COMMUNICATIONS TO THE EDITOR

Design of Catalysts: Application of Crystal-Face Orientation

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Remarkable strides in the past few years have provided the chemical engineer with valuable information and tools for use in selecting and improving catalysts. Briefly these include three major theories and several measuring techniques useful in gaining insight into catalyst characteristics.

THEORIES

1. The electronic factor in catalysis.
2. The influence of crystal face on catalytic activity.
3. Balandin's theory of surface geometry (volumes *7* and *10* of "Advances in Catalysis" give good summaries of these theories and associated experimental work.)

MEASURING TECHNIQUES

1. Thermal emf
2. Electrical conductivity
3. Electron microscopy
4. Electron diffraction
5. X-ray diffraction
6. Differential thermal analysis

STATUS

At the present state of development it is clear that none of the theories can be successfully applied to all catalytic phenomena. It must be concluded that they are empirical rules resulting from some yet undiscovered general theories. The literature will therefore continue to contain numerous contradictions as well as magnificient substantiations of the several factors said to govern catalytic activity. Complete resolution of this complex problem is not in sight.

THE INFLUENCE OF CRYSTAL FACE

As an example of engineering application, concepts proposed by Gwathmey, Beeck, and others (*1*, *4*, *6*) related to the effect of crystal face on catalysis are being applied in these laboratories in the postulation of a more active nickel-hydrogenation catalyst. Whether such a catalyst is needed is not the burden of this study. Our goal is the demonstration of a technique which can have many useful applications.

BACKGROUND

The reader is referred to other sources (*1* to *4*) for a detailed review of the literature of this field. The relevant facts related to nickel as a hydrogenation-dehydrogenation catalyst follow.

1. Beeck and his associates (*3*) in studying evaporated metal films found that the hydrogenation activity for ethylene on (110) oriented nickel films was five times that on unoriented films. The diffraction measurements used to establish orientation were made on fresh films (films not used in the reaction).

2. Sachtler and associates (*5*) found the (111) faces active in hydrogenation but not the (110) as found by Beeck. In this work Sachtler studied the orientation *in situ*.

3. Gwathmey and Cunningham (*4*) prepared single crystals and measured ethylene hydrogenation rates on the different crystal faces. They found the (321) face most active followed by the (111) face. Single crystals were prepared large enough so that individual faces might be identified and studied. Their data suggested that any tendency toward unoriented films particularly at low temperature would increase catalyst activity. This is contrary to Beeck's work on ethylene but can be explained by the fact that Beeck identified crystal faces on samples which were not used in the reaction studies. The very nature of Gwathmey and Cunningham's experiments suggests more careful control of the variables.

4. Schuit and van Reijen (*6*) have shown that the kinetics, activation energy, and specific rate constant do not differ greatly between nickel-on-silica catalysts and nickel films. Relative activities for other metals were found to be substantially equal for the two types of catalysts.

A TECHNIQUE FOR APPLICATION TO CATALYST DESIGN

The above outlined observations when used to propose various theories and hypotheses may generate numerous controversies. When used as empirical facts obtained by competent workers as a guide in the development of a catalyst, there should be no objection. Perhaps the most obvious application, and the one suggested here, is the creation or improvement of a catalyst by means of studies made with metal films.

The slower rate of propylene hydrogenation made it more convenient for use in our laboratories and further served to illustrate the extrapolation of the ethylene observations to an analogous system. Experimental procedures are described at the end of this paper. The results and thereby the proposed technique are outlined here.

1. On the assumption that hydrogenation activity is determined by the arrangement of crystal faces, an attempt was made to produce the optimum result suggested by Gwathmey's work. His findings indicated that a randomly oriented (unoriented) film might be the more active. Foreign atoms introduced in the film could produce both a change in the normal

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structural pattern of the film and the desired randomness.

2. A simple empirical procedure for finding such foreign atoms is to evaporate readily available commercial alloys of nickel and test their activity. The results of such a procedure are tabulated for batch hydrogenation of propylene in Table 1 as activities relative to nickel film at various conversion levels. The films prepared from nickel-chromium and nickel-chromium-iron alloys were the most active.

3. X-ray diffraction studies showed all films to be oriented in the $(1\bar{1}1)$ plane, but the nickel-chromium and nickel-chromium-iron films (the most active) showed some random orientation in agreement with the original hypothesis. Results were reproducible. Further studies could lead to even more randomly oriented and thus more active films.

4. The next step is the application of the findings of the film experiments to supported catalysts prepared by precipitation of mixtures of metal salts on kieselguhr followed by decomposition and subsequent reduction. It is postulated that nickel-chromium and nickel-chromium-iron supported catalysts will exhibit comparable superiority over nickel catalysts as that shown by the film studies. This work will be done, but these thoughts are presented here with the hope that other workers may be stimulated in employing orientation studies as a means of suggesting improved or new catalysts.

TABLE 1. ACTIVITIES OF VARIOUS NICKEL FILMS COMPARED WITH COMMERCIALLY PURE NICKEL FILMS

Conversion level	Film designation *A*	*B*	*C*	*D*	*E*	*F*
0.05	1.625	1.625	0.590	0.650	0.650	0.325
1.10	1.750	1.780	0.700	0.700	0.700	0.437
0.15	1.830	1.830	0.758	0.735	0.772	0.550
0.20	1.935	1.870	0.788	0.792	0.788	0.631
0.25	1.950	1.900	0.808	0.805	0.808	0.704

1. Activities expressed as ratio of reaction times at constant conversion for the pure nickel film to those of alloy film.
2. Designations indicate percentage of metal evaporated

A: 79.5 nickel, 13 chromium, 6.5 iron
B: 80 nickel, 20 chromium
C: 67 nickel, 30 copper, 1.4 iron, 1 manganese
D: 66 nickel, 29 copper, 2.75 aluminum, 0.9 iron
E: 95.5 nickel, 4.5 manganese

EXPERIMENTAL METHODS

Briefly, the films were evaporated from a tungsten filament to a 500-ml. flask with nickel and nickel-alloy wires wrapped around the helical filament. Other significant data include:

Vacuum: 0.1μ
Flask wall temperature: 103°F.
Current: 30 to 32 amp. at 10 v.

The reaction was carried out in the flask without prior contact with the atmosphere. Pretreatment for 6 hr. with hydrogen or propylene eliminated the induction period and permitted comparison of films on an equal basis.

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The Effect of Velocity Profile on Axial Dispersion in Packed Beds

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To my knowledge no treatment of axial dispersion in packed beds which accounts for the effect of the velocity profile has been published. Yet it seems possible that some of the axial dispersion observed in packed beds is caused by the combined influence of velocity profile and radial diffusion. Consider a pulse of dye flowing through a packed bed. The variation of axial velocity with radius causes the pulse to spread axially; however radial diffusion counteracts this by causing the dye that has been carried ahead in the faster flow to diffuse radially into slower flow, and likewise dye that has been held back in the very slow flow diffuses into faster flow. As the ratio of the bed diameter to the particle diameter is increased, these two counteracting effects vary as follows. The velocity profile becomes flatter and tends to cause less dispersion. The radial diffusion is also reduced because the particles are smaller in relation to the radius of the bed. This however tends to cause more dispersion. The following work is an attempt to evaluate these effects by calculating the N_{Pe} from a theoretical development similar to that used by Taylor (*1*) to evaluate these effects in pipe-line flow.

A material balance around a differential annular shell that moves with the mean superficial velocity of the stream yields

$$\frac{\partial}{\partial z}\left[zE\left(-\frac{\partial c}{\partial z}\right)\right]$$