Effect of Surrounding Atmosphere in the Transformation of Germanium Dioxide

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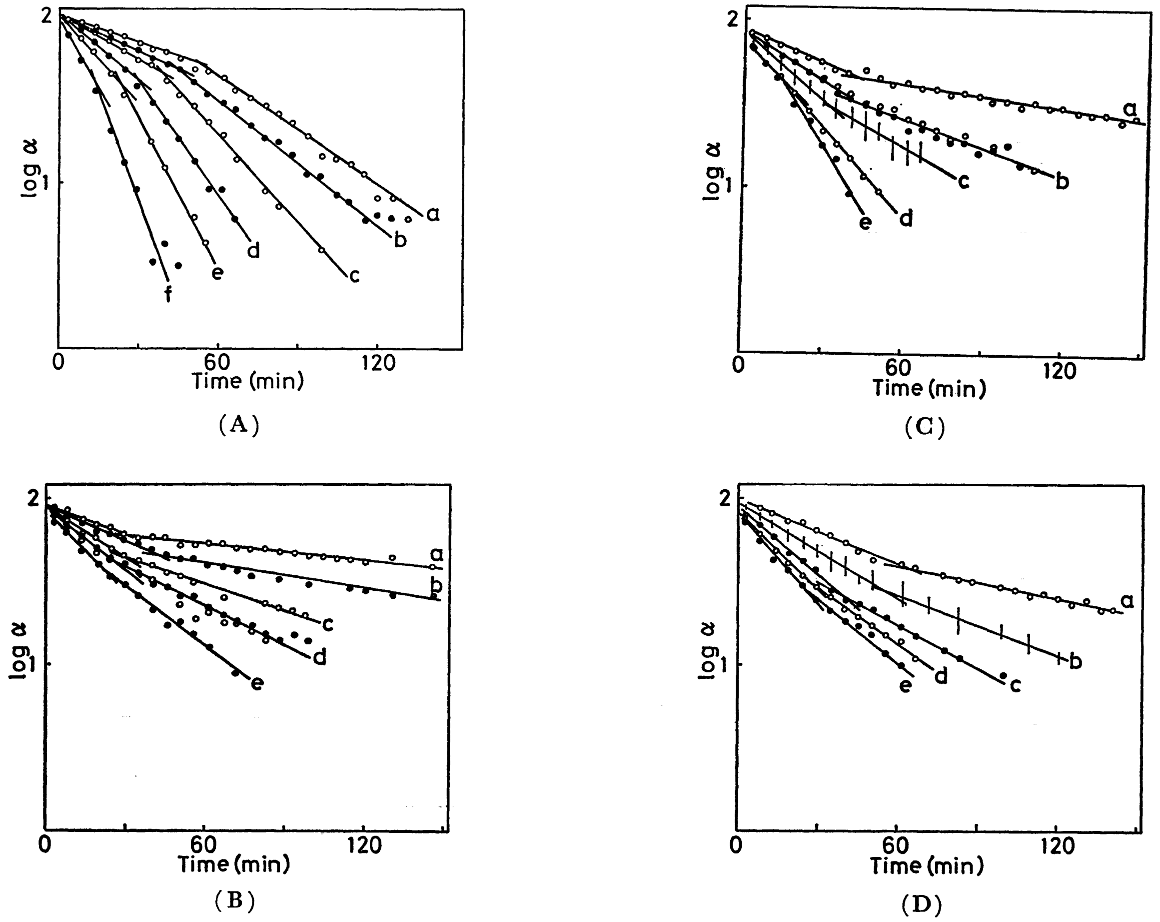
The effect of surrounding atmosphere on the phase transformation of germanium dioxide with alkali germanate catalysts was investigated by high temperature X-ray diffraction method. The catalysts were $Li_2O \cdot 7GeO_2$, $3K_2O \cdot 11GeO_2$, $K_2O \cdot 7GeO_2$ and $2Na_2O \cdot 9GeO_2$. The ambient atmospheres were dry or wet nitrogen and oxygen. The effect of atmosphere was found to be not so large as that of the catalyst. Water vapor has prominent effects upon the transformation as in other solid state reactions.

The role of the catalyst during the phase transformation of germanium dioxide was elucidated in a previous paper.[1] It is known that the surrounding atmosphere affects the rate and activation energy of the transformation singnificantly. It is thought that the atmosphere has a different effect on the transformation depending upon the catalyst used. In the present study the role of the surrounding atmosphere during the transformation was studied in detail under standardized conditions.

Experimental

The starting materials and the procedure of high-temperature X-ray diffraction were similar to those reported.[1] A high-temperature X-ray cell was filled with gas, dry or wet nitrogen and oxygen being used for the ambient atmospheres. Nitrogen and oxygen were dried by passing through concd. sulfuric acid and anhydrous calcium chloride; or wetted by allowing the gas to flow through water at 0 or 51±1 °C (water vapor pressure 5 or 100 mmHg, respec-



(A) (C)

(B) (D)

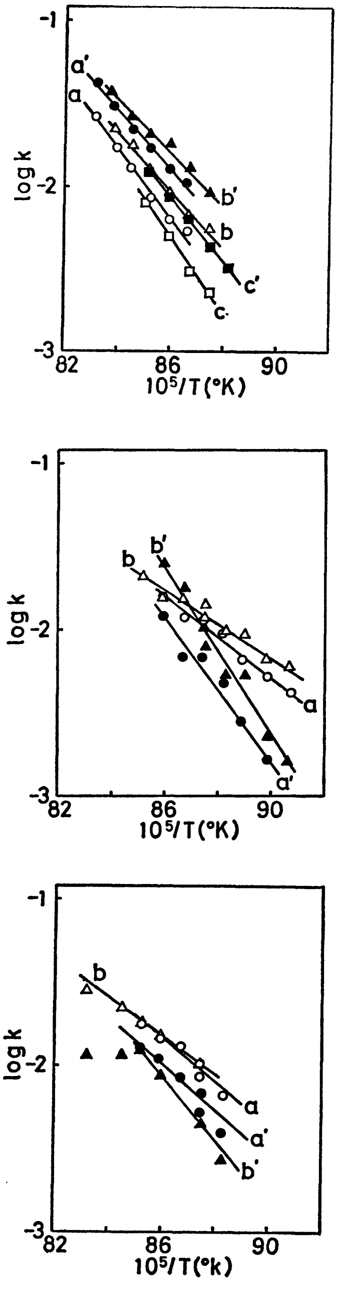
Fig. 1. First-order plot of conversion of hexagonal to tetragonal germanium dioxide.

(A) Catalyst: $Li_2O \cdot 7GeO_2$ 5wt%
Atmosphere: dry O_2
temperature a : 880 °C b : 890 °C c : 900 °C
d : 910 °C e : 920 °C f : 930 °C

(B) Catalyst: $3K_2O \cdot 11GeO_2$ 1 wt%
Atmosphere: wet N_2 (water vapor 5 mmHg)
temperature a : 840 °C b : 850 °C c : 860 °C
d : 870 and 880 °C e : 890 °C

(C) Catalyst: $3K_2O \cdot 11GeO_2$ 1 wt%
Atmosphere: wet O_2 (water vapor 5 mmHg)
temperature a : 840 °C b : 850 and 860 °C
c : 870 °C d : 880 °C e : 890 °C

(D) Catalyst: $K_2O \cdot 7GeO_2$ 2 wt%
Atmosphere: wet O_2 (water vapor 100 mmHg)
temperature a : 860 °C b : 870 °C c : 880 °C
d : 890 °C e : 900 °C



(A) a : initial stage of transformation (Fig. 1-A)
a' : final stage of transformation (Fig. 1-A)
b : initial stage of transformation[1)]
b' : final stage of transformation[1)]
c : initial stage of transformation[2)]
c' : final stage of transformation[2)]
1) Catalyst: $Li_2O \cdot 7GeO_2$ 5 wt%
Atmosphere: Wet O_2 (water vapor 100 mmHg)
2) Catalyst: $2Na_2O \cdot 9GeO_2$ 5 wt%
Atmosphere: Wet N_2 (water vapor 5 mmHg)

(B) a : initial stage of transformation (Fig. 1-B)
a' : final stage of transformation (Fig. 1-B)
b : initial stage of transformation (Fig. 1-C)
b' : final stage of transformation (Fig. 1-C)

(C) a : initial stage of transformation (Fig. 1-D)
a' : final stage of transformation (Fig. 1-D)
b : initial stage of tranformation[3)]
b' : final stage of transformation
3) Catalyst: $K_2O \cdot 7GeO_2$ 2 wt%
Atmosphere: Wet N_2 (water vapor 5 mmHg)

Fig. 2. Arrhenius plot of log *k* (*k* is obtained from the figures of log $\alpha - t$ plot) against reciprocal temperature.

TABLE 1. ACTIVATION ENERGY OF TRANSFORMATION

Atmosphere			Activation energy (kcal/mol)			
			$Li_2O \cdot 7GeO_2$ 5 wt%	$3K_2O \cdot 11GeO_2$ 1 wt%	$K_2O \cdot 7GeO_2$ 2 wt%	$2Na_2O \cdot 9GeO_2$ 5 wt%
N_2	Dry		83—91 (122—123)	70—98 (72—102)	50±5	157—149
	Wet	5 mmHg	96—91	55—98	52—90	101— 90
		100 mmHg	92—78			
O_2	Dry		93—80 (92—82)	47—130 (52—128)	40±5	142—106
	Wet	5 mmHg	83—90	46—114	115—119	107—83
		100 mmHg	81—74		60—65	

$\ln k = \ln A - E/RT$ *k*: rate const. *E*: activation energy (kcal/mol). *A*: pre-exponential factor

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) Data given in parentheses were calculated for $Li_2O \cdot 7GeO_2$ catalyst prepared at low temperature and $3K_2O \cdot 11GeO_2$ catalyst prepared at high temperature.

tively). The flow rate of gas was held constant by a tube flowmeter.

Results

Typical plots of logarithm of hexagonal fraction against time are shown in Fig. 1. Rate constant, *k*, was calculated in the same way as that described in the previous paper for the initial and final stages. The catalyst and atmosphere used are given in the Figures.

Activation energies were calculated from Arrhenius plots (Fig. 2). The experimental data with the atmosphere of dry nitrogen were reported.1) The values of activation energy and pre-exponential factor are given in Tables 1 and 2.

Discussion

It was found that lithium or potassium salt added reacts with germanium oxide to form a germanate compound,1,2) and that the surrounding atmosphere affects the rate and activation energy of the transformation significantly.3) In these cases a different effect depending on the kind of germanate was expected, especially between one acting in solid state and one in liquid state.

From the values of activation energy it was confirmed that the effect of the surrounding atmosphere upon the phase transformation is smaller than that of the catalyst. While the values of activation energy do not change so much, the pre-exponential factor of transformation was dependent upon the surrounding atmosphere (Table 1).

A comparison of the relative positions of initial and final stages in the Arrhenius plot (Fig. 2), shows that they do not intersect in the temperature range studied in the cases of $Li_2O\cdot 7GeO_2$, ((A) a and a′, b and b′), $2Na_2O\cdot 9GeO_2$ ((A) c and c′) and $K_2O\cdot 7GeO_2$ ((C) a and a′, b and b′) catalysts. Their positions are in contrast to those of the two former catalysts acting in a solid state and the latter in a liquid one. This indicates that the rate *k* is higher in the final stage than in the initial stage for solid catalysts and lower for liquid ones. In the case of $3K_2O\cdot 11GeO_2$ ((B) a and a′, b and b′) the lines cross, the points of intersection lying between 870 and 890 °C. These temperatures lie near the eutectic point between $K_2O\cdot 7GeO_2$ and GeO_2 in the phase diagram reported by Murthy *et al.*4) This salt would be formed by the reaction of $3K_2O\cdot 11GeO_2$ and GeO_2.

The effect of oxygen atmosphere is shown in Table 1, where oxygen makes the activation energy in the final stage small for $Li_2O\cdot 7GeO_2$ and $2Na_2O\cdot 9GeO_2$ which act in a solid state. However the difference between nitrogen and oxygen is not so large for liquid $K_2O\cdot 7GeO_2$ as in the two former catalysts. The effect of oxygen could be explained by the formation of germanium monoxide, which is assumed to be stable at high temperature. The effect of germanium monoxide seems to be more prominent on the transformation with a solid catalyst than with a liquid one.

The effects of the preparing conditions of solid catalysts upon the activation energy of the phase transformation, recognized in the nitrogen atmosphere,1) were not observed in the present experiment in which oxygen atmosphere was used. They were not observed for liquid catalysts independent of the atmosphere during the transformation. The effect upon the rate of transformation is independent of the atmosphere and a high rate was found for catalysts prepared at lower temperature. It seems that the effect of the surrounding atmosphere upon the transformation is larger than that of the preparing conditions of the catalyst.

The effect of water vapor was observed only for the initial stage for low pressure. It was found also for the final stage when its pressure is as high as 100 mmHg. We see that water vapor influences the pre-exponential factor (Table 2), such phenomena being often found in the solid state reaction. When the vapor pressure was as high as 500 mmHg, the transformation rate was found to be high especially in the final stage, but the lowering of X-ray intensity made accurate determination of the rate impossible.

The effect of oxygen or water vapor upon the transformation rate is observed to be similar by independent

TABLE 2. VALUES OF PRE-EXPONENTIAL FACTOR

Atmosphere			log *A* (*A* : pre-exponential factor) Catalyst							
			$Li_2O\cdot 7GeO_2$ 5 wt%		$3K_2O\cdot 11GeO_2$ 1 wt%		$K_2O\cdot 7GeO_2$ 2 wt%		$2Na_2O\cdot 9GeO_2$ 5 wt%	
N_2	Dry		13.4	15.3	11.3	16.9			27.2	26.0
			(21.6	22.1)	(11.7	19.9)				
	Wet	5 mmHg	15.9	15.0	8.7	16.7	8.0	14.8	18.0	14.8
		100 mmHg	15.1	12.6						
O_2	Dry		15.9	13.2	6.9	23.1	5.5		24.5	17.8
			(15.9	14.3)	(7.8	22.3)				
	Wet	5 mmHg	13.4	15.1	6.8	19.9	19.9	20.3	17.8	13.5
		100 mmHg	13.1	12.1	15.6	23.7	9.5	10.2		

Note: See Table 1.

of the catalyst; k is larger for oxygen than for nitrogen and for wet atmosphere than for dry one. However, the log α–t plot (Fig. 1) scatters more in the wet atmosphere than in the oxygen atmosphere.

The co-operative effect of oxygen and water vapor is so complicated that it is difficult to give an explanation. They might compensate each other when the catalyst is $Li_2O \cdot 7GeO_2$ and the vapor pressure of water as low as 5 mmHg. For the catalyst $3K_2O \cdot 11GeO_2$, the co-operative effect is very clear.

The so-called "compensation effect" was observed (Tables 1 and 2) and the linearity between activation energy and common logarithm of pre-exponential factor was established. This might be the first time for it to be found in the solid state reaction.

References

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