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Changes in the State of Water during Phase Transformations in Silica Exposed to Water Vapor

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Abstract—In the presence of supercritical water vapor (400°C, 20–30 MPa), amorphous silica transforms to SiO_2-*X* in a few hours, then to cristobalite in 5–20 h, and finally to quartz in 10–60 h. Changes in the state of constitutional water were found to closely correlate with the structural transformations of silica. Silica structurization and water desorption were followed by mass spectrometric measurements and ^{1}H NMR and ^{29}Si NMR. The water content of silica passes through a maximum (2–2.5 wt %) early in the formation of SiO_2-*X* and then decreases to 0.5 wt % in cristobalite and 0.01–0.03 wt % in quartz. The structural transformations include silica hydroxylation accompanied by the breaking of siloxane bonds and followed by dehydroxylation and structure rearrangement. The rate of water exchange between the silica matrix and supercritical water decreases with time, while the activation energy of water outdiffusion rises. The diffusion coefficient of water in quartz is determined. The states of constitutional water in quartz and corundum prepared in the presence of supercritical water are compared.

INTRODUCTION

Heat treatment of amorphous silica in air or vacuum produces no stable silica phases even at high temperatures. It was, however, reported [1, 2] that crystallization occurred very rapidly and at much lower temperatures if silica was exposed to water in a supercritical state. At 400°C and 20–30 MPa, the crystallization of amorphous silica into quartz in the presence of minor amounts of an activator took 10–60 h. However, the mechanism underlying the influence of supercritical water on silica structurization and the relations between the state of water in the silica matrix and the phase transformations of silica remain unclear.

EXPERIMENTAL

The state of water in silica and the mechanism of silica structurization in the presence of supercritical water were assessed by kinetic thermodesorption measurements with an MI-1311 mass spectrometer and also by solid-state ^{1}H and ^{29}Si NMR.

In mass spectrometric measurements, samples were heated from 200 to 1400°C in 100 or 200°C steps under vacuum. The amounts of water and other impurities were determined by integrating ion currents with the use of experimentally determined sensitivity factors. A similar procedure was used earlier to assess the kinetics of water loss and the diffusion coefficients of water and gaseous impurities in silicate glasses, quartz, and corundum [3–5].

^{1}H NMR spectra were measured at room temperature on a Bruker WP-80 pulsed Fourier-transform spectrometer. ^{29}Si NMR spectra (^{29}Si–^{1}H cross-polarization, proton locking, magic angle spinning) were obtained with a Bruker MSL-300 spectrometer.

Amorphous SiO_2 samples (extra-pure grade) were prepared by ammonolysis of tetraethyl orthosilicate, followed by heating in an air + oxygen mixture at 900°C (SiO_2-I), or by hydrolysis of silicon tetrachloride (SiO_2-II).

RESULTS AND DISCUSSION

When exposed to water vapor at 400°C and 20–30 MPa, amorphous silica transformed first into a SiO_2-*X* phase, then into cristobalite, and finally into quartz ranging in particle size from 0.1 to 0.3 mm. In the initial stage, a small amount of keatite was present together with SiO_2-*X*. Small additions of activators (e.g., nitrogen-containing bases) are known to accelerate crystallization of amorphous silica. In the presence of such activators, amorphous silica transforms to SiO_2-*X* in a few hours, to cristobalite in 5–20 h, and to quartz in 10–60 h. The exposure to water vapor reduces the specific surface of SiO_2 from 98 to 1 m^2/g in 0.5 h

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and to 0.2–0.4 m^2/g in 10 h. The specific surface of the resulting fine-particle quartz is 0.04 to 0.06 m^2/g.

In the course of silica structurization and crystallization, water content passes through a maximum (2–2.5 wt %) early in the formation of SiO_2-*X* and then decreases to 0.5 wt % when cristobalite begins to form and 0.01–0.03 wt % in quartz (Fig. 1).

The presence of supercritical water has a significant effect not only on the water content of silica but also on its state (Fig. 2). As a result, the water desorption peak shifts to higher temperatures: the peak is located at 200–300°C for the starting silica, 300–400°C in the initial stage of crystallization, 500–600°C for cristobalite, and 1000–1200°C for fine-particle quartz.

In the process of structurization, the activation energy of water desorption increases (table). The activation energy was evaluated from the change in ion signal *I* corresponding to a change in temperature from T_1 to T_2 at a constant water content of the sample [1]:

$$E_a(\mathrm{kJ/mol}) = \frac{8.31\ln(I_2/I_1)}{1/T_1 - 1/T_2}. \qquad (1)$$

A major fraction of the water leaves silica in the initial stage of structurization with E_a = 40–60 kJ/mol; the activation energy of water desorption from fine-particle quartz (around 1000°C) is E_a = 120–140 kJ/mol.

The starting, hydrated SiO_2-II was found to contain water in various forms: liquid water in micropores, water molecules (hydrogen-bonded to silanol groups), silanediol groups, and silanes. The ^{29}Si NMR spectrum of silica shows peaks at –90 (silanediol groups), –100 (silanol groups), and –110 ppm (siloxane bonds). During the dehydration of silica in vacuum or air, molecular water (^1H NMR peak at 4.3 to 5.0 ppm) vaporizes at 90–110°C in air or at room temperature in vacuum. At 400°C, we observe the maximum desorption of hydrogen-bonded hydroxyl groups (NMR peak at 2.7 to 3.6 ppm). Desorption of the hydroxyl groups incorporated in the silicon–oxygen network (NMR peak at 1 ppm) occurs mainly between 800 and 900°C and reaches completion in the range 1300–1600°C (in vacuum).

In the early stage (4 h) of silica structurization in supercritical water, we observe ^1H NMR peaks at 4.6 (molecular water) and 3 ppm (hydrogen-bonded hydroxyl groups). Holding this silica at 400°C for 3 h leads to the disappearance of the peak at 5 ppm. The ^{29}Si NMR spectrum shows two signals of roughly equal intensity: at –100 (silanol groups) and –110 ppm (siloxane bonds). After annealing at 1300°C, the ^1H NMR spectrum contains only one peak—that at 1 ppm.

In the ^1H NMR spectrum of fine-particle quartz—the final product of silica structurization—the major peak, located at about 5 ppm, persists after heating to 600°C. This peak seems to correspond to molecular water—clusterized or incorporated in the structure of quartz. High-temperature water desorption from fine-particle quartz is diffusion-controlled. With increasing specific surface (decreasing particle size), the water desorption peak shifts to lower temperatures.

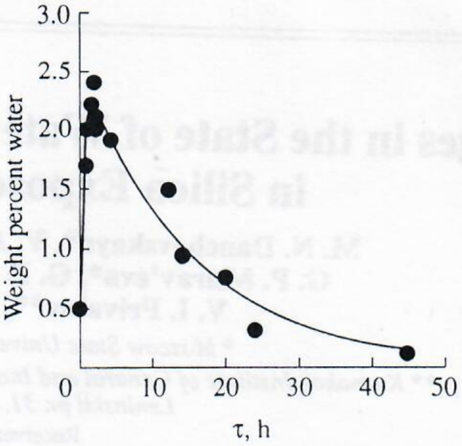

Fig. 1. Variation of water content during SiO_2-I crystallization in supercritical water (400°C, 20 MPa) in the presence of tetra-*N*-methylammonium hydroxide.

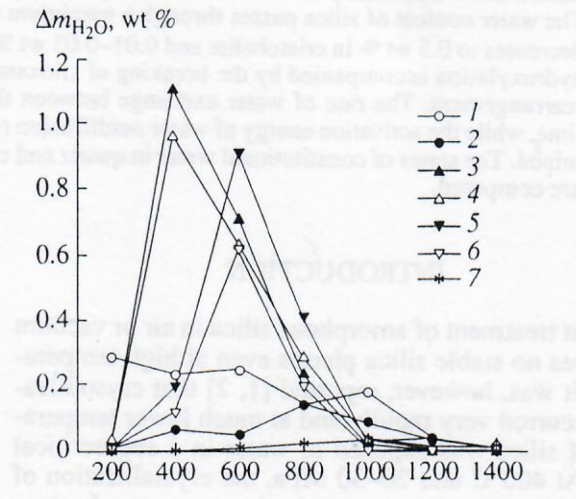

Fig. 2. Water desorption from SiO_2-I after exposure to supercritical water (400°C, 20 MPa) for (*3*) 2, (*4*) 4, (*5*) 12, (*6*) 14, and (*7*) 45 h; (*1*) original sample, (*2*) after adsorption of tetra-*N*-methylammonium hydroxide.

To evaluate the diffusion coefficient of water in silica, we used the equation describing isothermal water desorption from spherical particles in vacuum [6]:

$$I = \frac{2mC_0S^2\rho^2D}{3B}\sum_{n=1}^{\infty}\exp\left(-\frac{n^2\pi^2S^2\rho^2D\tau}{9}\right), \qquad (2)$$

where ρ is density, *S* is the specific surface, *m* is sample weight, *B* is the sensitivity factor with respect to mole-

Activation energy of water desorption at different stages of silica crystallization

Sample	E_a, kJ/mol					
	200–400°C	400–600°C	600–800°C	800–1000°C	1000–1200°C	1200–1400°C
Starting SiO_2-I	29	50	130	167		
SiO_2-*X* + cristobalite	59	56	113	103		
Cristobalite	55	65	75	68		
Cristobalite + quartz	39	41	65	85	136	
Quartz		38	54	118	155	142

cular water, *I* is the water ion intensity, τ is time, and C_0 and *C* are the initial and current water contents of the sample. In calculations, corrections were also made for the particle-size distribution and particle nonsphericity. The Arrhenius plot for the diffusion coefficient of water is displayed in Fig. 3. From the slope of the Arrhenius plot, the activation energy of water outdiffusion from quartz was found to be 133 kJ/mol, which is close to the E_a of high-temperature water desorption (table) evaluated by equation (1).

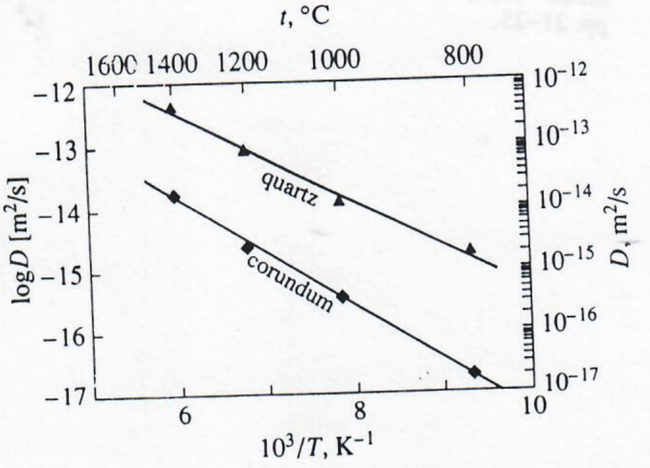

Fig. 3. Arrhenius plots for the diffusion coefficients of water in fine-particle quartz and corundum.

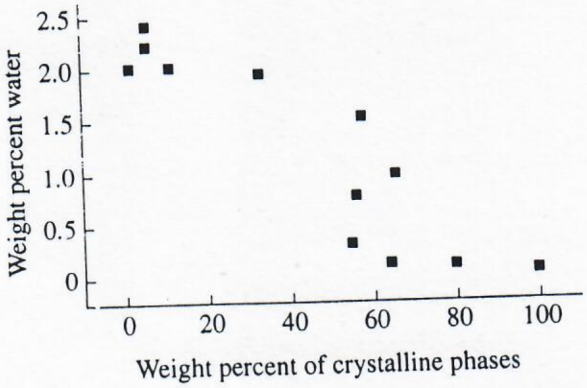

Fig. 4. Water content of SiO_2-I vs. extent of crystallization (content of crystalline phases) in the presence of supercritical water (400°C, 20 MPa).

Constitutional water has a crucial effect on the structural transformations of silica. In supercritical water, silica hydroxylation is accompanied by the breaking of siloxane bonds and accelerates the rearrangement of the silicon–oxygen network, resulting in the formation of thermodynamically stable silica phases. This rearrangement, involving the formation of new siloxane bonds during dehydroxylation, is accompanied by a reduction in the content of constitutional water. The rate of water exchange between the silica matrix and supercritical water decreases with time since the specific surface of silica drops and bulk density rises as a result of structurization. This process culminates in the formation of 100% quartz with a lower content of constitutional water (Fig. 4).

The presence of supercritical water has a similar effect on the structurization of amorphous aluminum hydroxide, resulting in fine-particle alumina. The activation energy of water outdiffusion from fine-particle corundum between 800 and 1400°C (164 kJ/mol) is higher than that for fine-particle quartz (133 kJ/mol) (Fig. 3), in agreement with density data. Although the solubility of alumina in supercritical water (400°C, 20 MPa) is more than two orders of magnitude higher than that of silica (3.2×10^{-4} and 1.7×10^{-2} mol/kg H_2O, respectively [7, 8]), the kinetics of the formation of fine-particle corundum [9] and quartz are closely similar, as would be expected given that the structural transformations of both alumina and silica in supercritical water are solid-state processes.

CONCLUSION

The presence of supercritical water has a crucial effect on the structurization of silica into fine-particle quartz, accelerating hydroxylation, accompanied by the breaking of siloxane bonds and followed by dehydroxylation and structure rearrangement. Changes in the state of water in the silica matrix perfectly correlate with the structural transformations of silica in supercritical water. The rate of water exchange between silica and supercritical water is controlled by the reduction of specific surface in the initial stages of silica structurization and the volume diffusion of water in the latter stages of quartz formation.

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