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Note

THERMAL AND PORE STRUCTURE CHARACTERISTICS CF SILICA MODIFICATIONS

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Keith and Tuttle [1] found that even well crystallized quartz of so-called optical quality is sometimes zoned with respect to a variation in the 573°C inversion and thus introduce the idea of shifting inversion points between the silica modifications. Ruddlesden [2] directly tackled this point and introduced the concept that the relative stability of crystobalite and tridymite can change sign with an increase in size of the crystalline unit. She assumed that the energy concerned in the homopolar bonding is the same in both of the structures. The results of her calculations revealed that the cubic close-packing arrangement characteristic of crystobalite is the more stable, as long as the crystalline nucleus is small. As it grows to longer dimensions, the tridymite structure becomes the more stable, but this is produced only with difficulty and with slow speed, because of the necessity of breaking bonds in the crystobalite structure before the tridymite can be reconstructed from its parts.

In the present study, crystobalite and tridymite modifications could be prepared using suitable mineralizers and their thermal and pore structure characteristics were critically compared.

EXPERIMENTAL

Natural quartz (silica-Q) in the low temperature form was used as representing the quartz modification. The crystobalite modification (silica-C) was prepared by firing a sample of fine silica gel containing 0.01 mole% FeO (equivalent to 2.49%

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$FeSO_4$ by weight) at 1450°C for 3 h. The tridymite form (silica-T) was prepared by firing a silica gel sample containing 0.01 mole% Na_2O (equivalent to 4.70% Na_2WO_4 by weight) at 1400°C for 3.5 h; the tridymite produced by this way was found to contain about 6–8% crystobalite.

Differential scanning calorimetric (DSC) analysis was done on the three silica modifications in the temperature range 20–600°C. The pore structure characteristics were derived from the adsorption isotherms of nitrogen at liquid nitrogen temperature using a BET volumetric apparatus of the conventional type; each sample was evacuated for one hour at 100°C prior to any adsorption run.

RESULTS AND DISCUSSION

The differential scanning calorimetric (DSC) thermograms obtained for the quartz (Q), crystobalite (C) and tridymite (T) modifications are shown in Fig. 1.

The DSC thermogram obtained for the quartz modification showed the existence of an endothermic peak at 573°C representing the transformation of the low-temperature quartz, characterized by a helical arrangement of tetrahedra, to the high-temperature quartz with the possibly somewhat disordered structure.

The thermogram obtained for the crystobalite form displayed an endotherm at 250°C, characterizing the transformation of the well-ordered crystobalite (high-temperature form) into the low-temperature crystobalite form.

For the tridymite modification the DSC thermogram demonstrated the existence of three endothermic peaks at 120, 165 and 245°C. The two endotherms located at

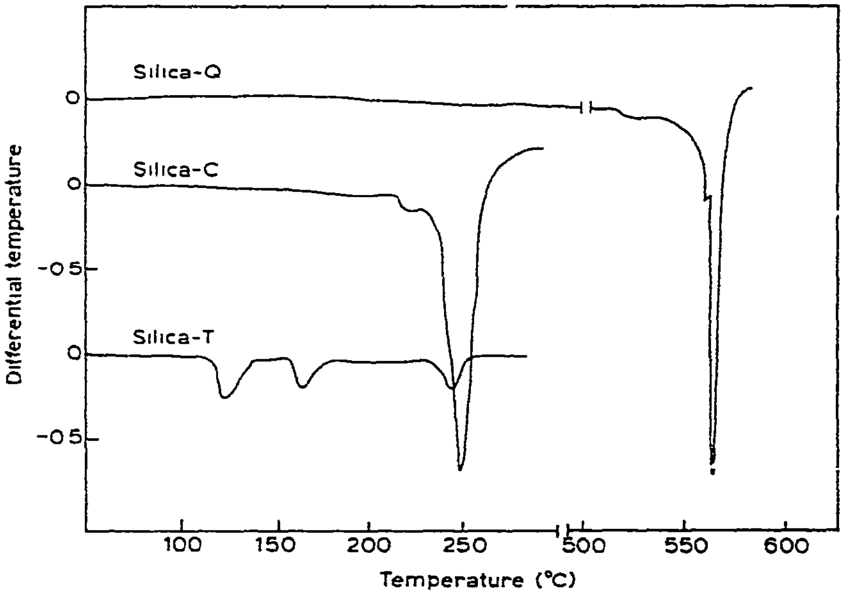

Fig 1 Differential scanning calorimetric (DSC) analysis of silica modifications.

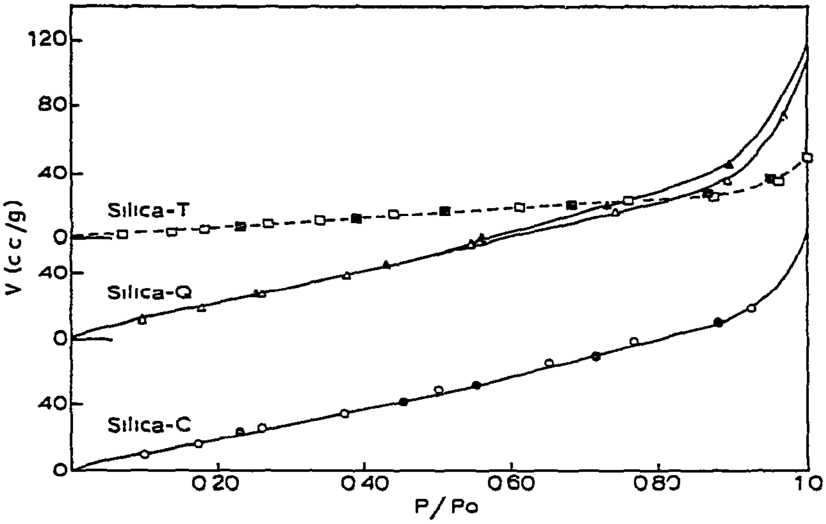

Fig 2. Adsorption–desorption isotherms of nitrogen on the silica modifications.

120 and 165°C represent the transformation of the tridymite phases, while the endotherm located at 245°C is characteristic for the crystobalite modification; the tridymite prepared in this study was found to contain about 6–8% crystobalite.

The adsorption–desorption isotherms of nitrogen gas at liquid nitrogen temperature (−195.8°C) are shown in Fig. 2 for the various silica modifications.

The nitrogen adsorption isotherms on the crystobalite (silica-C) and tridymite (silica-T) modifications are characterized by being fully reversible without any hysteresis indicating a pore system with a limited pore size in these adsorbents.

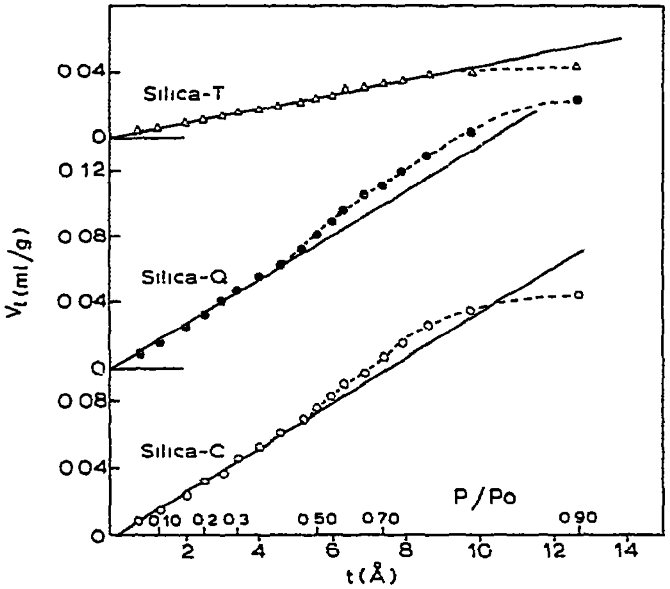

Fig. 3. V_l–t plots for the adsorption of nitrogen on the silica modifications

TABLE 1

Some pore structure characteristics of the silica modifications from nitrogen adsorption

Sample	S_{BET} ($m^2 g^{-1}$)	S_t ($m^2 g^{-1}$)	V_p ($ml\ g^{-1}$)	$\bar{r}_h$ (Å)
Silica-Q	155.7	139.7	0.2709	17.40
Silica-C	173.0	155.0	0.2295	13.27
Silica-T	51.8	46.0	0.0757	14.62

However, in the quartz modification, a closed hysteresis loop was noticed in the high pressure region, due to the existence of some mesopores in the pore system of quartz.

From the adsorption isotherms, the amount of nitrogen adsorbed, expressed in milliliters of the liquid adsorbate per one gram of the adsorbent, V_l ($ml\ g^{-1}$), could be constructed versus the statistical thickness of the adsorbed layer, t (Å), and the V_l–t plots are shown in Fig. 3. The t-values used are those obtained by Mikhail et al. [3].

From the adsorption isotherms and the V_l–t plots, shown in Figs. 2 and 3, some important pore structure characteristics could be derived and these are given in Table 1. These parameters are the specific surface areas derived from the BET equation, S_{BET} ($m^2 g^{-1}$), the specific surface areas derived from the V_l–t plots, S_t ($m^2 g^{-1}$), the total pore volumes, Vp ($ml\ g^{-1}$) and the mean hydraulic radius of the total pore system accessible to nitrogen molecules, $\bar{r}_h$ (Å), respectively.

The mean hydraulic radius of the total pore system accessible to nitrogen molecules was found to be 17.40 Å for the low temperature quartz, whereas the mean hydraulic radii of the total pore systems of the crystobalite and tridymite modifications were found to be 13.27 and 14.62 Å, respectively. The lower $\bar{r}_h$-values of the total pore systems of the crystobalite and tridymite modification is mainly due to the fact that larger fractions of the total pore system of these adsorbents are located in micropores or mesopores with limited pore sizes, the V_l–t plots shown in Fig. 3 indicate this criterion very well. The crystal growth of the hexagonal tridymite modification is associated with a marked drop in the specific surface area measured by nitrogen molecules

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