

SYNTHESIS OF VARIOUS CRYSTALLINE MODIFICATIONS OF SILICON DIOXIDE IN SUPERCRITICAL WATER FLUID.

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In the report the results of investigations of phase transformations of various modifications of silicon dioxide in water supercritical fluid and in soft hydrothermal conditions are imparted. As starting materials two kinds of amorphous silicon dioxide were utilized: silicon dioxide obtained by ammoniacal hydrolysis of tetraetoxisilan (K1) and silicon dioxide, obtained by aqueous hydrolysis of silicon tetrachloride in acidic medium (K2). Samples of raw materials differed by the structural performances. In all cases the significant hydration of starting material preceded the start of transformation of amorphous silicon dioxide into one of crystalline modifications. For producing one of crystalline modifications of silicon dioxide: cristobalite, keatite or quartz, the various activators of crystallization and various performance of synthesis were utilized. The investigations of the mechanism of phase transformations of silicon dioxide in hydrothermal conditions and in supercritical water fluid has shown, that in a case large-globular of silicon dioxide (K1) structural transmutations with formation of new modifications were fixed at temperatures above 370°C in atmosphere of water fluid (P=200 - 280 MPa) with the additives of activators. Thus, during synthesis in supercritical water fluid cristobalite, keatite and then quartz were sequentially formed. At usage of silicon dioxide (K2) the formation of new crystalline modification started already at 230°C in water solution 0.1 % NaOH under pressure of water vapor 2.6 MPa. The process was considerably accelerated at adding of silicon dioxide sol.

INTRODUCTION

Now the usage of supercritical water fluid (SCWF) for the obtaining of the various scarce materials is widely covered in the literature¹⁻⁴. At comparison between mechanism of the hydrothermal process and process in SCWF becomes apparent that these mechanisms have certain common features⁵⁻⁷.

In present paper are given the results of investigations of metamorphic transformations process of silicon dioxide in SCWF and in soft hydrothermal conditions.

It was shown earlier, that in medium of supercritical water fluid at temperature higher 370°C and pressure above 20MPa the amorphous silicon dioxide undergoes a change of structure with formation of various crystalline modifications. The process flows past in a solid phase with involvement of water molecules of supercritical water fluid. Changing composition of fluid or additives in raw material it is possible to govern a direction of structural changes of silicon dioxide^{8,9}. The adding in water fluid nitrogen-containing organic bases allows leading the process to cristobalite formation. If the water fluid contains aliphatic alcohols the process occurs mainly with the formation of keatite. In synthesis conditions, indicated above, the thermodynamic stable modification of silicon oxide is the quartz. Therefore both modifications are transmuted finally into quartz¹⁰.

The mass spectrometric and electron paramagnetic resonance study have shown¹¹, that under supercritical water fluid the activating agents interact with surface hydroxides of silica with formation

amino- or methoxy- and ethoxy-groups. In the case the using the activating additives containing $C_mH_{2m+1}O$ groups, promote the formation of quartz through an intermediate state primarily of keatite. The habitus of these quartz crystals are needle – prismatic primarily. Nitrogen – containing additives direct the structurization of silica through intermediate crystalline phase of cristobalite. In this case final crystals of quartz had isometric bipyramidal habitus¹².

The influence of the various composition additives in water fluid was apparent not only in kind of modification of intermediate phase of silicon dioxide, but also in increase of phase changes rate and rate of structure perfection of modifications of silicon dioxide¹³.

The purpose of these investigations was study of the process of phase transformations of various modifications of silicon dioxide in water supercritical fluid and in soft hydrothermal conditions.

MATERIALS AND METHODS

Synthesis of solid oxides was carried out in laboratory autoclaves (18 mL). As raw material was used amorphous silicon dioxide (purity 99.999%) of two kinds: silicon dioxide (K1) obtained by ammoniacal hydrolysis of tetraetoxisilan and heated at 850°C and silicon dioxide (K2), obtained by aqueous hydrolysis of tetrachloride of silicon in acidic medium and heated at 300°C. The raw material was placed into a special container within the autoclave and for making fluid water into the space between the walls of autoclave and the container with starting material the water was added. The transformation of amorphous silicon dioxide was putted into effect at water vapor pressure 3.0 - 26.0 MPa and at temperature 400°C and 230°C. Into reactionary medium the activators of phase transformation of silicon dioxide: water solution NaOH (0.1 % NaOH in relation to mass of raw material) or intermixture of this water solution NaOH with water suspension of the fine-dispersed stabilized sol silica (20% mass silica/raw material) were added. The fine-dispersed stabilized by NaOH silica sol represents water suspension polysilicon acids.

The synthesized products were investigated by physical-chemical methods. The electron microscopic photographs were carried out on the device «Cam Scan Series 2». For the X-ray analysis of the synthesis products was using «STOE Powder Diffraction System» (CuK α radiation). A size and form of crystals were determined using optical and electronic microscopes. Water content in transformation products were determined by the use derivatograph Q - 1500 D and mass-spectrometer MI-1311.

RESULTS AND DISCUSSION

The Synthesis in supercritical fluid and in hydrothermal conditions allows obtaining various materials utilizing ecologically pure technologies¹⁻⁶.

Under water vapor pressure 26.0 MPa and temperature 400°C the transformation of amorphous silicon dioxide K1 (Fig.1) with the activating agent tetra-N-methylammonium hydroxide or aliphatic alcohol occurs in direction of formation of one of a number of modifications: cristobalite floccules (Fig. 2), keatite fibres (Fig. 3) or quartz (Fig. 4), depending on composition of a fluid and regime of synthesis [9].

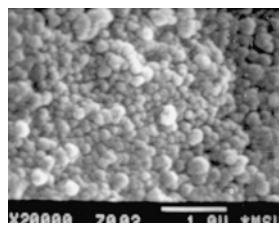


Fig.1. Amorphous SiO₂ K1

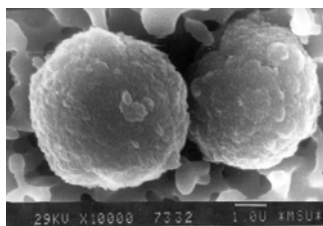


Fig.2. Cristobalite

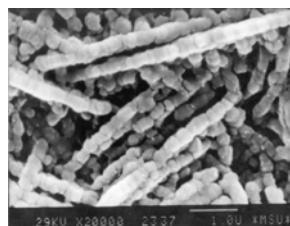


Fig.3. Keatite fibres

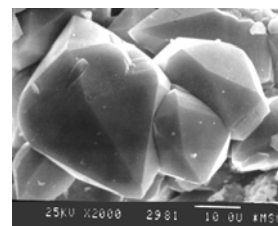


Fig. 4. Quartz

Kinetics and the energy performances of metamorphic transformations of amorphous silicon dioxide depend on its properties and kind of used activator. The activator takes part in making of defects in structure SiO_2 and promotes its reorganization.

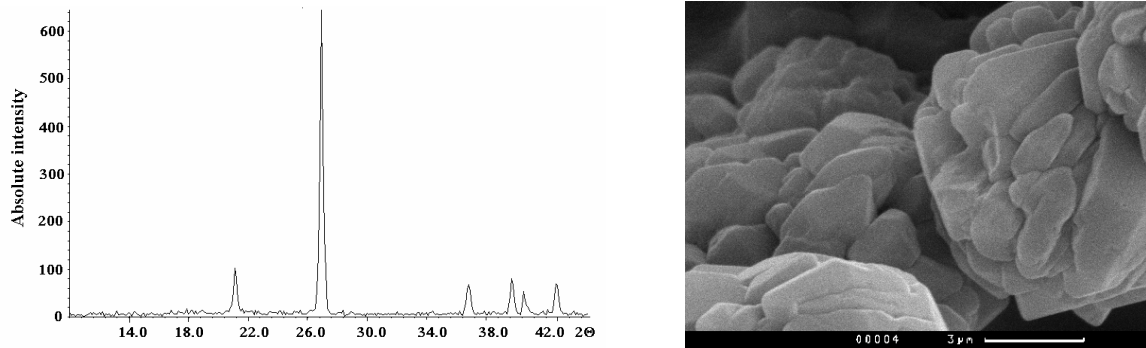


Fig. 5. Diffractogram of quartz, synthesized from silica K2 under supercritical condition ($T=400^\circ\text{C}$, $P=22$ MPa) during 2 hours with addition of polymeric silicon acid sol in reaction system and electronic micrograph of this sample.

Fig. 5 is presented the X-ray diffractograms of transformation products of SiO_2 K2 in supercritical water fluid during $t = 2$ hours at $T=400^\circ\text{C}$, $P=26$ MPa, with additive of intermixture of water solution NaOH (0.1%) with suspension of the fine-dispersed silica sol (20%). Diffraction peaks with the main peak at $2\Theta=26.6^\circ$ indicate that using of silica sol in these conditions for 2 hours the complete transformation amorphous SiO_2 K2 into fine crystalline quartz occurs. Whereas in presence only additive of NaOH, in the same conditions for 2 hours will be obtained not only quartz, but and cristobalite. At decreasing of temperature up to 230°C , i.e. at the going into the area of hydrothermal synthesis, the transformation of amorphous silicon dioxide K2 also occurs in the direction of formation of disordered cristobalite ($2\Theta=21.7$) and quartz, but transformation passes more slowly (Fig. 6). Only after 15 hours of hydrothermal treatment of starting material K2 is obtained fine crystalline quartz (Fig.7) with crystals size in the range of 1 - 3 μm (Fig. 10d). As is evident from diffractograms of the transmutation products of the start material K2, in these conditions the quartz starts to form only after 12 hours (Fig. 6).

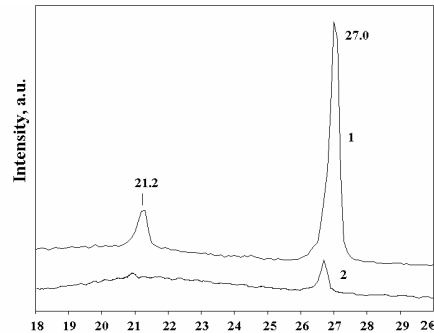
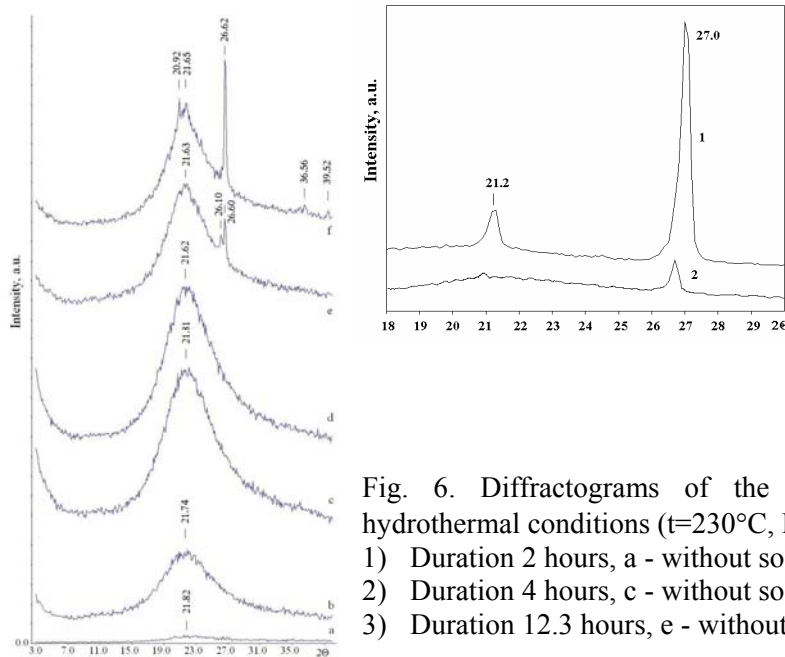


Fig. 7. Diffractograms of the products, synthesized under the hydrothermal conditions ($T=230^\circ\text{C}$, $P=2.6$ MPa) from SiO_2 K2, during 15 hours. 1 – with addition of polymeric silicon acid sol, 2 - without sol.

Fig. 6. Diffractograms of the products synthesized under the hydrothermal conditions ($t=230^\circ\text{C}$, $P=2.6$ MPa) from SiO_2 K2:
 1) Duration 2 hours, a - without sol, b – with sol;
 2) Duration 4 hours, c - without sol, d – with sol;
 3) Duration 12.3 hours, e - without sol, f – with sol.

The process of transformation silicon dioxide K2 in hydrothermal conditions with and without sol passes through formation flocculated disordered cristobalite, containing considerable amount of water in structure. The water content in silicon dioxide K2 before hydrothermal treatment is equal 5.5 %. During hydrothermal treatment of SiO₂ K2 at a heating of autoclave up to 230°C the water containing increases from 5.5 % up to 10.7 % (Fig. 8).

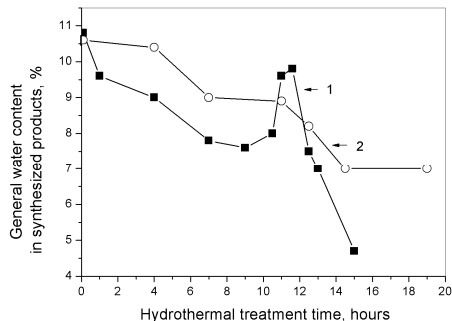


Fig. 8. The water content in the products, synthesized under the hydrothermal condition (T=230°C) versus hydrothermal treatment time: 1 – with addition of polymeric silicon acid sol, 2 – without sol.

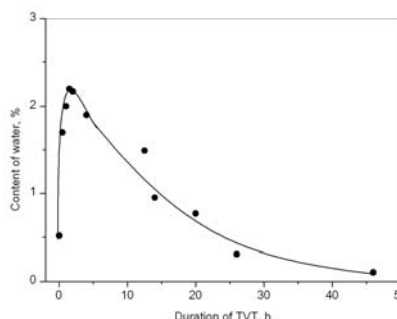


Fig. 9 The water content in products obtained during SiO₂ K1 metamorphic transformations in supercritical water fluid at T=400°C, P=26 MPa.

As shown mass-spectrometry, the water in structure of silica after hydrothermal treatment is in the form of hydroxyl groups¹⁴. After hydration of silicon dioxide K2 the dehydration accompanying with the formation of cristobalite structure was started. At further hydrothermal treatment of silica K2 at 230°C (in all about 11 hours) the new secondary increasing of water content was preceding to restructuring of cristobalite into quartz. At formation of quartz the drastic decrease of water content in transformation products of silicon dioxide was observed (Fig.8). The similar appearance is observed also at metamorphic transformations of silicon dioxide in supercritical water fluid (Fig. 9).

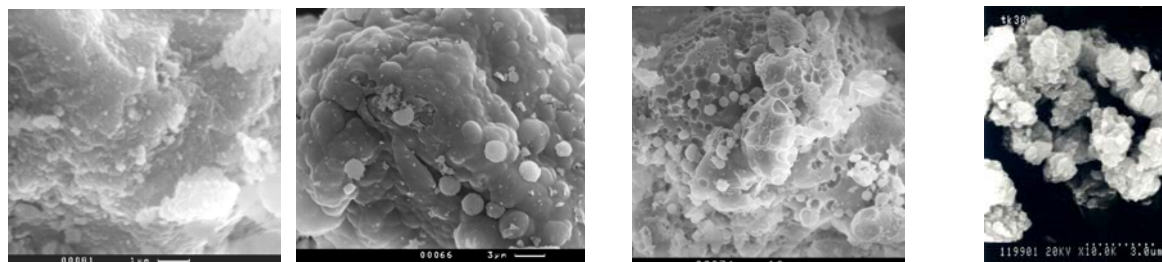


Fig.10 a. SiO₂ K2 till hydrothermal treatment (HT).

b. SiO₂ K2 after HT at 230°C during 12.3 hours, without sol.

c. SiO₂ K2 after HT at 230°C during 12.3 hours, with sol.

d. Quartz obtained from SiO₂ K2 after HT at 230°C during 15 hours, with sol.

Fig. 10 shows scanning electron micrographs of microstructures of transformations products of amorphous silicon dioxide K2. Fig.10 (a) relates to initial material SiO₂K2, (b) - to cristobalite synthesized without sol, (c) - to cristobalite synthesized with sol and (d) – to quartz. Start material SiO₂ K2 is fine-globular xerogel with specific surface 300 m/g and bulk weight 0.6 g/cm³. After hydrothermal treatment without sol at 230°C during 12.3 hours the specific surface of silica decreases and bulk weight increases to 0.8 g/cm³, the pore size increments, but total volume of pores remains to stationary values (0.84 cm³/g). As evident from Fig. 10b, the flocculation of silica K2 occurs with formation of floccules with size 1 – 3 μm, from which at more long-term treatment the fine quartz crystals will be formed. In case using silicon acids sol simultaneously with flocculation the

coalescence of floccules occurs and then, during formation of quartz, the aggregates were in abundance.

CONCLUSION

The activation of process of metamorphic transformations of silicon dioxide was observed as in hydrothermal conditions as well as in supercritical water fluid.

The role of sol of polysilicon acids can be exhibited in two ways: as a siliceous matrix during formation of crystallization nucleus of a new phase of the crystalline modification of silicon dioxide and as a conglomerating agent during oriented cocrystallization of generated submicron crystals with formation of larger crystals and the aggregates.

The process of the restructuring of one modification of silicon dioxide in another occurs with immediate involvement of water molecules, which are breaking "silicon-oxygen" bonds during hydration of silicon dioxide with the subsequent closure of these bonds into other configuration.

Dehydration of lattice of amorphous silicon dioxide results in formation of defects, mainly of oxygen vacancies. The defects are a source of a long-range elastic field. The scope of force field much more exceeds distance between defects and leads to shear deformation of a lattice with formation of fragments of structure of a new phase. The incipient phase boundaries also are a source of an elastic disturbance.

The results of investigations, described in the present paper, lead to conclusion about similarity between the mechanism of phase changes of silicon dioxide in a supercritical water fluid and in hydrothermal conditions.

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