica samples (5.0–5.8 OH/nm^2) is larger than the calculated value (4.55 OH/nm^2) assuming that the sample surface consists of (100) planes of cristobalite and surface Si atoms have one OH group [17]. The difference in the surface hydroxyl groups would be attributed to the appearance of the other planes which have more surface density of atoms and formation of geminal hydroxyl groups ($=Si(OH)_2$).

The heat of immersion of amorphous silica sample was similar to those values which were measured for amorphous pyrogenic silica [10] and silica gel [11]. The heats of immersion of the crystallized silicas were larger than that of the amorphous silica, and increased with advancing of crystallinity. Generally the increase of surface hydroxyl groups is considered to cause the increment of immersion heat. However, the difference among the heats of the three crystallized samples cannot be explained by only the difference in the number of surface hydroxyl groups. Fig. 1 shows the heats of immersion of the samples in water as a function of crystallinity. The heats of immersion of the silicas steeply increased in the large of 15%–30% crystallinity and slightly increased above 30% crystallinity. The crystallite sizes of the crystallized silicas estimated from peak widths of X-ray diffraction patterns are shown in Table 1. The crystallite size increased with crystallinity. Presumably, the crystallization by heating of the samples containing sodium chloride first occurs at surface and gradually proceeds inside of the particles; therefore the crystallinity estimated from a DSC does not always indicate crystal-

Table 1
Characteristics and heats of immersion of samples

Sample	Heating time/h	S_{N_2}/(m^2/g)	S_{H_2O}/S_{N_2}	n-OH(/nm^2)	Crystallinity (%)	Crystallite size/nm	ΔH_{imm}/(mJ/m^2)
A	0	7.1	0.21	3.4	0	0	158
B	6	4.5	0.38	5.8	13.5	34	181
C	18	3.3	0.44	5.0	30.9	41	263
D	26	3.1	0.61	5.4	61.4	60	303

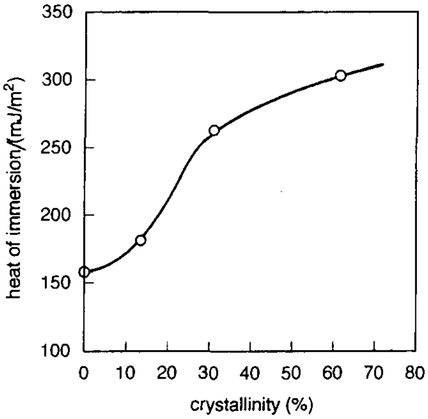

Fig. 1. Heat of immersion of silicas in water as a function of the crystallinity.

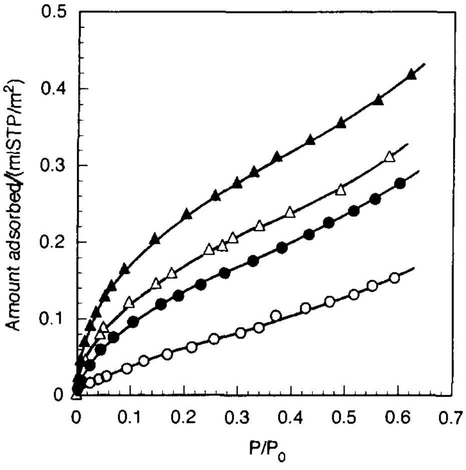

Fig. 2. Adsorption isotherms of water vapor on the amorphous and crystallized silicas at 293 K. ○, amorphous silica; ●, crystallized silica (13.5% crystallinity); △, crystallized silica (30.9% crystallinity); ▲, crystallized silica (61.4% crystallinity).

linity at surface. Since the 13.5% crystallinity sample may have small crystalline patches at the surface, the effect of crystallization on heat of immersion is small. The surface of the 30.9% crystallinity sample is considered to be almost covered with crystalline patches. Thus the effect of crystallinity markedly appeared in spite of low crystallinity. Above 30% crystallinity, the extension of crystalline patches by crystal growth contributed to slight increase in heat of immersion. The increase in heat of immersion with crystallinity is due to the change in surface structure by crystallization. Silica surfaces consist of siloxane and hydroxyl groups. Surface siloxane groups are nonpolar groups, so the interaction with water is very weak. On the other hand, surface hydroxyl groups which are polar groups strongly interact with water. The change in types of surface hydroxyls by crystallization will occur and be described later in detail.

3.2. Water adsorption properties

Hydrophilicity of the samples was investigated by measurement of water adsorption isotherms. Fig. 2 shows the water adsorption isotherms on the amorphous and crystallized silicas.The shape of the adsorption isotherm on the amorphous silica was close to Type III isotherm and those of the crystallized silicas were classified into Type II isotherm (BDDT classification [18]). The amount of water adsorbed at same relative pressure increased with increase in crystallinity. It is expected that the heat of immersion in water strongly depends on the interaction between water molecules and solid surfaces. So hydrophilicity of a solid surface is related to the heat of immersion in water. Hydrophilic character of solid surfaces is represented by the ratio of S_{H_2O} to S_{N_2}, where S_{H_2O} and S_{N_2} are the surface areas calculated from water adsorption and nitrogen adsorption, respectively. The value of 0.105 nm^2 was used as the cross-sectional area of a water molecule. The S_{H_2O}/S_{N_2} value, as well as the heat of immersion, increased with increase in crystallinity (Table 1). The heat of immersion in water as a

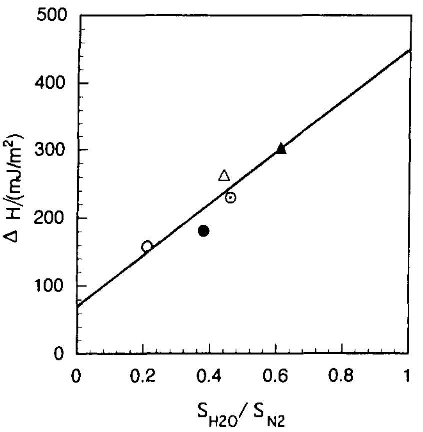

Fig. 3. Heat of immersion of various silicas in water as a function of S_{H_2O}/S_{N_2}. ○, amorphous silica; ●, crystallized silica (13.5% crystallinity); △, crystallized silica (30.9% crystallinity); ▲, crystallized silica (61.4% crystallinity); ⊙, quartz;

function of S_{H_2O}/S_{N_2} is shown in Fig. 3. The heat of immersion in water increases linearly with S_{H_2O}/S_{N_2}. The heats of immersion at $S_{H_2O}/S_{N_2} = 0$ and $S_{H_2O}/S_{N_2} = 1.0$ are estimated by extrapolation to be 73 and 444 mJ/m^2, respectively. In the case of $S_{H_2O}/S_{N_2} = 0$, silica surface consist of only siloxane groups, whereas silica surface of $S_{H_2O}/S_{N_2} = 1.0$ means fully hydroxylated silica surface. Egorov et al. [19] reported the relationship between heat of immersion of silica gel and the degree of surface hydroxylation:

$$\Delta H_{\text{imm}} = q_1 S_1 + q_2 S_2$$

where q_1 and q_2 are the heat of immersion of a perfectly dehydroxylated silica (the surface consist of only siloxane groups) and that of fully hydroxylated silica, respectively. S_1 and S_2 value are the fraction of a dehydroxylated area and a hydroxylated area, respectively ($S_1+S_2=1$). The values of q_1 and q_2 were estimated to be 50 and 250 mJ/m^2, respectively. The heat of immersion of a perfectly dehydroxylated silica (q_1) in our study was close to the value in Egrove's study. However the heat of immersion of a fully hydroxylated silica (q_2) in our study did not agree. The disagreement in the heat of immersion of a fully hydroxylated silica is considered to be attributed to the differences in the condition of substrates such as silica gel (amorphous) and crystalline silicas.

3.3. Change in surface hydroxyl groups by crystallization

The surface hydroxyl groups on silicas play a important role in interaction with water molecules. The change in the heat of immersion of silicas with crystallinity will relate to the change of the type of surface hydroxyls by crystallization. The surface hydroxyl groups on silicas are classified into two types: (1) free (non-hydrogen bonded) hydroxyl groups (abbreviated as OH$_f$ groups), (2) hydrogen bonded hydroxyl groups (abbreviated as OH$_b$ groups). Infrared spectroscopy is easy to distinguish the difference between these two hydroxyl groups. Fig. 4 shows the infrared spectra of the amorphous silica, crystallized silicas and quartz in the region of hydroxyl stretching vibration. All samples had relatively sharp peaks about 3740 cm^{-1} corresponding to the OH$_f$ groups and broad bands corresponding to the OH$_b$

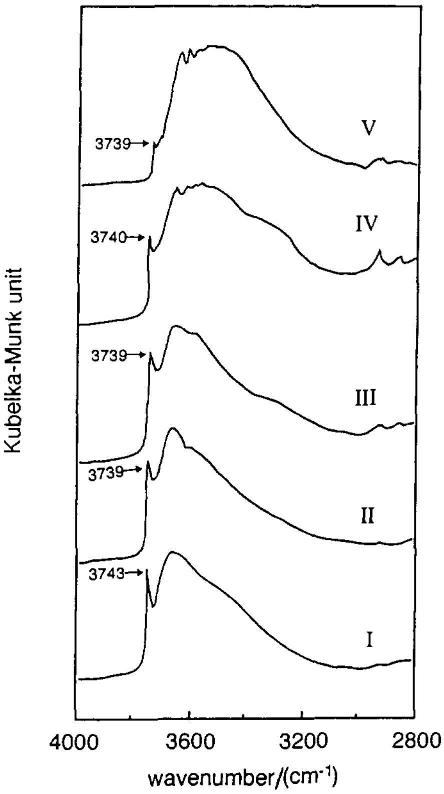

Fig. 4. FTIR spectra of (I) amorphous silica; (II) crystallized silica (13.5% crystallinity); (III) crystallized silica (30.9% crystallinity); (IV) crystallized silica (61.4% crystallinity); (V) quartz.

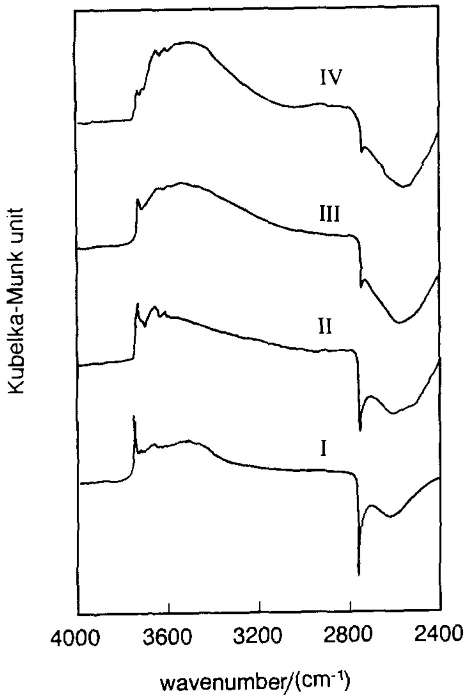

Fig. 5. FTIR difference spectra of (I) amorphous silica; (II) crystallized silica (30.9% crystallinity); (III) crystallized silica (61.4% crystallinity); (IV) quartz before and after deuterium exchange.

groups around 3600 cm^{-1}. By the crystallization, the peak of the OH_f groups observed on the amorphous silica sample shifted to slightly lower wavenumber and the band corresponding to OH_b groups, especially in the region of lower wavenumber, grew up with increase of the crystallinity. The spectrum of the 61.4% crystallinity sample is similar to that of quartz sample. There is a possibility that the infrared spectra in Fig. 4 detect not only surface but internal hydroxyl groups which are not related to the heat of immersion in water. These two types of hydroxyl groups can be differentiated by deuterium exchange using D_2O vapor. The difference spectra of the samples before and after the deuterium exchange are shown in Fig. 5. After deuterium exchange, some hydroxyl groups which could not be exchanged with deuterium were observed. These hydroxyl groups were attributed to internal hydroxyl groups. Fig. 5 confirmed that the peak of surface OH_f groups shifted to low wavenumber and the surface OH_b groups increased with crystallinity.

The peak shift of OH_f groups was observed in quartz powder. The peak shifts of OH_f groups are attributed to two reasons. The first a peak shift of OH_f groups has been reported to depend on the relative surface coverage of OH_f and OH_b groups [20]. The shift was assigned to lateral interaction of neighboring surface hydroxyl groups. Therefore the increase in OH_b groups by the crystallization causes a peak shift of OH_f groups. The second, the change in surface structure from amorphous to crystal are considered. The stretching frequencies of surface OH_f groups have been shown to relate to the electronegativity of the atom to which OH_f groups bonded [21]. Namely, the strength of OH bonding energy is affected by the electronegativity of the Si atom. If the bond angle and bond length of Si–O–Si change with crystallization, the electronegativity of Si atom will slightly change. Consequently, a peak shift of OH_f groups occurs.

As mentioned above, the increase in the OH_b groups by the crystallization accounts for the bond rupture of Si–O–Si by heating with sodium chloride. However, types of the OH_b groups of the crystallized silicas are expected to differ from those of amorphous silicas. As crystalline silicas have a regular array of atoms, the distance between neighboring surface hydroxyl groups is relatively constant. If the neighboring surface hydroxyl groups can form hydrogen bonds each other (actually the distance between neighboring surface hydroxyl groups on (100) planes of cristobalite enables to form hydrogen bonds [22]), long chains of hydrogen-bonded hydroxyl groups are formed extensively. The peak shift of the OH_b groups to low wavenumber by the crystallization means that the hydrogen-bonding energy is increasing with crystallinity.

3.4. Mechanism of adsorption of water on silica surface

Fig. 6 shows the adsorption isotherms of water on the amorphous and crystallized silicas. In this figure the amount of water adsorbed was represented with the number of adsorbed water molecules per one hydroxyl group. The adsorption isotherm of the 13.5% crystallinity sample, which exhibited slight increase of immersion heat by the crystallization, is similar to that of the amorphous silica. In spite of the

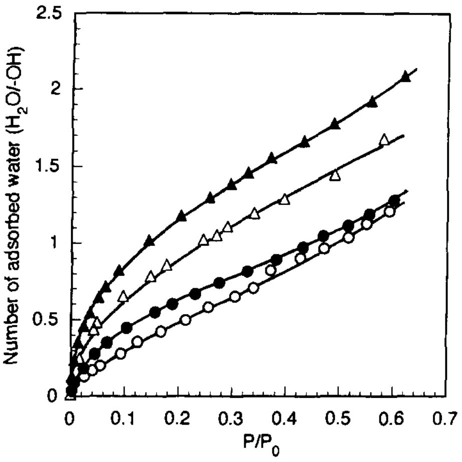

Fig. 6. Adsorption isotherms of water vapor on the amorphous and crystallized silicas at 293 K. ○, amorphous silica; ●, crystallized silica (13.5% crystallinity); △, crystallized silica (30.9% crystallinity); ▲, crystallized silica (61.4% crystallinity).

increase in hydroxyl groups by the crystallization, adsorption mechanism of water on the 13.5% crystallinity sample is analog to that of the amorphous silica. The two silicas have the similar type of surface hydroxyl groups. In contrast, the adsorption isotherms of the 30.9% and 61.4% crystallinity samples, which exhibited large increase of immersion heat by the crystallization, are different from that of the amorphous silica. This means that adsorption mechanism of water on hydroxyl groups changed by progress in the crystallization.

As water molecules interact strongly with OH_b groups rather than OH_f groups [23] the increase in OH_b groups by the crystallization is responsible for the increase in the heat of immersion. A water molecule forms only a single hydrogen bond with OH_f groups, whereas a water molecule can form two hydrogen bonds with OH_b groups (Fig. 7) at low surface coverage. OH_b groups have less ability of hydrogen bond to some organic adsorbates than OH_f groups because of forming strong hydrogen bonds one another [24]. However, water molecules can such break the hydrogen bonds among OH_b groups and can form again hydrogen bonds to hydroxyl groups. The structure of water adsorbed layer will change to more stable structure at high surface coverage, because adsorbed water molecules interact each other. Fig. 8 shows the IR spectra of the amorphous silica and crystallized silica sample C before and after adsorption of water.

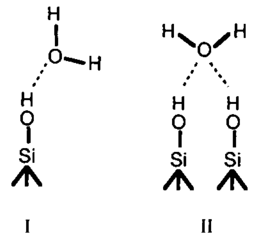

Fig. 7. Adsorption mechanism of a water molecule on hydroxyl groups. (I) free hydroxyl group; (II) hydrogen-bonded hydroxyl group.

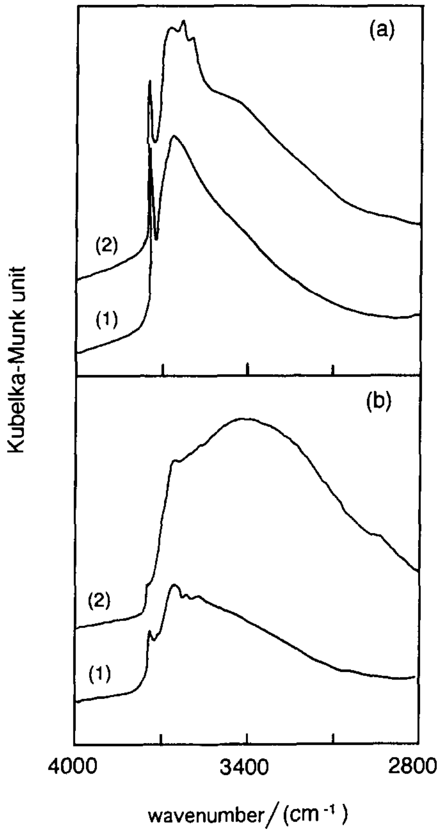

Fig. 8. Change in FTIR spectra of (a) amorphous silica; (b) crystallized silica (30.9% crystallinity) before and after adsorption of water. (1) outgassed at 473 K; (2) adsorption of water at $P/P_0 = 0.5$.

After adsorption of water on the amorphous sample, the slight decrease in the peak strength of OH_f groups and slight increase in broad band of OH_b groups mean the formation of hydrogen-bond with water molecules. However, no considerable change of the band shape were observed. On the other hand, after adsorption of water on the sample C the appearance of the new broad band of OH_b groups suggests the strong hydrogen bond with water molecules. Furthermore the regularity of surface lattice of crystalline silica induce the regular long chain of surface hydroxyl groups. The surface hydroxyl groups on the crystallized or crystalline silicas may have the optimum arrangement which stabilizes adsorbed water layer extensively, so the heats of immersion of the crystallized or crystalline silicas in water is larger than those amorphous silicas.

Considering dipole–dipole interaction between water molecules and surface hydroxyl groups, the change in polarity of surface hydroxyl groups by crystallization will also contribute to the heat of immersion.

4. Conclusion

The heats of immersion of the crystallized silicas in water increased with crystallinity. The crystallization caused the change in types of surface hydroxyl groups. The crystallization enhanced the formation of OH_b groups which are different from those of amorphous silicas. The OH_b groups on crystalline silicas have a regular arrangement and form long chains. These hydroxyl groups stabilize the liquid structure of adsorbed water layer at silica surfaces and contribute to the increment of the heat of immersion of crystalline silicas compared to that of amorphous silicas.

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