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MICROCALORIMETRIC STUDY OF THE THERMODYNAMICS OF THE DEHYDRATION OF AMORPHOUS SILICA

V B LAZAREV, G P PANASYUK, G P BUDOVA and Ya A KESLER

Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Moscow, (U.S S R)

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ABSTRACT

The experimental determination of the heat of dehydration [$\Delta H^0_{T(\mathrm{dehydr})}$] of amorphous SiO_2 has been carried out in a double differential high-temperature Calvet-type microcalorimeter According to the results obtained, $\Delta H^0_{T(\mathrm{dehydr})}$ is much less than the heat of water evaporation and decreases with increase of dehydration temperature It also decreases after hydrothermal treatment of SiO_2 in the autoclave This may be due to the increase in the number of water molecules weakly bound to the amorphous SiO_2, resulting from the change in the silica gel structure

INTRODUCTION

Investigation of the thermodynamics and kinetics of the dehydration of amorphous silica allows data concerning the energetic state of various kinds of bound water and its role in the formation of the silicon–oxygen structure to be obtained.

Earlier we investigated the silica dehydration using the methods of differential thermal analysis [1] and mass spectrometry [2]; this enabled us to estimate the enthalpy and activation energy of water evaporation from silica gel in various temperature intervals. The microcalorimetric method allows direct determination with sufficient reliability of the integral thermal effects of dehydration. A comparison of the results of thermodynamical measurements obtained by the integral and differential methods will allow the more correct identification of various kinds of combined water in an amorphous silica.

EXPERIMENTAL

The heat of dehydration was determined using a Calvet-type double differential high-temperature microcalorimeter. The design of the calorimeter and the experimental technique have been described previously [3,4].

During the experiment the specimens of silica gel, placed in a nickel container, were thermostated at 298 K, then plunged into the calorimeter's cell, whose operating temperature was maintained with the accuracy of ±0.1°C. Determination of the heats of dehydration was performed at temperatures of 447, 909 and 975 K. The self-recorder KCP-4 was used and a curve of the dependence of the heat evolution on time was plotted.

The thermograms were calculated using a "MOM"-type planimeter with an accuracy of ±0.5%. The thermal effect was calculated according to the formula

$$Q = \frac{\rho M S}{m} \tag{1}$$

where ρ is the heat-exchange factor (calμkV^{-1} min^{-1}), m is the weighed amount (g), M is the molecular weight of the substance, and S is the area corresponding to the thermal effect of reaction, (μ kV min^{-1}). The calorimeter was calibrated by plunging the quartz single crystals under experimental conditions followed by calculation of the thermal effects according to the data of Kelley [5]. The duration of each experiment did not exeed 45 min. Each specimen was plunged into a cell three times. On the first plunge the thermal effect of reaction was equal to the sum of the enthalpy of dehydration of silica gel and change of heat content of the specimen

$$\Delta H_1 = (H_T - H_{298})_{SiO_2 \cdot x H_2O} + (H_T - H_{298})_{contain} + \Delta H_{T(dehydr)} \tag{2}$$

On repetition of the plunge the thermal effect of reaction was equal only to the change of heat content of the calorimetrically annealed specimen

$$\Delta H_2 = (H_T - H_{298})_{SiO_2 (x-y) H_2O} + (H_T - H_{298})_{contain} \tag{3}$$

By neglecting the error caused by the change of heat content of evolved water (y H_2O), whose amount in all cases does not exceed 0.05 kcal mole^{-1} of water, the dehydration enthalpy of silica gel may be calculated according to the formula

$$\Delta H^0_{T(dehydr)} = \frac{\Delta H_1 - \Delta H_2}{y} \tag{4}$$

The loss of water (y) was determined by a gravimetric method with the accuracy up to 10^{-5} g Completeness of dehydration was checked by the third plunge of the specimen.

"Analytical" grade aqueous silicic acid was used for the investigation. A change in the silica structure was attained by means of hydrothermal treatment with silicic acid in water inside an autoclave at 350°C for 6 h

RESULTS

The experimental results are given in Table 1. The errors given are the standard deviations. After conducting the calorimetric experiments the specimens were kept in air at room temperature for 6 days. The loss of water by silica gel after annealing at 447° K (174°C) was found to be reversible, since after 2 days the specimens annealed in a calorimeter acquired their original weight.

In all the remaining specimens dehydration proceeds irreversibly, since the weight of the specimens does not change significantly with time.

Table 1

Experimental results

N, *N*	Initial specimen	Number of experiments in a set	*T* exp (K)	ΔH_T^0 (kcal mole^{-1} H_2O	Loss of water (wt %)
1	$SiO_2 \cdot xH_2O$	8	447	6.7 ± 0.9	5 ± 1
2	$SiO_2 \cdot xH_2O$	6	909	5.6 ± 0.6	11 ± 2
3	$SiO_2 \cdot xH_2O$	6	975	5.4 ± 0.9	12 ± 2
4	Hydrothermally treated	8	975	3.7 ± 0.6	6 ± 1

DISCUSSION

The results obtained show that for all the specimens studied the enthalpy of dehydration is considerably less than the heat of evaporation of water, thereby its value decreases with increase in temperature of dehydration. Hydrothermal treatment leads to a considerable decrease in the thermal effect. It is most probable that during the experiment evaporation of various kinds of water takes place, while the integral thermal effect is determined by the sum of contributions given by each kind. This corresponds with the results obtained by a thermogravimetric method, which permits the determination of the differential thermal effects of dehydration of amorphous silica corresponding to evaporation of various kinds of combined water. On the basis of the investigation carried out by Panasyuk et al. [1], three kinds of water have been identified: the first, which evaporates in the interval 100–300°C (dehydration enthalpy is about 10 kcal mole^{-1}), is water condensed in the pores of silica gel in a capillary manner; the second, which evaporates in the interval 250–400°C (dehydration enthalpy is about 5 kcal mole^{-1}) is presented by the water molecules combined by hydrogen bonds with the hydroxyl groups of the silica gel surface; the third, which evaporates in the interval 350–600°C (dehydration enthalpy is about 1 kcal mole^{-1}) has been identified as the water molecules present in the volume of globules and connected by a coordination bond with the silicon atoms of randomly disposed silicon–oxygen tetrahedrons. In spite of its low dehydration enthalpy, this kind of water evaporates at a rather high temperature, caused by the difficulty of diffusion of the water molecules from the volume of the globules. The results of the microcalorimetric analysis agree quite well with the data obtained by the method of differential thermal analysis. Each integral effect is determined by the sum of contributions from three kinds of water. At 447 K the main contribution to the dehydration enthalpy is from the water in open pores, while the share of the remaining kinds of water evaporated at this temperature is not high. With increasing temperature the contribution of weakly combined water is increased and hence, the value of the integral thermal effect decreases. An analogous result is achieved by the hydrothermal treatment, at which the dimensions of the globules are considerably enlarged and the amount of inner-globular water increases sharply.

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