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CHANGES IN THE CATALYTIC PROPERTIES CAUSED BY THE CRYSTALLIZATION OF A VANADATE GLASS ON THE DECOMPOSITION OF FORMIC ACID

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The difference in the catalytic activity between vitreous and crystalline state of a vanadate (V_2O_5-BaO-ZnO) was observed for the decomposition of formic acid. The results suggested that the surface net work structure formed by V_2O_5 is extremely inactive in the dehydration in comparison with the surface in the crystallized state.

There have been published many studies concerning the influence of crystallographic variation or phase transformation of a solid on its catalytic activity.$^{1)}$ We can expect that the similar situation will be existent between the vitreous and crystalline form of a solid. So far as we are aware, no experiments on this problem have been reported. The purpose of the present work was to elucidate this question by using a vanadate glass (V_2O_5 - BaO - ZnO , mol ratio = 55.0 : 27.5 : 17.5) as a catalyst for the decomposition of formic acid. The reason for selecting this substance was that this glass can be readily crystallized at about 360° - 380° C and these temperatures lie above the range which is convenient for the kinetic study of the reaction.

Reagent grade materials (V_2O_5, $BaCO_3$, ZnO) were obtained from Nakarai Chemicals LTD. A mixture of these materials was melted in a platinum crucible at 700° C and refined at 1000° C for 2 hr until bubble free. The vitreous sample was prepared by rapid cooling this melt to room temperature and then crushed or pulverized in a dry atmosphere.$^{2)}$ Formic acid was purified by sublimation at -30° C under reduced pressure after removal of water with anhydrous boric acid and finally condensed into a storage bulb in the reaction apparatus. The rate of reaction ($HCOOH \begin{matrix} \nearrow H_2 + CO_2 \\ \searrow H_2O + CO \end{matrix}$) was obtained by measuring the pressure increase in a closed vessel at temperatures 240° - 260° C and at an initial pressure of 20 Torr. In order to determine the selectivity of the reaction, analysis of the reaction products was carried out by a gas chromatograph, using a silica gel column and helium as carrier gas. Heat-treatment of specimens was carried out in the reaction vessel in helium for 2 hr at temperatures 240° - 450° C. The observation of crystallization was made by differential thermal analysis (DTA), X-ray powder diffraction and scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was also used to obtain precise information on the surface composition of the catalyst. The changes in surface area due to heat-treatment were followed by nitrogen adsorption at -195° C using a Cahn electrobalance and by application of the B.E.T. method.

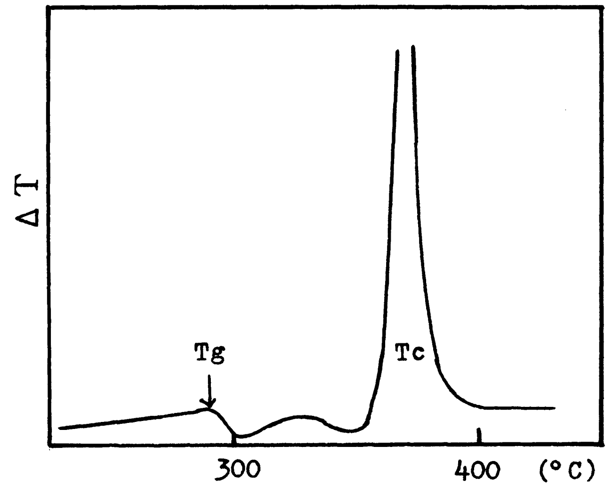
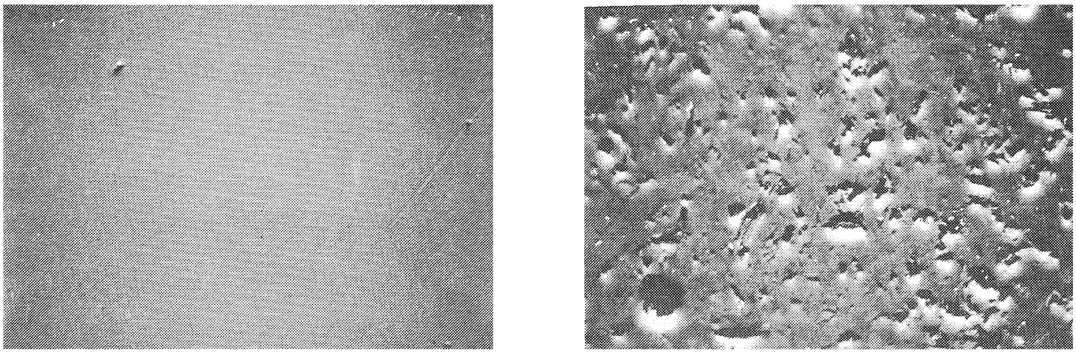


Fig. 1 DTA of vanadate glass

Figure 1 shows a typical DTA curve obtained at a heating rate of 5°/min for this specimen. The result indicates that the glass transition and the crystallization occur at about 290° C (Tg) and in the range 360° - 380° C (Tc), respectively. The range of Tc was also in fair agreement with that detected by X-ray diffraction. Scanning electron micrographs shown in Fig. 2 reveal that the surface of glass is featureless on a scale resolvable in the microscope but on heat-treatment above Tc crystallines appear.



A B

Fig. 2 Electron micrographs (× 2000),
Heat-treatment in helium for 2 hr (A) at 240°, (B) at 355° C

Figure 3 shows changes in the surface area (A) and the catalytic activity (B), initial rate per unit area, as a function of the temperature of heat-treatment for a powdered specimen (> 200 mesh). The catalytic activity was remarkably increased by the treatment above 350° C, suggesting that the activity appears to be parallel to the crystallinity. The result obtained by use of a massive specimen is given in Fig. 4. It is clear that the difference in the activity patterns between both specimens is not significant. In addition, the rates of two reactions, dehydrogenation and dehydration, were obtained separately from the measurements of CO_2/CO ratio in the reaction products.

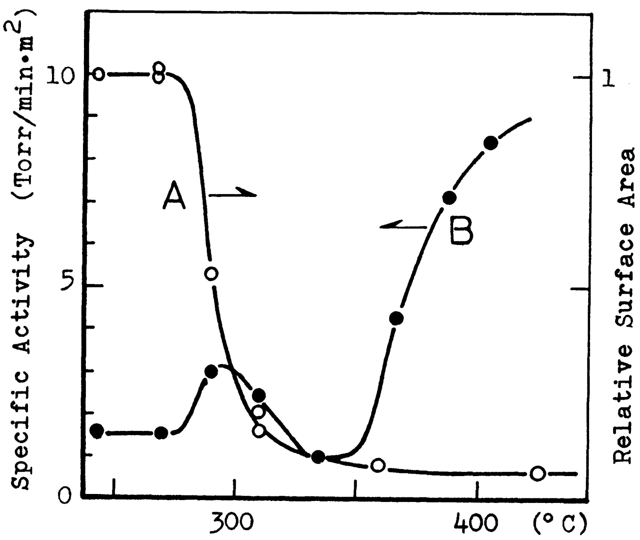


Fig. 3 Dependence of the surface area (A) and catalytic activity (B) on the temperature of heat-treatment (powder specimen, reaction temperature, 240° C)

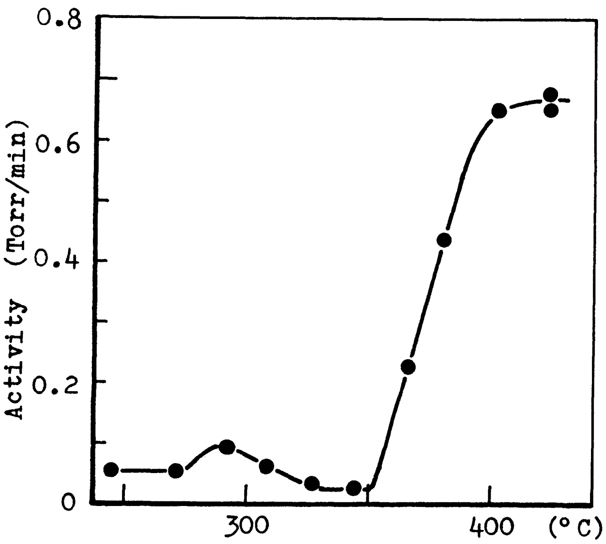


Fig. 4 Dependence of the catalytic activity on the temperature of heat-treatment (massive specimen, reaction temperature, 240° C)

Figure 5 indicates that the former is independent of the heat-treatment, while the latter is predominantly enhanced by the crystallization. The origin of the difference in the activity is uncertain at present, but it seems likely that the surface network structure formed by V_2O_5 in the vitreous state is chemically stable and inactive in this reaction in comparison with the surface in the crystallized state.

On the other hand, it may be considered that other possible reasons for affecting the activity are the changes in the surface compositions of the catalyst and the deposition of impurities at the surface during the heat-treatment. Table 1 shows data of XPS observed for the catalysts after the treatment at three temperatures.

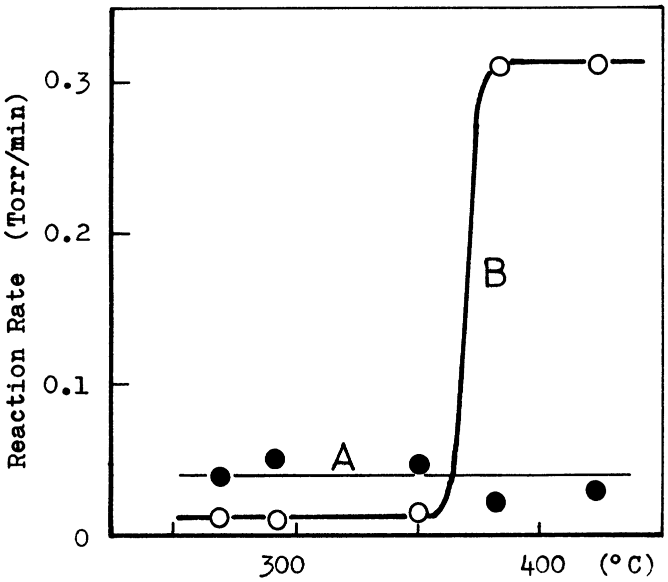


Fig. 5 Changes in the reaction rates by heat-treatment. (A)dehydrogenation, (B)dehydration (reaction temperature, 240°C)

Table 1. Binding Energies for $V(2p_{3/2})$, $Ba(4d_{5/2})$, $Zn(2p_{3/2})$ and O(1s), and Relative Intensities of Their Signals

Treatment	E_b (eV) [a]				Signal Intensity		
(°C)	V	Ba	Zn	O	V	Ba	Zn
240	516.2	88.6	1020.1	529.2	100	15	7
355	516.2	88.8	1020.3	529.2	100	14	5
425	516.3	88.9	1020.3	529.2	100	13	5
Pure V_2O_5	516.8	—	—	529.9	-	-	-

a) E_b was referenced to C(1s) impurity as 284.0 eV.

No appreciable differences between the vitreous and crystalline specimens are recognized in binding energies and relative intensities. A catalyst crystallized at above Tc was removed from the reactor, ground in a mortar and then was used for the reaction. The specific activity was unaffected by this treatment. The results above indicate that under the conditions of the present experiment these factors do not seem to account for the changes in the activity.

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References

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