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Active Sites for the Dehydrogenation of Ethyl Alcohol on Lithium Fluoride Single Crystal

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The dehydrogenation of ethyl alcohol on LiF single crystal surfaces has been investigated to determine the role of surface dislocations and another defects on the catalysis. The catalytic activity of the single crystal of LiF was greatly influenced by the surface treatments such as the manners of cleaving of the crystal and vacuum heating and so on. After radiation quenching subsequent to vacuum anealing at 350°C for 2 hr, the catalytic activity was greatest in the present work, being over seven times greater than that of nontreated crystal. The catalytic activity after the quenching treatment was found to increase in proportion to logarithm of the dislocation density. In observations with the electron microscope, the small spots concentrated in the center of dislocation was found on the highly activated crystal surface. From the results of kinetic and microscopic observations discussion was made on the catalytic sites of the LiF single crystal.

Many workers have considered the causal relation between dislocation or other defects and catalysis. Quantitative data, however, have not been given sufficiently as yet. Hall and Rase1) carried out experiments leading to the very interesting conclusion that the increase of dislocation density with various treatments resulted in increased catalytic activity of a single crystal of LiF in the dehydrogenation of ethyl alcohol. In their results, however, there were only two points to show the causal relationships.

In our laboratory, work has been undertaken to obtain a more quantitative relationships between dislocation density and catalytic activity. Observations of the surface state made by means of

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1) J. W. Hall and H. F. Rase, *Ind. Eng. Chem. Fundamentals*, **3**, 158 (1964).

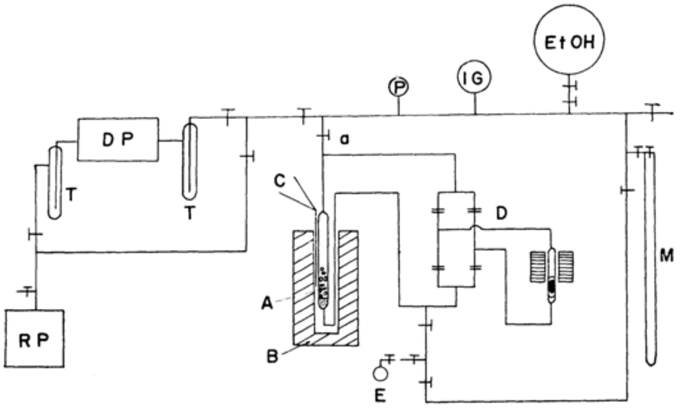

Fig. 1. Block diagram of apparatus.

A	Reaction chamber	DP	Diffusion pump
B	Electric furnace	RP	Rotary pump
C	Thermocouple	M	Manometer
D	Circulation pump	IG	Ionization gauge
E	Sampler	P	Pirani gauge

optical and electron microscopy, showed an increase in an understanding of the role of dislocations and of the nature of high active sites on the crystal.

Experimental

Kinetic data in the dehydrogenation of ethyl alcohol were obtained in a batch recirculation system which was made of Pyrex glass with a non-contaminating magnetic pump schematically shown in Fig. 1. The total volume of the reaction vessel was about 200 m*l* and the initial pressure of ethanol gas was 15 mmHg. An oil diffusion pump was used and residual pressure of 1×10^{-4} mmHg, measured with an ionization gauge, was obtained.

Gas samples were withdrawn from the system periodically and were analyzed by a gas chromatograph. The reaction velocity was determined by using the equation for the first-order reaction with respect to ethyl alcohol, $\log(a/(a-x))=Kt$, where a is the initial pressure of ethyl alcohol, $(a-x)$ is the pressure at time t and K is the rate constant in hr^{-1}.

The lithium fluoride single crystal used as the catalyst was pure LiF (over 99.999%) with normal cleavage planes {100} for the prisms, from the Horiba Manufacturing Co., Kyoto, Japan. The crystal catalyst was used in the form of $7\times6\times1$ mm of which total surface area was 20 cm^2 in each experimental run. Before the catalytic reaction, the crystal samples were etched for 80 sec and rinsed in ethanol and in anhydrous ethyl ether several times repeatedly. The etching procedure was same as that reported by Gilman and Johnston,[2,3] and dislocation densities were determined by means of an optical photomicrograph.

Ethyl alcohol as the reactant gas was prepared by evaporating a G. R. grade ethyl alcohol from the Kanto Kagaku Co., Ltd. The summary of the reaction procedure is as follows. After the crystal catalyst was put into the reaction vessel at position *a* in Fig. 1, the vessel was then evacuated down to 1×10^{-4} mmHg, the reactor was filled with 15 mmHg of ethyl alcohol vapor, and taken to the reaction temperature, 350°C. The temperature was controlled within ±2.0°C. Then the crystal catalyst was dropped into the reaction zone, magnetically. The reproducibility in the determination of the reaction velocities was found to be better than about 10%.

Experimental Results

The typical plots in Fig. 2 show agreement with the first-order assumption, no difference in the velocities between the not etched surface just

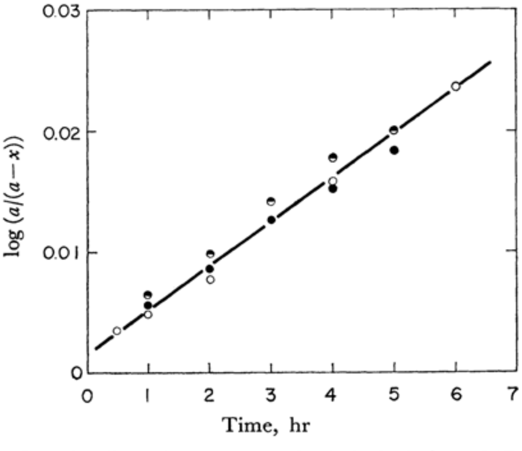

Fig. 2. Dehydrogenation of ethyl alcohol on LiF single crystal (reaction temperature 350°C): the effect of etching treatment, ○, not etched surface; ◓●, etched surface.

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[2] J. J. Gilman and W. G. Johnston, *J. Appl. Phys.*, **27**, 1018 (1957).

[3] J. J. Gilman, W. G. Johnston and G. W. Sears, *ibid.*, **29**, 747 (1958).

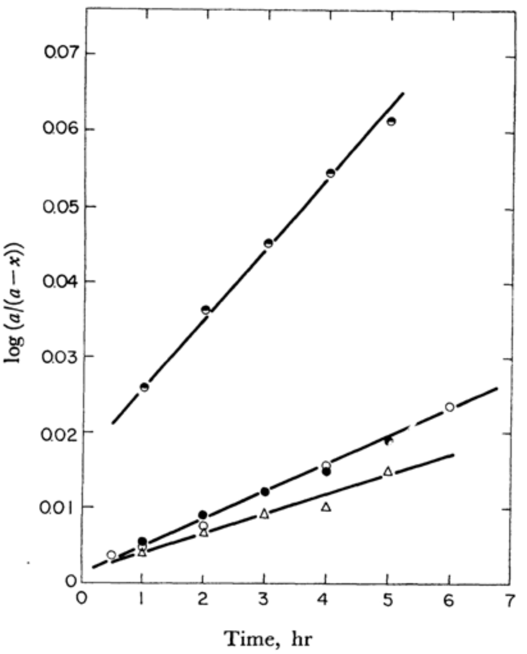

Fig. 3. Dehydrogenation of ethyl alcohol on LiF single crystal (reaction temperature 350°C): the effect of pretreatment, ○, no treatment; ◓, 2 hr heating (350°C) and quenching *in vacuo*; ●, 2 hr heating (350°C) and slow cooling (14°C/hr); △, 2 hr heating (350°C) quenching *in vacuo*, then etching.

after cleavage and the etched surface being found. It can be expected that the changes in the surface area due to the formation of the etch-pits with dislocations could be neglected. All of the crystal catalysts in the experiments were used after the etching treatment subsequent to the cleaving, the etched surfaces being called the *non-treated* surfaces, in the present paper.

The catalytic reaction curves after various pretreatments are summarized in Fig. 3. The thermal treatments prior to the reaction were made in another vacuum apparatus, in which a pressure of 1×10^{-6} mmHg could be reached, to avoid the formation of the condensed films of LiF crystal on the glass wall during the thermal treatment at over about 500°C. In Fig. 3, it is to be noted that the reaction velocity is greatly influenced by the pretreatment of the crystal catalysts, being remarkable in the catalyst quenched from 350°C and reaching a level over three times greater than the *non-treated* one. On the other hand, the crystal catalyst cooled very slowly (14°C/hr), was not activated, just same as that of *non-treated*. The highly activated catalyst quenched from 350°C was found to show an abrupt decrease in catalytic activity by re-etching slightly. The observation by optical microscopy showed that the surface dislocation densities did not change with any thermal treatment at 350°C and no difference between the density before and after the reaction was detected, the dislocation density being hold about 1×10^5 cm^{-2} in the usual cases.

When the crystal catalysts were quenched *in vacuo* from higher temperature than 450°C, the catalytic activity decreased drastically. Figure 4 shows the effect of the quenching temperature, the activity in hr^{-1} being plotted as a function of the quenching temperature. The activity was decreased with the increase of the temperature of annealing and became lower than that of *non-treated* crystal at 550 and 650°C.

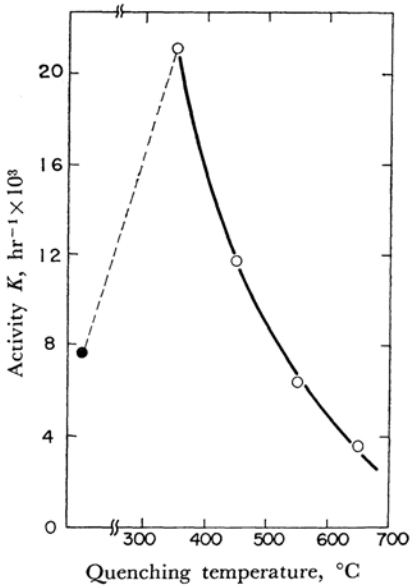

Fig. 4. Catalytic activity as a function of the quenching temperature (reaction temperature, 350°C) ●, no treatment.

The dislocation density in the crystal surface could be controlled by the manner of cleaving, stressing, or thermal treatment. For example, if the crystal was re-etched after quenching subsequent to two hours of vacuum heating at 650°C, the dislocation density was found to increase over twenty times that of the *non-treated* crystal. In such a manner, the crystal catalysts containing the desired density of dislocaions can be obtained. The catalytic activity as a function of dislocation density is plotted in Fig. 5. The open circles show the activities of the *non-treated* crystals, just after etching. It is evident that the catalytic activity of the etched samples is constant regardless of the different dislocation densities. On the other hand, when the crystal catalyst was quenched from 350°C prior to the each experimental run, the catalytic activity increased with the dislocation density, being in proportion to the logarithm of the density.

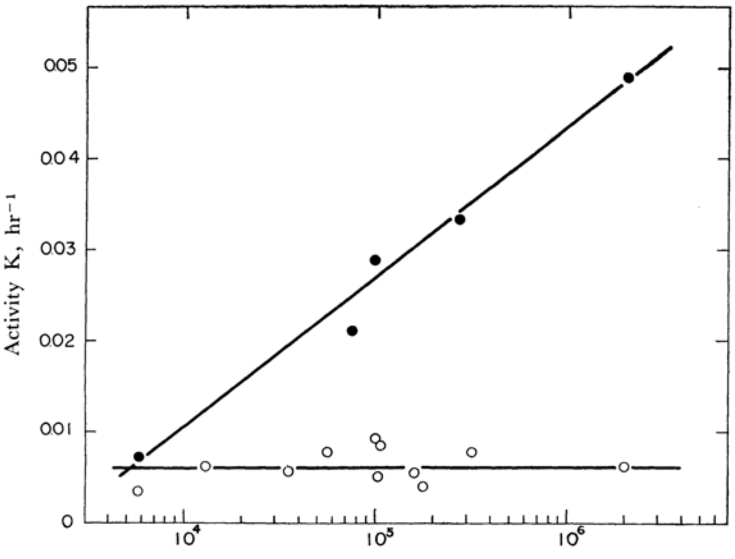

Fig. 5. Catalytic activity as a function of surface dislocation density. (Reaction temperature 350°C)
○ No treatment ● After quenching from 350°C

The typical photomicrographs of the crystal surfaces after the various treatments are shown in Figs. 6, 7 and 8. Figure 6 shows the surface of the *non-treated* crystal just after etching, with a dislocation density of $2\times10^5\,\mathrm{cm}^{-2}$. Almost the same photomicrographs as Fig. 6 were obtained also in the cases of the thermal treatments at 350°C and before and after the reaction. In the case of the higher quenching temperatures, for example at 650°C (Fig. 7), a very different surface much like a fused surface was observed, corresponding to very low catalytic activity as seen in Fig. 4. However, after the crystals were re-etched, a lot of the etch-pits due to the dislocations over than twenty times in density appeared as shown in Fig. 8.

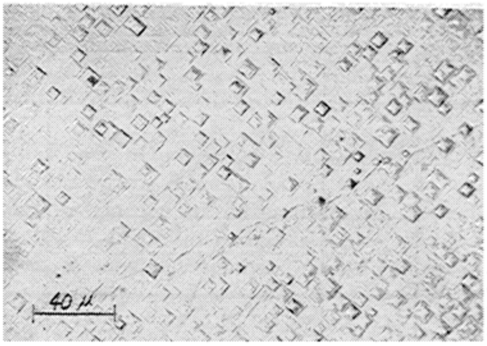

Fig. 6. Photomicrograph of no treatment surface (dislocation density, about $2\times10^5\,\mathrm{cm}^{-2}$).

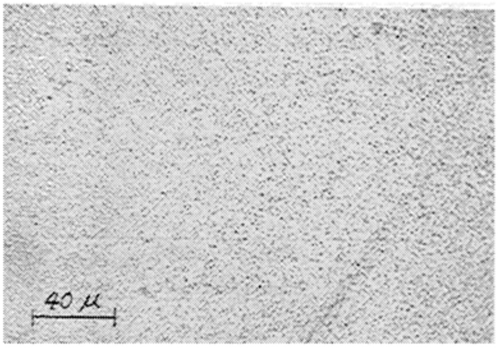

Fig. 7. Photomicrograph of the surface after quenching from 650°C.

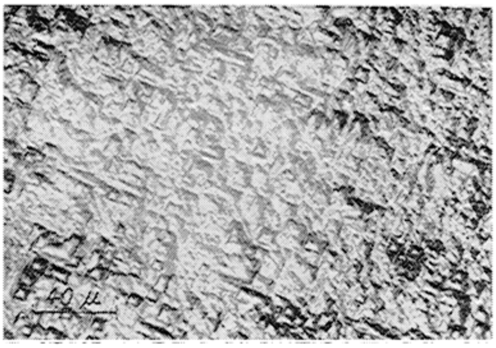

Fig. 8. Photomicrograph of the re-etched surface after quenching from 650°C.
(dislocation density, about $2\times10^6\,\mathrm{cm}^{-2}$)

In order to extend the knowledge on the highly activated catalyst surface quenched from 350°C, electron microscopic photographs of each surface are compared in Figs. 9, 10 and 11. The surface state as seen in Fig. 10 which gave the very high catalytic activity is characterized by several small

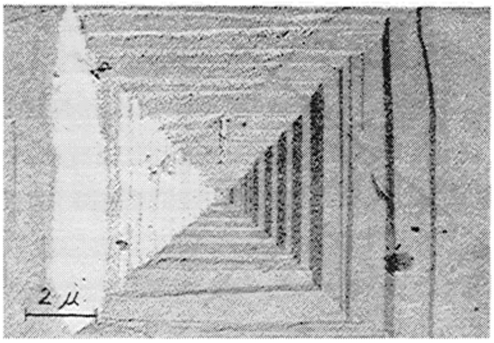

Fig. 9. Electron micrograph of replica of no treatment surface.

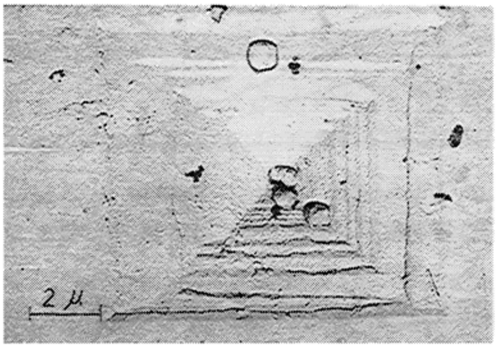

Fig. 10. Electron micrograph of replica of the surface after quenching from 350°C. (high active surface)

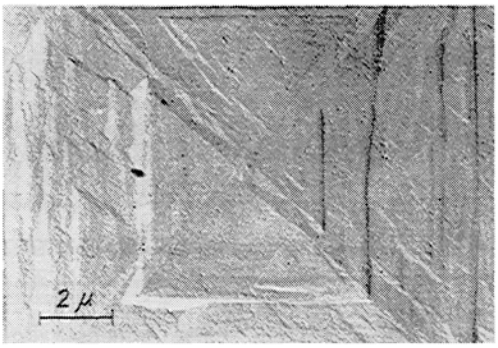

Fig. 11. Electron micrograph of replica of the surface after slow cooling from 350°C (14°C/hr).

spots which are inclined to concentrate at the center of the etch-pit corresponding to a dislocation. These spots were not found on the surface after slow cooling (14°C/hr) which did not increase in the catalytic activity.

Discussion

Hall and Rase[1)] showed a very striking relation between dislocation density and catalytic activity for LiF in the dehydrogenation of ethyl alcohol. They obtained an increased activity of about one hundred times for the sample with five times of dislocation density. In their experiments, the crystal catalysts had dislocation densities in the range of 4×10^6 to 2.5×10^7 cm^2, a much greater range than in the present study. Accordingly, the results can not be compared with each another directly. In our investigation, it has been found that in the case of the *non-treated* samples no difference was detected in the correlation between dislocation density and catalytic activity of LiF crystal, but after quenching, such a correlation appeared that the catalytic activity was proportional to the logarithm of the density. Based on the above experimental facts that the catalytic activity was greatly influenced by the thermal treatment, though the dislocation density did not changed by 350°C treatment, it should be stressed that factors other than dislocations act as the enhanced catalytic sites for the dehydrogenation of ethyl alcohol. In the present study, the crystal catalysts were exposed to the air after the various thermal treatments, then the catalytic activity tests were carried out in another vacuum system. Consequently, the substance other than LiF such as LiOH or Li_2O formed preferentially at the terminations of dislocations as a result of the exposure to the air might act as the active centers.

The graphical summary of catalytic activities as a function of surface treatment is presented in Fig. 12. The point a shows the catalytic activity of the *non-treated* crystal, *i. e.*, the etched surface

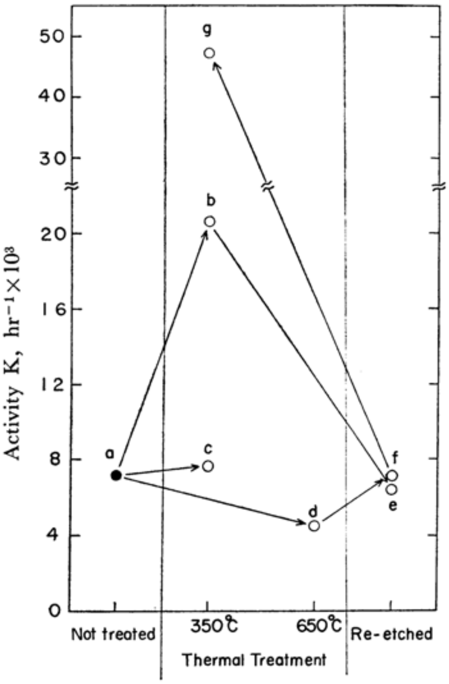

Fig. 12. Graphical summary of catalytic activities as a function of pretreatment (reaction temperature 350°C).

after cleaving. The activity was found to be increased by quenching (point b) and not changed by slow cooling subsequent to 2 hr vacuum heating at 350°C (point c), no change in dislocation density being observed in any case at 350°C treatment.

The quenching from a higher temperature (650°C) gave a lower activity (point d) than that of the non-treated surface, giving the surface like a fused as shown in Fig. 7. When the crystal catalyst after any thermal treatment was re-etched, its catalytic activity recovered to the one before the treatment (b→e, d→f). The dislocation density in point f was more than twenty times of that in point a and e, *i. e.* 2×10^6 cm^{-2}, which might be increased by the thermal treatment at higher temperature. When the re-etched crystal catalyst containing the surface dislocation in higher density (point f) was quenched again from 350°C, the catalytic activity was found to increase up to seven times as great as that in point f, as shown by point g.

From these facts, it seems reasonable to assume that the increase in the dislocation density on crystal surface could not result in the increase of catalytic activity, but the surface dislocations might be worthy of the activation of crystal catalyst with the thermal treatment, for example, vacuum quenching from 350°C.

Although many investigations have been carried out on the surface reactivity of alkali halide,[4] a very few attempts have been made on heterogeneous catalysis of alkali halide.[1,5] In such cases as the nucleus formation and growth during exchange reaction with another halogen vapors, no correlation has been found between nucleation sites and the points where dislocations or low-angle grain boundaries emerge at the crystal surfaces.[4] On the roles of the dislocations as active centers of catalysis in metallic catalysts, much information have been taken by many investigators.[6-8] For instance, Uhara and his co-workers[8] found that active centers of catalysis for several reactions on Ni or Ag, could be the surface terminations of dislocations by means of the thermal deactivation method. However, attempts to obtain the quantitative correlation between the catalytic activity and the dislocation density on metallic catalysts has not been successful. The mechanism of the action of dislocation in catalytic reaction has also not been clear yet.

In view of the above facts, however, the most reasonable conclusion to be drawn from the available data is as follows.

1) The catalytic activity of the LiF single crystal in the dehydrogenation of ethyl alcohol is greatly changed by the thermal treatment prior to catalytic reaction, even though dislocation density not changed. The catalytic activity after the quenching subsequent to the heating at 350°C *in vacuo* was found to increase in proportion to the logarithm of dislocation density. 2) In the electron microscopic observation, the small spots concentrated in the center of dislocation was found on the highly activated crystal surface after quenching. Dislocation which might lead to these spots could be assumed to play a secondary role for the induced catalytic activity. 3) The enhanced active sites formed by quenching is thought to be distributed in only the thin surface layer, because the catalytic activity is removed easily by reeching slightly.

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[4] J. A. Morrison and K. Nakayama, *Trans. Faraday Soc.*, **59**, 2560 (1963) and many papers associated with the nucleus formation on alkali halides.

[5] A. A. Tolstopyatova, Vestnik Moscow Univ., **6** (No. 3), Ser. Fig. Mat. i Estestven Nauk No. 2, 49 (1951), *Chem. Abstr.*, **46**, 3382 g (1952).

[6] H. M. C. Sosnovsky, *J. Phys. Chem. Solids*, **10**, 304 (1959).

[7] T. Yamashina and H. E. Farnsworth, *Ind. Eng. Chem. Prod. Res. Dev.*, **2**, 34 (1963).

[8] I. Uhara, S. Kishimoto, Y. Yoshida and T. Hikino, *J. Phys. Chem.*, **69**, 880 (1965).