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The effect of alkali halides and silver nitrate on the crystallization of silica powders

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The effect of alkali halides on the crystallization of amorphous silica powders has been investigated. Normally crystallization does not occur below 1000° C, but in the presence of about 20% by weight of lithium chloride, α-quartz forms within 2 h at 700° C. In the presence of sodium and potassium salts, α-cristobalite forms at about 800 to 850° C. It appears that quartz is formed in the presence of the lithium salt because Li^+ can enter the quartz lattice, whereas Na^+ and K^+ can penetrate the more expanded polymorphic form, cristobalite. It is possible that the cations are accompanied by oxide ions in all cases to maintain electrical neutrality. Limited penetration of the amorphous particles is sufficient to nucleate the new phase. Other properties of silica products treated with salts are reviewed.

1. Introduction

Certain silica powders heated at temperatures up to 850° C in the presence of alkali halides and silver nitrate, give crystalline forms of silica. For example, a 1/5 (wt/wt) mixture of sodium chloride and silica powder gave α-cristobalite at 800° C and quartz at 700°C after 2 h heating, whereas crystallization to cristobalite of silica heated alone does not occur below about 1000° C. The effects of salts on silica crystallization, including the findings of other workers, are discussed in this paper.

It is also interesting that the same silica powders heated to about 650° C (i.e. below the temperature of bulk crystallization) in the presence of sodium chloride become effective substrates for the formation of ice from supercooled vapour [1-3]. An important characteristic of these powders is that they are only partially receptive to water vapour molecules.

2. Materials, heat-treatment and product analysis

The samples of silica which have been previously described [2, 3] were HiSil233 (Pittsburgh Plate Glass Co) prepared by precipitation from aqueous solutions, and CabOSil H5 (Cabot Corp) prepared by the flame-hydrolysis of silicon tetrachloride. Inorganic salts were Baker Analysed grade reagents.

Samples were in most cases prepared by grinding the inorganic salt to powder and mixing it with the silica. Most heat-treatments were carried out in a muffle furnace controlled to ± 10° C.

Products were analysed for crystalline materials with a General Electric X-ray diffractometer (Model XRD-3 using Cu $K\alpha$ radiation) and an SPG-4 scintillation counter.

3. Results

When heated at 800° C for 2 h, mixtures in the ratio 1/5 (wt/wt) salt to silica showed the presence of cristobalite from HiSil and a trace of cristobalite from CabOSil. Mixtures in the ratio 1/2 gave well-defined diffraction peaks from both silicas. The heating period of 2 h is about the minimum needed to effect crystallization at the temperatures employed. When heated alone for 2 h at 1000° C, HiSil gave a trace of cristobalite but CabOSil remained amorphous, and when 1/5 mixtures of NaCl+ silicas were heated at 1000° C for 2 h, both silicas gave tridymite as well as cristobalite.

Crystalline products arising from 2 h heat-treatments with various salts are given in Table I.

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TABLE I Effect of salts on the crystallization of silica powders

Salt	Salt/silica ratio	2 h at temperature (°C)	Products	
			HiSil	CabOSil
LiCl	1/5	650	(quartz)*	—
LiCl	1/5	700	quartz	amorphous
NaCl	1/5	800	cristob	(cristob)
NaCl	1/5	1000	cristob + trid	cristob + trid
NaBr	1/5	800	cristob	—
KCl	1/5	850	cristob	(cristob)
KBr	1/5	850	cristob	—
CaO	1/2	800	amorphous	—
$AgNO_3$	1/5	650	AgCl, (Ag)	—
$AgNO_3$	1/5	800	cristob AgCl, (Ag)	amorphous
$AgNO_3$	1/2	800	cristob, AgCl, Ag	—

*Parentheses indicate that main X-ray peaks were present.

The temperatures are the lowest at which a crystalline phase could be detected for the particular mixtures. The principal findings are that mixtures containing sodium or potassium halides give α-cristobalite, and those containing lithium chloride give α-quartz. HiSil in the presence of sodium chloride and sodium bromide gives cristobalite at 800° C. With the corresponding potassium salts, cristobalite is not produced until 850°C. HiSil and silver nitrate (decomp. 444°C) mixtures heated to 650°C for 2 h gave some silver chloride, indicating that HiSil contains chloride ions which are probably occluded during preparation. At 800°C, the same mixture also gave cristobalite. Generally, HiSil crystallizes more readily than CabOSil, owing possibly to impurities within the solid particles.

4. Discussion

In studies similar to those reported here, de Keyser and Cypres [4] reported that sodium oxide aided the formation of cristobalite from amorphous silica at 700° C, and at about 800° C the cristobalite was converted to tridymite.

Tridymite is the form of silica stable in the range 867 to 1470°C [5], although amorphous silica invariably forms cristobalite when heated to above 1000°C [6]. There is some evidence that tridymite is stabilized by foreign oxides [7] or that it is a solid solution [8].

Silica gel was found by Papailhau [9] to crystallize with difficulty at about 1000° C, but in the presence of sodium carbonate and potassium carbonate the temperatures of cristobalite formation were 780 and 840°C, respectively. In the presence of the fluorides, the gel formed tridymite at 1000°C. Flörke [10] found similar results when heating silica gel and glass with alkali metal carbonates. At 850° C, gel and glass with lithium carbonate both gave quartz, with sodium and potassium carbonates they both gave tridymite and some cristobalite, and with rubidium and caesium carbonates they gave cristobalite. At 950°C, the products were cristobalite with lithium carbonate, tridymite with sodium carbonate, and tridymite with potassium carbonate, respectively, It is also interesting to note that Brun [11] reported that the mixed vapours of NaCl and KCl caused vitreous silica to crystallize between 700 and 1000°C to what was probably cristobalite or tridymite.

Mougey, Francois-Rossetti, and Imelik [12] found that the adsorption on silica gel of Na^+ and K^+ from aqueous solutions caused enlargement of pores, and loss of surface when the gel was subsequently heated to 400°C, whereas in the range 800 to 850°C, the gel crystallized to cristobalite. It was suggested that adsorbed cations entered the lattice at elevated temperatures causing rupture of the Si-O-Si bridges, thereby collapsing the structure and lowering the devitrification temperature. Recently, Sawyer and co-workers [13] have used silica gel and porous silica beads coated with sodium chloride and heated at temperatures in the range 250 to 700°C in gas-solid chromatography columns. They claim that the treatment with sodium chloride reduces the well-known problem of the "tailing" of elution peaks.

All the halides are near their melting points (e.g. LiCl, 614°C; NaCl, 801°C) during the heat-treatment and can be expected to be mobile at the temperatures at which crystallization occurs in about 2 h. The fact that silicas in the presence of bromides and chlorides of a given alkali metal crystallize at the same temperature (800°C for Na^+ and 850°C for K^+) suggests that the cation is responsible for determining the structure formed. This view is substantiated by comparison of ionic radii (Li^+ 0.7Å, Na^+ 0.96Å, Ag^+ 1.3Å, K^+ 1.3Å, O^{2-} 1.4Å, Cl^- 1.8Å, Br^- 1.95Å) with the radii of structural voids in the phases [14] (quartz 1.4Å, tridymite 1.3Å, and cristobalite 1.7Å). Thus, of the ionic species examined, only Li^+ is in fact easily capable of entering the quartz lattice. Mixtures containing salts of Na^+, K^+ and Ag^+ produced cristobalite which can accommodate these cations, but the lattice voids are too small for Cl^-, Br^- and O^{2-}. The temperature of rapid crystallization (in about 2 h) increases with increase in cation size, $Li^+ < Na^+ < Ag^+ < K^+$, which is also the order of increasing diffusion coefficients for the ions in glass at 350°C[15]. The suggestion that the cation is the structure-stabilizing ion is in accordance with the work of Flörke [7] and Buerger [8]. Holmquist [14] attributed the phase formed to the nature of the anion, since alkali oxides lowered the quartz/cristobalite conversion to about 900°C irrespective of the cation involved. Here it should be remarked that both constituents of the mixture contain oxygen. O^{2-} can enter the tridymite and cristobalite lattices and is mobile in glass. A difficulty arises with an explanation based on incorporation of the cation, since, to maintain electrical neutrality, anion incorporation is also required: chloride and bromide ions are larger than the structural voids in the silica.

Sodium chloride decomposes slightly [16] when heated to fusion (801°C). The gaseous products from the interaction of sodium chloride with silicas have been identified for different conditions in the range 559 to 1045°C by Clews and Thompson [17]. At temperatures near 1000°C, the products were: in dry air – chlorine and some hydrogen chloride; in moist air – hydrogen chloride and some chlorine; in dry nitrogen – some hydrogen chloride; and in moist nitrogen – hydrogen chloride. In the presence of water vapour the formation of hydrogen chloride is favoured. The reaction of sodium chloride with surface hydroxyl groups giving SiONa and HCl may be important. Also silicas, and especially precipitated silicas such as HiSil, contain internal water which slowly evolves on heating.

Four additional sets of experiments were performed to examine the importance of water and oxygen on the transitions: (a) the silicas and sodium chloride were pre-dried separately for 2 h at 800°C before being mixed; (b) mixtures of the silicas and sodium chloride were made into aqueous slurries before heat-treatment; and mixtures of pre-dried components were heated in a Vycor tube in a stream of (c) dry air, and (d) dry nitrogen. In all cases cristobalite formed at 800°C as in previous experiments, suggesting that if oxidation, e.g. of NaCl to Na_2O, is a precursor of the transformation of amorphous silica to one of its polymorphs, oxygen may be available other than from water or the air.

5. Conclusions

Only tentative conclusions can be reached. It seems that the nature and particularly the size of the cation determines the particular form of silica produced. Thus, quartz is formed with lithium salts because only lithium can enter the quartz lattice. The cations Na^+, K^+ and Ag^+ lead to the less dense cristobalite structure below 1000°C, while tridymite (which may be so impure as not to be a true polymorph) forms at 1000°C and above. It is not certain whether the penetrating anion in all cases is the oxide. Penetration of the amorphous silica by the cation (and the anion to maintain electrical neutrality) need not be very deep to produce nuclei of the new phase from which the complete particles are then converted.

Furthermore, the changes in surface properties, particularly with respect to the physical adsorption of gases and vapours, brought about by heating silicas with inorganic salts at lower temperatures than are required for bulk crystallization, increase the range of uses of silica powders. Partially hydrophobic silica surfaces can nucleate ice from supercooled water vapour [1-3] thus behaving similarly to the cloud-seeding agent silver iodide, and treated silicas reduce the problem of tailing in gas-solid chromatography [13].

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