Thermochimica Acta, 93 (1985) 271-274
Elsevier Science Publishers B.V., Amsterdam

DSC STUDY OF THE THERMODYNAMICS AND THE KINETICS OF STRUCTURAL TRANSFORMATIONS OF SILICA IN A WATER VAPOUR ATMOSPHERE

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ABSTRACT

The enthalpies of dehydration and crystallization of amorphous silica with the formation of quartz have been determined by the differential scanning calorimetry method in a water vapour atmosphere. It has been found that the dehydration enthalpy value depends on the character of the preliminary treatment of silica. The effective activation energy of the growth of quartz nuclei has been estimated based on the Kolmogorov-Kazeev equation for the silica crystallization kinetics.

INTRODUCTION

Pure amorphous silica is an extremely stable compound. In the air under atmospheric pressure it crystallizes only at temperature above 1400-1500 K into cristobalite, but in the presence of alkali metal compounds crystallization proceeds at about 1100 K with the formation of quartz, tridymite or cristobalite. In active media, for instance in a water vapour atmosphere, the silicon-oxygen sceleton destabilizes resulting in relaxation of the silica structure into quartz that in general case proceeds through several successive stages. The determination of thermodynamic and kinetic parameters of silica structural transformations gives a possibility for the directed changing of silica structure and preparation of materials with desirable properties.

MEASURING METHOD

DSC method was used to study the thermodynamics and the kinetics of structural transformations of silica in a water vapour atmosphere in the temperature range of 620-750 K. Amorphous silica of special purity grade with the specific surface of 200 $m^2\ g^{-1}$ and the total metal impurity contents $3 \cdot 10^{-4}$ mass % was taken as initial. Silica was treated in an autoclave in a water vapour atmosphere under isothermal conditions. Preliminary treatment of silica with a crystallization activator solution resulted

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Proceedings of ICTA 85, Bratislava

in the following mechanism of structural changes, enlarging of the globules, glassing, formation of quartz. The stage of the formation of cristobalite was excluded.

The experiments were performed on a differential scanning calorimeter DSC 111 "SETARAM".

To study the thermodynamics of structural transformations, initial amorphous silica with the addition of a given amount of water was placed into a sealed stainless steel cell with nickel joint meant for 100 bars at 873 K. The pressure in the cell was evaluated with the use of the Vukalovitch tables [1] taking into account the total mass of water introduced into the cell and that contained in the silica sample (according to the TGA data). The heating curves were recorded in the temperature range 300-1000 K at a rate of 10 K min^{-1} and a sensitivity range of 35 mJ sec^{-1}.

To study the crystallization kinetics, the samples of amorphous silica treated preliminary with a solution of crystallization activator were placed into an autoclave, where a certain amount of water was also added, and kept for different time intervals at 623, 648 and 673 K, respectively. The samples treated in the autoclave were placed into the calorimeter in an alumina boat and heated up to 873 K at a rate of 10 K min^{-1}. The crystallization percentage was determined as the ratio of the enthalpy measured for the $\alpha \rightleftharpoons \beta$ quartz phase transition to that found for the complete crystallization (0.628 kJ mol^{-1}).

RESULTS AND DISCUSSION

The heating curves of the silica samples in sealed cells are shown in Figure 1. The endothermal effect corresponding to the total effect of silica dehydration and water evaporation was observed for all samples of amorphous silica in the temperature range from 340-700 K. For the untreated samples of amorphous silica the DSC heating curves reveal only a diffused endothermal effect (curve 2). Other curves plotted for the samples preliminary treated with a crystallization activator solution show in addition to the dehydration minimum near 563 K the exothermal effect corresponding to the crystallization of amorphous silica in the temperature range 700-820 K and the endothermal effect of the $\alpha \rightleftharpoons \beta$ quartz phase transition at 853 K. The dehydration enthalpy $\Delta H^\circ(T)$ is from 9.3 to 25.7 kJ mol^{-1} H_2O depending on the conditions of the preliminary treatment and the crystallization enthalpy is -1.63 kJ mol^{-1} SiO_2.

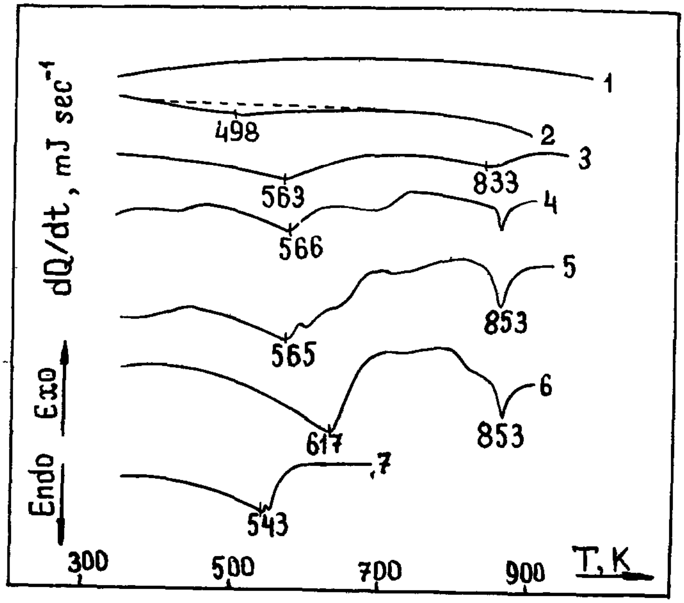

FIGURE 1

DSC heating curves for the SiO_2 + H_2O samples.

(1) empty cells; (2) without activator, specific volume of water vapour $v = 36.0$ cm^3 g^{-1}; (3) weak activator, $v = 16.9$ cm^3 g^{-1}; (4), (5) and (6) strong activator, $v = 23.6$, 14.9 and 6.75 cm^3 g^{-1}, respectively; (7) water without silica, $v = 34.1$ cm^3 g^{-1}.

Figure 2 illustrates the crystallization percentage as the function of duration of thermovaporous treatment at 623, 648 and 673 K, respectively for the samples treated preliminary with a crystallization activator solution. The kinetic curves are described by the Kolmogorov-Kazeev equation:

$\alpha(t) = 1 - \exp(-kt^n)$

where $n = 4$

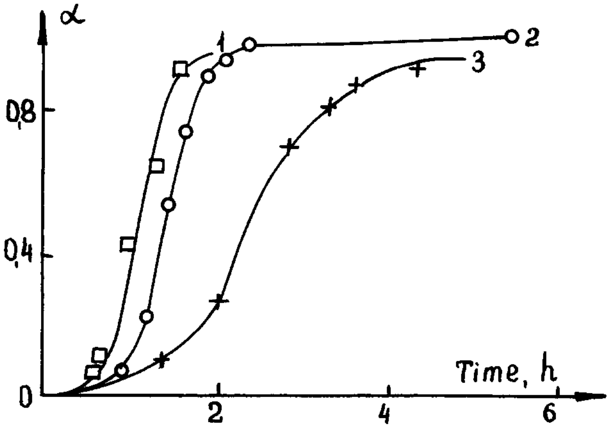

FIGURE 2

Crystallization percentage of silica vs. duration of thermovaporous treatment. (1) 623 K; (2) 648 K; (3) 673 K.

The activation energy found by the Arrhenius equation is 272 ± 20 kJ mol^{-1}. This value can be interpreted as an effective one which includes the activation energies of nucleation and crystal growth. The activation energy and the enthalpy of crystallization allow one to evaluate the activation energy of the transport through the surface of the growing crystal [2] which is 67 ± 5 kJ mol^{-1}.

The data obtained demonstrate that the thermal treatment in a water vapour atmosphere gives the crystallization activation energy by the order of magnitude lower than that calculated for the high-temperature crystallization with the formation of cristobalite [3] that probably due to an essentially different mechanism of the transport processes caused by the presence of water vapour.

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