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Role of Germanate Catalyst in the Transformation of Germanium Dioxide

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The role of alkali germanates as catalysts in the polymorphic transformation of germanium dioxide was investigated by high-temperature X-ray diffraction method. Lithium germanate and sodium germanate catalyze the transformation in a solid state, the activation energies being larger than 80 kcal/mol. Potassium germanate catalyst plays its role in a liquid state, the activation energy being smaller than that of other catalysts.

It was found[1)] that pure germanium dioxide does not undergo transformation on being heated up to 1000 °C, but it is transformed into tetragonal modification from hexagonal modification in the presence of lithium carbonate or potassium chloride. It was confirmed by means of DTA and high-temperature X-ray diffraction that a solid state reaction first occurs between the alkali salt and germanium dioxide to form germanate compounds which, in a crystalline or glassy state, catalyze the transformation.[2)] Since it is expected that the occurence of such a reaction may disturb the determination of the transformation rate, it is necessary to investigate the transformation with an alkali germanate salt which is prepared by separate procedure. The phase diagrams of alkali oxide and germanium dioxide having been studied by Murthy *et al.*,[3–5)] it was possible to elucidate the role of alkali germanate salts during the course of transformation.

We have studied the role of the alkali germanate salt during the course of phase transformation in detail under standardized conditions. It was found that lithium germanate and sodium germanate catalyze the transformation in solid state, while potassium germanate does so in liquid state, the activation energy being smaller than that of other salts.

Experimental

The starting materials were much the same as previously reported. Alkali germanate was prepared by a solid state reaction between Li_2CO_3, K_2CO_3 or Na_2CO_3 and GeO_2, as follows.

1) Lithium germanate: Li_2CO_3 and GeO_2 were mixed in a 1 : 7 mole ratio and ignited at 750 °C for 5 hr or at 1020 °C for 40 min. The end point of formation of $Li_2O\cdot 7GeO_2$ was confirmed by comparing the X-ray diffraction patterns of the product with the data given by Murthy and Ip.[3)] The catalyst ignited at high temperature is of a larger crystal size than that at low temperature.

2) Potassium germanates: In order to prepare $3K_2O\cdot 11GeO_2$, K_2CO_3 and GeO_2 were mixed in a 3 : 11 mole ratio and ignited at 800 °C for 4 hr or at 1020 °C for 30 min, while K_2CO_3 and GeO_2 were mixed in a 1 : 7 mole ratio and ignited at 940 °C for 30 min, the product being $K_2O\cdot 7GeO_2$.[4)] The end point of formation of these salts was confirmed by the same procedure as described above. In the case of $K_2O\cdot 7GeO_2$, the sintering was observed to occur, and the salt was used as catalyst after being finely ground.

3) Sodium germanate: $2Na_2O\cdot 9GeO_2$ was prepared by igniting a mixture of Na_2CO_3 and GeO_2 in a 2 : 9 mole ratio at 1050 °C for 40 min and the X-ray diffraction patterns of the product were compared with that reported by Murthy and Aguayo.[5)]

High-temperature X-ray diffraction and measurements of transformation rate were carried out as reported.[2)] All the experiments were carried out in dry nitrogen atmosphere.

Results

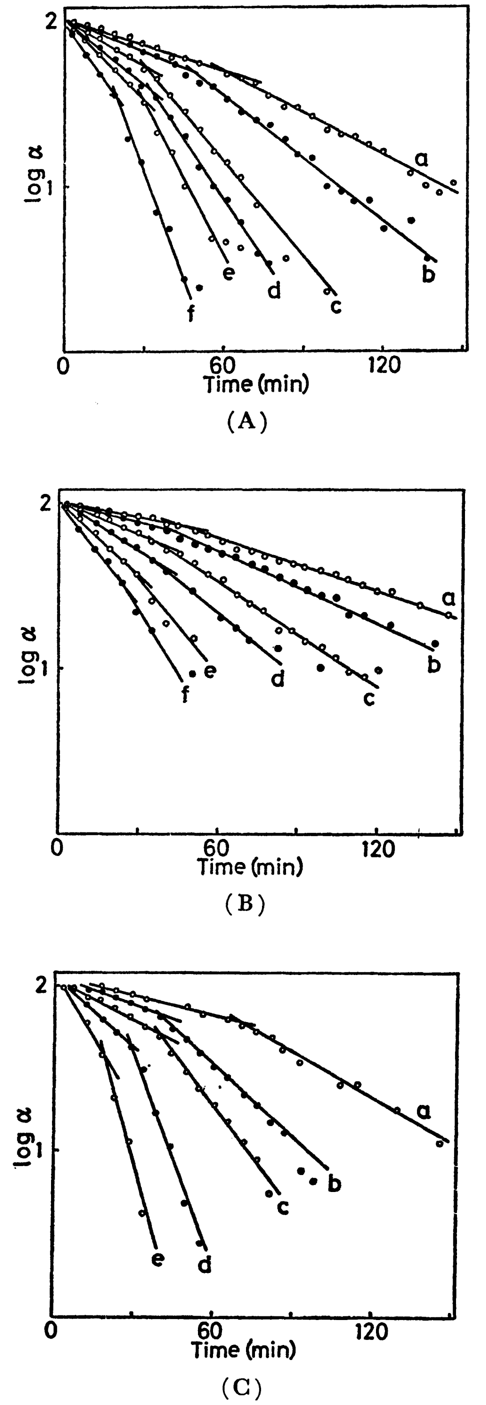
Some typical plots of logarithm of a hexagonal fraction, α, against time are shown in Figs. 1 and 2, where α was calculated by $H/H+T$, H or T being the peak height of hexagonal or tetragonal modification. The catalyst and its amount in weight percentage are given in the figures.

Activation energies were calculated from the Arrhenius plots (Figs. 3 and 4), where k was determined from the slope of straight lines. The results are given in Tables 1 and 2.

Discussion

From the study on the role of catalyst during the phase transformation of germanium dioxide[2)] it was found that lithium and potassium salts added react with germanium dioxide to form germanate compounds. It was clarified for lithium salt that the formation of lithium germanate, $LiO_2\cdot 7GeO_2$, occurs at a lower temperature than that of the transformation. Lithium germanate thus formed seems to catalyze the transformation in solid state. Potassium germanate, in contrast, seems to act as a catalyst in liquid state. It is expected that the kinetics of the transformation differ for the two cases. Murthy *et al.*[4)] reported that there are many stable or metastable states in the K_2O-GeO_2 system, but since the added amount of potassium salt is rather small, it is desirable to select stable compounds rich in GeO_2. $3K_2O\cdot 11GeO_2$ and $K_2O\cdot 7GeO_2$ were prepared and used as catalysts, and it was found that the difference exists between them.

The phase transformation proceeds with alkali germanate salts. The plots of $\log \alpha$ against time (Figs. 1 and 2) consist of two straight lines, which can be explained by the assumption that the transformation proceeds in two stages, probably nucleation and propagation. However, activation energies calculated for two stages (Figs. 3 and 4) do not differ as much for lithium and sodium germanate as in the case of potassium germanate. This might be accounted for by the difference of solid and liquid catalyst. It could be concluded that lithium and sodium germanate remain in solid state even during the course of transformation, while potassium germanate turns to liquid.



(A)

(B)

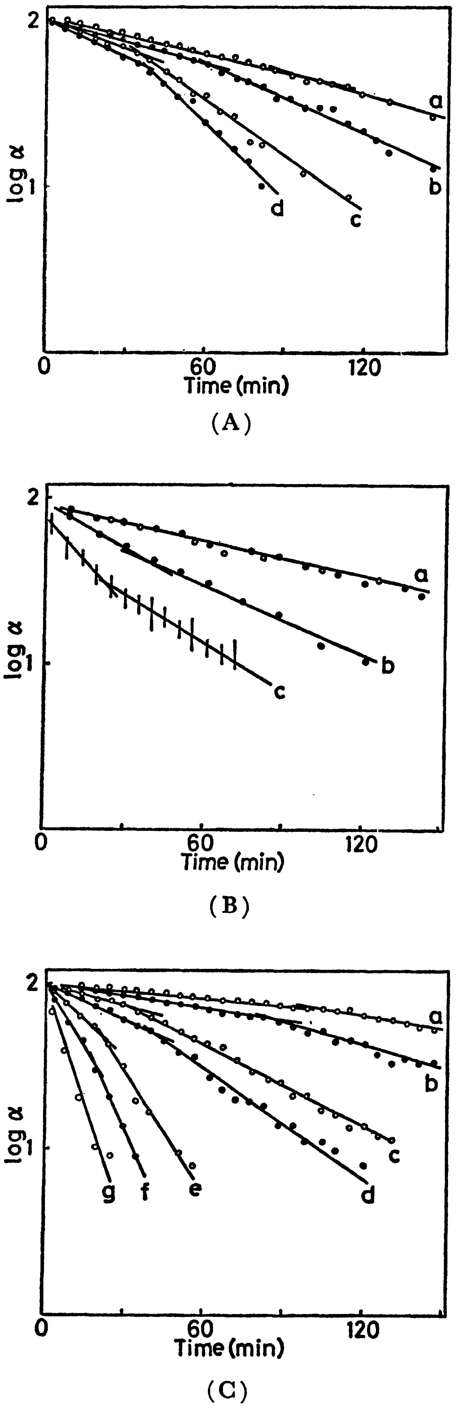
(C)

Fig. 1. First-order plot of conversion of hexagonal to tetragonal germanium dioxide (with catalyst of lithium germanate; $Li_2O \cdot 7GeO_2$); α is the percentage of hexagonal form present.

(A) Catalyst amount: 5 wt%
temperature a : 880 °C b : 890 °C c : 900 °C
d : 910 °C e : 920 °C f : 930 °C

(B) Catalyst amount: 10 wt%
temperature a : 870 °C b : 880 °C c : 890 °C
d : 900 °C e : 910 °C f : 920 °C

(C) Catalyst was prepared at low temperature and added amount was 5 wt%
temperature a : 840 °C b : 850 °C c : 860 °C
d : 870 °C e : 880 °C



(A)

(B)

(C)

Fig. 2. First-order plot of conversion of hexagonal to tetragonal germanium dioxide (with catalyst of potassium or sodium germanate).

(A) $3K_2O \cdot 11GeO_2$ catalyst was prepared at low temperature and added amount was 1 wt%
temperature a : 840 °C b : 850 °C c : 860 °C
d : 870—890 °C

(B) Catalyst amount: 2 wt% of $K_2O \cdot 7GeO_2$
temperature a : 850—860 °C b : 870 °C
c : 880—940 °C

(C) Catalyst amount: 5 wt% of $2Na_2O \cdot 9GeO_2$
temperature a : 870 °C b : 880 °C c : 890 °C
d : 900 °C e : 910 °C f : 920 °C
g : 930 °C

Table 1. Activation energy of transformation (in N_2)

Catalyst wt%	$Li_2O \cdot 7GeO_2$ 5	$3K_2O \cdot 11GeO_2$ 1	$K_2O \cdot 7GeO_2$ 2	$2Na_2O \cdot 9GeO_2$ 5
Activation energy	83— 91(A) 122—123(B)	72—102(A) 70— 98(B)	50±5	157—149

Note: 1) The first number denotes the value for the initial stage of the transformation, and the second number that for the final stage. 2) Catalyst A was prepared at 1020 °C for 30—40 min. Catalyst B was prepared at 750—800 °C for 4—5 hr.

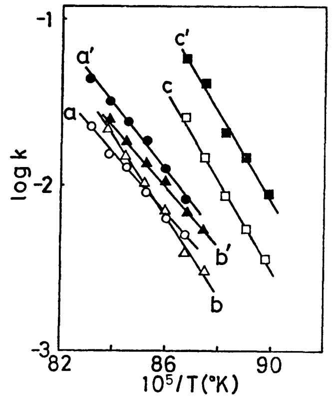


Fig. 3. Arrhenius plot of log k (k is obtained from Fig. 1) against reciprocal absolute temperature.
- a : initial stage of transformation (Fig. 1-A)
- a' : final stage of transformation (Fig. 1-A)
- b : initial stage of transformation (Fig. 1-B)
- b' : final stage of transformation (Fig. 1-B)
- c : initial stage of transformation (Fig. 1-C)
- c' : final stage of transformation (Fig. 1-C)

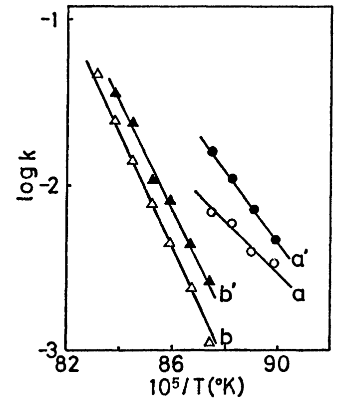


Fig. 4. Arrhenius plot of log k (k is obtained from Fig. 2) against reciprocal absolute temperature.
- a : initial stage of transformation (Fig. 2-A)
- a' : final stage of transformation (Fig. 2-A)
- b : initial stage of transformation (Fig. 2-C)
- b' : final stage of transformation (Fig. 2-C)

Table 2. Effect of amount of catalyst upon activation energy (in N_2)

Catalyst	$Li_2O \cdot 7GeO_2$	$3K_2O \cdot 11GeO_2$
1 wt%	110—100	70—98
5 wt%	83— 91	92—
10 wt%	109— 83	—

This is also supported by the fact that the temperature where the phase transformation occurs is lower in the case of liquid than in solid catalyst.

In the case of $K_2O \cdot 7GeO_2$ the results seem to be caused by the change of its state, as shown in Fig. 2 (B). The mean value of activation energy obtained from the Arrehnius plot is 50±5 kcal/mol between 850 °C and 900 °C (Table 1). Such a phenomenon was not observed with germanates other than $K_2O \cdot 7GeO_2$.

In the case of $3K_2O \cdot 11GeO_2$ it is probable that the interaction between the salt and germanium dioxide would occur during the course of the transformation and $K_2O \cdot 7GeO_2$ is formed.[4] However, this change was not detected by high-temperature X-ray diffraction, probably because of an insufficient amount of the catalyst for detection. The small values of the activation energy obtained for $3K_2O \cdot 11GeO_2$ may be the result of such an interaction. The catalyst, whose melting point is known to be 1055 °C, would be solid during the transformation so far as no interaction took place.

In the case of sodium germanate the results shown in Figs. 2(C) and 4 are much the same as in the case of lithium germanate. The activation energy obtained is 157 and 149 kcal/mol for first and final stages, respectively. The large values of activation energy would be explained by the fact that sodium germanate is stable and would catalyze the transformation in solid state.

The effect of the preparative method of catalysts on the transformation was observed for lithium germanate as an example for the solid catalyst (Table 1). The rate constant, k, was larger for the catalyst prepared at low temperature than prepared at high temperature, the activation energies differing a great deal from each other. No such effects were observed when potassium germanate was used. It would be concluded that the transformation carried out with solid catalysts is affected by characteristics such as particle size and morphology of the catalyst.

The amount of catalysts used in the transformation has in general no influence upon the activation energy of the transformation (Table 2). In the case of $LiO_2 \cdot 7GeO_2$, the transformation rate increased with 1—5 wt% increase in amount and it becomes saturated at 5—10 wt%. In the case of $3K_2O \cdot 11GeO_2$, the increase in amount causes the sintering of germanium dioxide. This would be accelerated by the presence of the catalyst in liquid state. As a result the calculation of activation energy could not be carried out in the case of large amounts of $3K_2O\cdot 11GeO_2$.

The role of lithium salt in this transformation was recently reported.⁶⁾ The intermediate phase found by the same method as that applied in the transforma- of silicon dioxide⁷⁾ increased during the course of the transformation of germanium dioxide.

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