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Differences between Glassy and Crystalline Germanium Dioxide for the Catalytic Decomposition of Formic Acid

At present little is known about the difference in the catalytic properties between glassy and crystalline substances. Recent reports indicate that metallic glasses are catalytically active (*1*) and uniquely selective (*2, 3*). An oxide glass of the Si–Al–Na system was successfully used as a support for making highly dispersed metal catalysts (*4, 5*). Previously we studied the catalytic properties of a vanadate glass (V_2O_5–BaO–ZnO) (*6*). However, the details of its catalytic properties could not be clarified owing to the many components of the system. Now we have extended our studies to the catalytic decomposition of formic acid on germanium dioxide, which is typical of the glass-forming oxides. We found that the surface of this glass is extremely inactive compared to the surface in the crystalline state, in contrast to the results of the metallic glasses (*1–3*).

The GeO_2 was hexagonal reagent grade (99.99% pure) from Nakarai Chemicals. Glassy samples were prepared by melting in a platinum crucible at 1300°C for 6 h, air-quenching to room temperature, and grinding. The glass transition temperature ranged from 500 to 550°C, according to differential thermal analysis. Hexagonal crystal samples were obtained by crystallizing the glass powder at 900°C overnight and regrinding (denoted as sample H-g). Changes in the catalytic activity caused by the crystallization of the glass were observed by isothermal and temperature-programmed decomposition (TPD) techniques. The purification of HCOOH and the procedures for the isothermal reaction employed in the present study were described previously (*6*). The reactions were carried out at an initial pressure of 20 Torr and at temperatures of 220–260°C, using samples pretreated with dry air at different temperatures between 240 and 900°C for 4 h. The BET-surface area was measured gravimetrically using a Cahn RG electromicrobalance to determine nitrogen adsorption at −196°C. The procedure for TPD was as follows: After dry air treatment and evacuation at 500°C for 1 h, the sample was cooled to room temperature, exposed to 10 Torr of HCOOH for 1 h, and reevacuated for 20 h. Then, under 100 ml/min He flow, the temperature was programmed at different heating rates from room temperature to 500°C. Desorbing gases were monitored with a thermal conductivity detector.

Figure 1 shows X-ray diffractograms of a glassy sample treated with dry air at 700°C (*A*) and 800°C (*B*) for 4 h. Crystallization to the hexagonal form occurs just below 800°C. Figure 2 shows changes in the catalytic activity represented by the initial rate of HCOOH decomposition per unit area (*A*), the surface area (*B*), and the selectivity to dehydrogenation (*S*), $S = CO_2/(CO_2 + CO)$, as a function of the temperature of pretreatment for a glass sample.

The catalytic activity was abruptly increased by the treatment above 800°C. These results indicate that the surface of the crystalline sample is a more active catalyst than that of the glassy one, similar to the results obtained for the vanadate glass (*6*). The *S* values were not appreciably changed by the crystallization.

Figure 3 shows TPD curves of HCOOH on glassy and hexagonal crystalline samples having the same surface area.

Two peaks are distinguished in both

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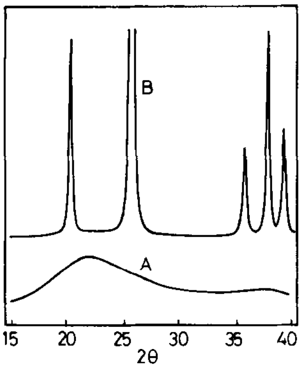

FIG. 1. X-Ray diffractograms of a glassy sample heat-treated at 700°C (A) and at 800°C (B) for 4 h, in the same range.

curves. Gas chromatographic analyses revealed that the first peak (I) arises from adsorbed HCOOH and the second peak (II) from the decomposition products, CO, CO_2, H_2O.

Figure 4 shows the product desorption peaks obtained by cooling a U-shaped trap in a flow path between the TPD cell and the detector at −78.5°C. The results are summarized in Table 1 together with the kinetic data obtained from the isothermal reactions.

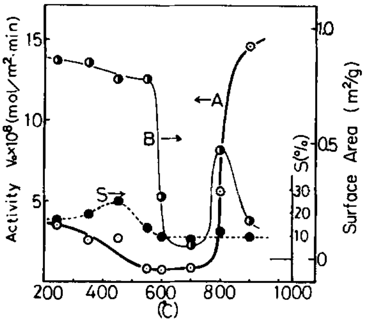

FIG. 2. Changes in catalytic activity (*A*), surface area (*B*), and selectivity to dehydrogenation (*S*) by heat-treatment of glassy sample (reaction temperature = 240°C).

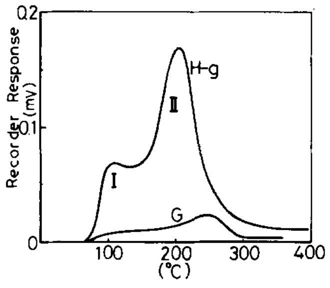

FIG. 3. TPD curves on hexagonal crystalline (H-g) and glassy sample (G), heating rate = 10°C/min.

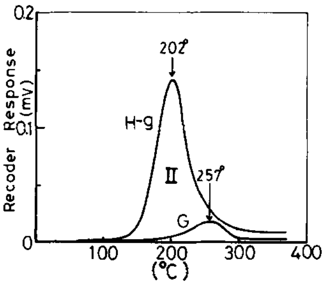

FIG. 4. Desorption curves of decomposition products on hexagonal crystalline (H-g) and glassy sample (G), heating rate = 10°C/min.

TABLE 1

Isothermal Reaction at 240°C and TPD at a Heating Rate of 10°C/min

Sample	Isothermal			TPD (second peak)		
	Cat. act. (mol/min · m^2)	Act. ratio	E_a (kcal/mol)	T_m (°C)	Ratio of peak area	E_d (kcal/mol)
Glass	0.8–2.8 × 10^{-8}	1	24–26	257	1	24
Hexagonal	14–19 × 10^{-8}	9.2	26–29	202	8.7	21

Note. E_a is the activation energy obtained from the data of the reaction temperatures of 220–260°C. E_d is the desorption energy of the products evaluated by applying first-order formulation to the TPD results at heating rates of 4–15°C/min (*7*). T_m is the maximum temperature in the desorption curve.

The TPD data show that the chemisorbed species on the hexagonal crystalline sample is present in greater amounts and decompose more easily than on the glassy sample. The ratio of the catalytic activities agrees closely with the ratio of the peak areas. No appreciable differences can be found between the activation energies (E_a and E_d) on the two samples. These results suggest that the difference in the catalytic activity between the two samples results mainly from the difference in the number of active sites which are effective in decomposing the chemisorbed species. We believe that the reason for the inactivity of the glassy surface is probably found in the suggestions (*8*) that the surface structures of glasses are relatively homogeneous, e.g., free of grain boundaries, and are chemically stable compared with the surface structure in the crystalline state.

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