## Dislocations and Catalysis

CAUSAL connexions between dislocations and catalysis have been suggested by a number of workers over the past twenty years[1–6]. Conclusive evidence, however, has often been lacking because of surface contamination or other effects which could not be implicated as factors in catalysis. Recently an unusual amount of valuable results have been obtained on dislocations and mechanical properties of lithium fluoride crystals. Gilman[7–16], Forty[17] and Benson *et al.*[18] have determined the role of cleavage in nucleating dislocations in lithium fluoride and described the character of dislocations and stresses needed to produce them. This wealth of experimental results offers a fertile ground for exploring the role of dislocations in catalysis on this simple and well-documented crystalline substance. By using Gilman's[8,10,11,15] techniques for cleaving, etching, and stressing crystals it is possible to control the introduction of dislocations to a satisfactory degree and to identify them without spending a major effort on what could be a most illusory problem.

We are, therefore, examining dislocations and catalysis using this background on lithium fluoride and utilizing the reaction of dehydrogenation of ethyl alcohol. A precise reactor system similar to that described by Pozzi and Rase[19], but now made automatic and reduced greatly in size, is being used. Very pure (less than 1 p.p.m. impurities) grade lithium fluoride crystals obtained from the Harshaw Chemical Co. are cleaved into pieces approximately (1 mm × 2 mm × 2 mm) and tested in various ways.

A recent series of experiments has proved interesting as shown by the results in Fig. 1. Crystals of lithium fluoride were cleaved and treated in various ways in order to produce dislocation densities of different orders of magnitude (Table 1 outlines the history of each sample). The samples were then tested in the reactor at 260° C for acetaldehyde production. The differential-type reactor results enabled direct calculation of rates. These results represent the first quantitative representation of a correlation between catalytic activity and dislocation density.

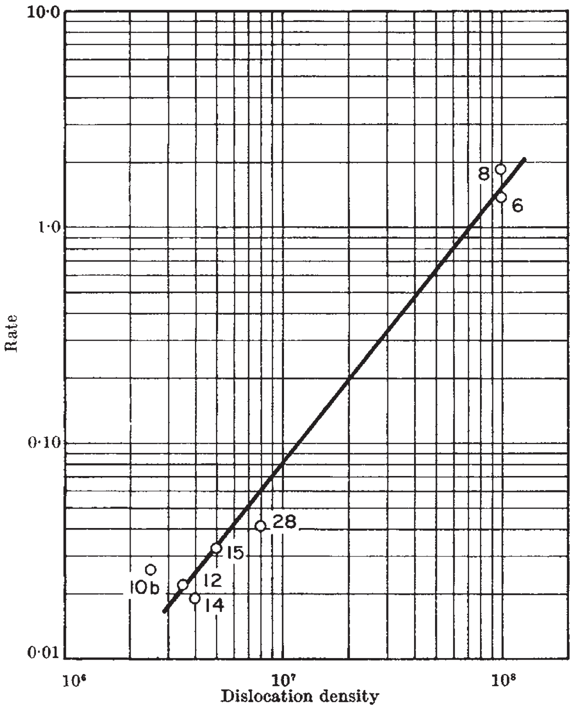


Fig. 1. Effect of dislocation density on catalytic activity of lithium fluoride crystals.

$$\text{Rate} = \frac{\left(\dfrac{\text{moles converted}}{\text{mole charged}}\right)\left(\dfrac{\text{c.c. ethanol}}{\text{h}}\right)}{\text{cm}^2 \text{ of surface.}}$$

Dislocation density = No. of dislocations per cm².

Table 1

| Run No. | Treatment | Comments |
|---|---|---|
| 6 | As–cleaved | These samples exhibited unusually large numbers of dislocations when cleaved slowly |
| 8 | As–cleaved | |
| 106 | Cleaved, annealed and cooled rapidly | These samples showed moderate dislocation densities upon cleaving as shown in Fig. 1. Activity and dislocation density remained relatively constant before and after treatment |
| 12 | Cleaved, annealed and cooled rapidly | |
| 14 | Cleaved, annealed and cooled rapidly | |
| 15 | Cleaved, annealed and cooled rapidly and then each piece stressed | Prior to stressing no activity was observed |
| 28 | Annealed and cooled rapidly and then stressed prior to leaving | Samples of this material which had not been stressed showed no activity upon cleaving and testing. Dislocation densities in unstressed material were ~ $10^5$ |

Equally as significant, however, is the rather dramatic production of activity in inactive and relatively dislocation-free crystals (for example, runs 15 and 28) by stressing annealed and rapidly cooled crystals. Gilman has shown that annealed and rapidly cooled lithium fluoride crystals are soft and moderate stresses can be applied to multiply dislocations profusely. We have observed this same phenomenon and seen the vastly increased numbers of dislocations on the etched crystals and the corresponding appearance of catalytic activity. Annealing and rapid cooling without stressing do not produce changes in dislocation density or catalytic activity.

Work is continuing to define these effects more precisely; but the value of the known techniques with lithium fluoride when applied to reaction studies has already been demonstrated, and the role of dislocations on catalytic activity of lithium fluoride has been demonstrated quantitatively.

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JAMES W. HALL*
HOWARD F. RASE

Department of Chemical Engineering,
University of Texas, Austin 12.

* Humble Oil and Refining Company Fellow.

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## METALLURGY

### Growth and Nucleation of the β→α Transformation in Uranium 0·45 per cent Chromium Alloy

THIS communication describes some experiments with uranium 0·45 per cent chromium, the purpose of which was to measure the growth and nucleation rates of α-uranium during the β → α transformation. To the best of our knowledge, these results are the first quantitative measurements of growth-rate of the β → α transformation.