

## Activation of Supported Nickel Oxide by Platinum and Palladium

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Received August 1, 1966

Small amounts of platinum or palladium incorporated in alumina-supported nickel catalysts have been observed to enhance activation of the nickel by hydrogen. Hydrogenolysis, isomerization, and aromatization reactions of *n*-heptane with hydrogen, used for characterizing catalytic activity, were carried out in a pulse-flow reactor coupled with a gas chromatograph. Platinum or palladium in atom ratios to nickel as low as  $\sim 5 \times 10^{-3}$  were sufficient to cause severalfold increases in conversion over the nickel component. These large effects appear to be due to precious-metal-catalyzed hydrogen reduction of supported nickel oxide. Alternative mechanisms and a possible role of surface diffusion in the reduction process are discussed.

### INTRODUCTION

Nickel catalysts are used for a variety of reactions including hydrogenation, dehydrogenation, hydrogenolysis, and steam reforming. For reactions requiring high temperatures, nickel is supported to help prevent loss of active nickel area by sintering. Support materials are often refractory metal oxides such as alumina and silica-alumina.

Preparation of supported nickel catalysts usually involves procedures which take the metal to its oxide form. Such procedures are commonly impregnation of a nickel salt onto a solid support material, or coprecipitation of nickel and support metal oxides, followed by incorporation of promoters, drying, and calcining.

Subsequent activation of such catalysts is usually done by heating in a hydrogen-rich atmosphere, which presumably reduces some or all of the nickel to its metallic form. High ultimate activity depends on maintaining the nickel well dispersed during activation and any subsequent regenerations. Loss of

dispersion by sintering can be minimized by activating and regenerating at a low temperature. It is apparent, then, that catalyzed reduction of the nickel oxide could result in increased activity by lowering the required activation temperature. At a given temperature, catalyzed reduction could also enhance the degree of reduction, producing a more active catalyst.

A report of enhanced activity and selectivity of supported nickel and cobalt steam-reforming catalysts by addition of very small quantities of platinum-group metals has appeared in a recent patent to Imperial Chemical Industries, Ltd. (1). The patent discloses enhanced activity and selectivity to methane as well as decreased coke formation. Significant effects are reported for as little as 0.01 wt % platinum metal in a catalyst containing close to 20 wt % NiO. Moreover, more than approximately 0.1 wt % platinum has little additional effect on the activity and the selectivity, indicating a promoter-like function for the platinum-group metal.

An activating and stabilizing effect of platinum in a commercial supported nickel catalyst has also been reported by Sakaida (2, 3) for the decomposition of nitric oxide.

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It is the purpose of this paper to report additional evidence for a cooperative interaction between nickel and platinum-group metals. Activating effects of platinum and palladium on supported nickel catalysts were observed, with the hydrogenolysis of *n*-heptane as a test reaction. Converted material was analyzed for products of hydrogenolysis, isomerization, and aromatization, and from these data the individual catalytic contributions of nickel, platinum, and palladium were deduced.

Arguments are also presented for an activation mechanism involving platinum- (or palladium-) catalyzed reduction of supported nickel oxide by hydrogen.

### EXPERIMENTAL

Reactions were carried out in a pulse-flow tubular catalytic reactor directly coupled with a Perkin-Elmer Model 154 gas chromatography apparatus. Hydrogen gas flow was continuous first through the reactor and then through the chromatograph column in series, thereby serving both as a reactant and as a carrier for chromatographic separation of products. Pulses of liquid feed were injected into the hydrogen flow through a septum upstream from the catalyst bed. Each 1  $\mu$ l pulse was separated from the next one by a 20–30 min interval, during which hydrogen eluted separated products from the chromatographic column. The catalyst bed consisted of 0.3–0.6 g of catalyst powder (through 60-mesh screen) retained between two quartz wool plugs. Catalyst temperatures were maintained with an electrical heater coupled with the reactor by a common well-insulated aluminum block, and the temperatures were measured by a thermocouple in contact with the 1/4-inch stainless steel tubing reactor wall. The 21-ft chromatograph column was packed with DC-200 Dow Corning silicone oil on A. T. Chromosorb and was isothermal at 76°C.

Catalysts were prepared by impregnating  $\eta$ -Al<sub>2</sub>O<sub>3</sub> (formed by calcining Davison  $\beta$ -trihydrate in air for 4 hr at 590°C) with aqueous solutions of suitable metal salts: H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, PdCl<sub>2</sub>·2H<sub>2</sub>O, and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Impregnation by just wetting the alumina support with solution was followed

by drying overnight at 120°C and then calcining in air at 290°C for 2–4 hr. The bimetallic catalysts were prepared in all cases by first impregnating with aqueous Ni(NO<sub>3</sub>)<sub>2</sub> solution, drying and calcining, and then impregnating with aqueous H<sub>2</sub>PtCl<sub>6</sub> (or PdCl<sub>2</sub>) solution, drying, and calcining again at the same conditions. All catalysts were prereduced *in situ* with flowing hydrogen at 370° to 480°C, as specified in the data tables.

The heptane liquid feed was Phillips pure grade (99 mole% minimum) normal heptane. Hydrogen gas purchased from Linde was specified to be 99.984% pure.

### RESULTS

Results demonstrating cooperative interaction of platinum and palladium with nickel are given in Table 1. Catalysts consisting of an alumina support impregnated with nickel, platinum, and palladium, individually and as the pairs nickel-platinum and nickel-palladium, were used. Each catalyst was reduced in hydrogen according to the specifications in the table. Results are given in terms of mole fraction *n*-heptane converted and the molar composition of the product (excluding unreacted *n*-heptane). The mole ratios of isomerized to normal C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> hydrocarbons are also given as an index of isomerization activity. Catalyst A, containing both 0.6 wt % nickel and 0.3 wt % platinum, caused a higher conversion of *n*-heptane than would be expected from a linear combination of catalysts C and D, containing 0.6 wt % nickel and 0.3 wt % platinum, respectively. Catalyst B, containing 0.6 wt % nickel, but only 0.01 wt % platinum also caused unexpectedly high conversion, the mole fraction *n*-heptane converted being four times that for Catalyst C after reduction of both at 430°C for 1 hr. The compositions of products from Catalyst A show the high conversion to methane characteristic of nickel and the appreciable aromatization and isomerization characteristic of platinum; both metals appear to be contributing their characteristic activities. However, Catalyst B contains insufficient platinum to contribute appreciable activity, as shown by the absence of isomerized and

TABLE I  
 INTERACTION OF Pt AND Pd WITH NiO SUPPORTED ON Al<sub>2</sub>O<sub>3</sub>

| Catalyst <sup>a</sup>  | Periods <sup>b</sup> of reduction at 370°C (hours) | Mole fraction <i>n</i> -C <sub>7</sub> reacted <sup>c</sup> | Product composition <sup>d</sup> (mole %) |                                    |                      |                    | Mole ratio isomerized to normal C <sub>4</sub> , C <sub>5</sub> , C <sub>6</sub> |
|--|--|---|---|------------------------------------|----------------------|--------------------|--|
|  |  |   | C <sub>1</sub>                            | C <sub>2</sub> thru C <sub>4</sub> | Benzene plus toluene | Iso-C <sub>7</sub> |  |
| A. 0.6% Ni and<br>0.3% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.46 g)  | 2  | 0.46  | 39.                                       | 52.                                | 5.                   | 4.                 | 0.3  |
|  | 3  | 0.47  | 40.                                       | 53.                                | 4.                   | 4.                 | 0.3  |
|  | 16   | 0.67  | 49.                                       | 46.                                | 3.                   | 2.                 | 0.2  |
| B. 0.6% Ni and<br>0.01% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.32 g)   | 1  | 0.07  | 65.                                       | 35.                                | 0.                   | 0.                 | 0.   |
|  | 3  | 0.12  | 64.                                       | 36.                                | 0.                   | 0.                 | 0.   |
|  | 1 hr @ 430°C                                       | 0.22  | 59.                                       | 41.                                | 0.                   | 0.                 | 0.07   |
| C. 0.6% Ni/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.51 g)   | 1  | 0.03  | 71.                                       | 29.                                | 0.                   | 0.                 | 0.   |
|  | 2  | 0.05  | 69.                                       | 31.                                | 0.                   | 0.                 | 0.   |
|  | 1 hr @ 430°C                                       | 0.06  | 74.                                       | 26.                                | 0.                   | 0.                 | 0.   |
| D. 0.3% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.52 g)   | 1  | 0.25  | 24.                                       | 49.                                | 12.                  | 15.                | 0.2  |
|  | 16   | 0.18  | 22.                                       | 44.                                | 13.                  | 22.                | 0.2  |
| E. 0.6% Ni/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>0.3% Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>A physical mixture of<br>-60-mesh particles<br>(0.63 g) | 16   | 0.19  | 20.                                       | 37.                                | 18.                  | 26.                | 0.3  |
|  |  |   |   |                                    |                      |                    |  |
| F. 0.6% Ni and<br>0.3% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.57 g)  | 1.5  | 0.70  | 82.                                       | 18.                                | 0.                   | 0.                 | 0.03   |
|  | 3  | 0.85  | 78.                                       | 22.                                | 0.                   | 0.                 | 0.02   |
| G. 0.6% Ni and<br>0.01% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.53 g)   | 1  | 0.74  | 82.                                       | 18.                                | 0.                   | 0.                 | 0.07   |
| H. 0.3% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.52 g)   | 1  | 0.16  | 47.                                       | 40.                                | 0.                   | 13.                | 0.1  |

<sup>a</sup>  $\eta$ -Al<sub>2</sub>O<sub>3</sub> prepared from Davison  $\beta$ -trihydrate by calcining at 590°C for 4 hr.

<sup>b</sup> Periods as listed here are individual and consecutive.

<sup>c</sup> Reaction conditions: 370°C, 1.7–1.9 atm H<sub>2</sub>, 1.4–1.7 cc/sec H<sub>2</sub> flow rate.

<sup>d</sup> Excluding unreacted *n*-heptane.

aromatized products. Therefore, it appears that a very small concentration of platinum enhances the catalytic activity of nickel even though the platinum is not itself present in sufficient quantity to alter the course of the catalyzed reaction. It is noteworthy that an atom ratio of platinum to nickel as low as  $5 \times 10^{-3}$  is sufficient for the observed enhancement of nickel activity in Catalyst B. When platinum is combined with nickel in much higher proportion, as in Catalyst A, nickel is activated, after which both metals function as independent catalytic factors coupled only by the chemical kinetics of the occurring reactions.

A physical mixture of one part by weight 0.6 wt % Ni/Al<sub>2</sub>O<sub>3</sub> (Catalyst C) with one part by weight 0.3 wt % Pt/Al<sub>2</sub>O<sub>3</sub> (Catalyst D), both passed through a 60-mesh screen, did not exhibit the cooperative activity behavior observed for Catalyst A. Nickel and platinum must therefore be in more intimate contact to interact in the manner observed. This result eliminates the possibility of interaction via long-lived species in the gas phase and suggests the possibility that direct physical contact of platinum with nickel is required, or that a short surface path between particles of platinum and nickel oxide is needed.

TABLE 2  
DEGREES OF ACTIVATION AT VARIOUS TEMPERATURES

| Catalyst <sup>a</sup>  | Sequence of reduction periods, time, and temperature (°C) <sup>b</sup> | Mole fraction <i>n</i> -C <sub>7</sub> reacted |
|--|--|--|
| C. 0.6 wt % Ni/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.51 g)                     | 1 hr @ 370°  | 0.03   |
|  | 1 hr @ 370°  | 0.04   |
|  | 1 hr @ 430°  | 0.05   |
|  | 1 hr @ 450°  | 0.08   |
|  | 1 hr @ 480°  | 0.09   |
| B. 0.6 wt % Ni and<br>0.01 wt % Pt/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.32 g) | 1 hr @ 370°  | 0.06   |
|  | 2 hr @ 370°  | 0.12   |
|  | 1 hr @ 430°  | 0.20   |
| G. 0.6 wt % Ni and<br>0.01 wt % Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub><br>(0.53 g) | 1 hr @ 370°  | 0.74   |
|  | 1 hr @ 430°  | 0.74   |
|  | 1 hr @ 480°  | 0.84   |

<sup>a</sup> For preparation details see Experimental section.

<sup>b</sup> Periods as listed here are individual and in some cases consecutive. The activity shown after reduction at a given temperature results from reduction at that temperature plus some reduction at lower temperatures.

An even more striking activation effect is observed when palladium is substituted for platinum. As little as 0.01 wt % palladium is sufficient to nearly completely activate 0.6 wt % nickel on the same support (Catalyst G) during reduction for 1 hr in hydrogen at 370°C. Little, if any, higher conversion is reached with as much as 0.3 wt % palladium in the catalyst (Catalyst F). Product distribution patterns again indicate that the nickel is being activated by the palladium.

Effects of 0.01 wt % platinum and palladium on the degree of activation of nickel at various temperatures are demonstrated in Table 2. Nickel alone on alumina was only very slowly activated by reduction in hydrogen, even at temperatures as high as 480°C. Addition of 0.01 wt % platinum accelerated the rate of activation, with an advantage of about twofold in mole fraction *n*-heptane converted after prerduction of the catalyst for 1 hr at 430°C. The presence of 0.01 wt % palladium caused a drastic increase in rate of activation, 1 hr at 370°C being sufficient to nearly completely activate the catalyst. Further reduction for 1 hr at 480°C caused only a slight increase in activity.

#### DISCUSSION

A likely mode of activation of supported nickel oxide-platinum and nickel oxide-

palladium catalysts is precious-metal-catalyzed reduction of nickel oxide with hydrogen. All catalysts were calcined in air at 290°C, causing the nickel to be in an oxide form before *in situ* activation with hydrogen. The oxide form was evidenced by a change in catalyst color from faint blue-green to faint gray after calcining. Also, heating unsupported Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in the calcining oven at 290°C for 2 hr resulted in complete conversion to a black powder characteristic of nickel oxides in appearance. Finally, Dr. D. J. C. Yates in our laboratory has found by microbalance measurements that bulk Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and also this salt impregnated both onto alumina and onto silica (10 wt % Ni) decompose abruptly between 210° and 230°C *in vacuo* and in hydrogen (4). Thus, the existence of nickel as oxide in our catalyst preparations is substantiated. Yet the pattern of hydrogenolysis products from the supported nickel catalysts with and without 0.01 wt % platinum shows the high selectivity to methane that is characteristic of metallic nickel (5, 6), and not of nickel oxide, or of platinum (7). The catalytic nature of the activation is evidenced by the low ratio of platinum or palladium to nickel (as low as  $\sim 5 \times 10^{-3}$ ) which brings about a large activating effect. Further supporting evidence for this hypothesis is to be found in literature reports of autocatalytic NiO re-

duction and of platinum-catalyzed partial reduction of  $\text{WO}_3$ , which are discussed and documented below.

Reduction of bulk NiO with hydrogen has been studied by Benton and Emmett (8), who found that the reaction is autocatalytic, being catalyzed by metallic Ni at the interface between the Ni and NiO phases. Their experimental technique was based on that of Pease and Taylor (9), who carried out an early study of the autocatalytic reduction of copper oxide by hydrogen. Subsequently, Bandrowski, Bickling, Yang, and Hougen (10) made a thorough kinetic study of the reduction reaction, finding that the overall rate can be expressed as the sum of two rates, one proportional to the fraction of unconverted NiO, and the other proportional to the product of the mole fractions of Ni and NiO. They postulate that the former is the reaction of NiO with hydrogen adsorbed on NiO, and the latter the reaction of NiO with hydrogen adsorbed on Ni. They give the following rate equation for their data below 300°C:

$$r = k_1(1 - \theta)p^{0.43} + k_2(1 - \theta)(\theta)p^{0.05} \quad (1)$$

where  $r$  is the overall rate in g moles  $\text{H}_2\text{O}$  formed per g mole of initial NiO per min;  $k_1$  and  $k_2$  are the rate constants for the direct reduction of NiO and for the Ni-catalyzed reduction of NiO, respectively;  $\theta$  is the fraction of original NiO that has been reduced to Ni; and  $p$  is the partial pressure of hydrogen. The contribution by Ni-catalyzed reduction is substantial,  $k_2$  being roughly five times greater than  $k_1$ . The order 0.43 in hydrogen pressure for the direct reduction is indicative of dissociative adsorption of hydrogen on the NiO at low surface coverage. On the other hand, the very low order of 0.05 for the Ni-catalyzed reaction under the postulated mechanism indicates saturation of the reactive Ni-NiO interface with hydrogen. Since Ni is well known to dissociatively adsorb hydrogen in large quantities, it is likely that the mode of catalysis here is activation of hydrogen in the atomic form. However, activation of oxygen atoms in NiO at the interface with Ni, as suggested by Benton and Emmett (8), is not definitely ruled out. At any rate, catalysis of the

reduction by a metal known to readily adsorb hydrogen is clearly in evidence.

Platinum catalyzes the partial reduction of  $\text{WO}_3$  by hydrogen, a finding somewhat similar in nature to the observed Ni-catalyzed reduction of NiO. Benson, Kohn, and Boudart (11) have found that physical contact with particles of platinum lowers from 400° to 100°C the temperature for hydrogen reduction of  $\text{WO}_3$  to  $\text{H}_{0.33}\text{WO}_3$  and/or  $\text{H}_{0.5}\text{WO}_3$  at comparable rates. They also found that water vapor acts as a co-catalyst, causing the reduction to occur rapidly even at room temperature. They attribute co-catalysis by water to enhanced transport of hydrogen from platinum to  $\text{WO}_3$  through an adsorbed water layer. These results clearly demonstrate platinum catalysis of a metal oxide reduction by hydrogen.

Nickel oxide supported on alumina is more difficult to reduce than bulk NiO, a fact which accounts for the low activity of our Ni/ $\text{Al}_2\text{O}_3$  catalyst even after reduction for 1 hr in hydrogen at 480°C. Benton and Emmett (8) observed reduction times of the order of an hour at 200°C for *bulk* NiO in hydrogen, and at 295°C Bandrowski, Bickling, Yang, and Hougen (10) measured 99% reduction in a few minutes. By contrast, nickel oxide *on alumina* (3–6% Ni) requires reduction at 510°C for completion in times of the order of an hour, as reported by Hill and Selwood (12). They combined quantitative reduction and magnetic susceptibility measurements to show that there is a definite interaction between the nickel oxide and the alumina support which affects the chemistry of the nickel oxide; a substantial fraction of the supported nickel oxide has a valence state of nickel higher than two. Interactions with rutile and magnesia rendering the supported nickel oxide incompletely reducible at 510°C were also observed. This type of interaction affecting valence state and reducibility is general for a large group of metal oxides. Another example of this sort of interaction is to be found in the hydrogen reduction of supported  $\text{WO}_3$  and  $\text{MoO}_3$ . Complete reduction of bulk  $\text{WO}_3$  and  $\text{MoO}_3$  occurs at 500°C, but significantly higher temperatures are required when these oxides are supported

on activated alumina (13). Metal oxide-support interactions of this kind adequately account for the difficult activation of our Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (Catalyst C).

Finally, the mechanism by which platinum and palladium catalyze hydrogen reduction of metal oxides must be examined. Both platinum and palladium are well known to dissociatively adsorb hydrogen in considerable quantities. Aston (14) has shown that the hydrogen atoms adsorbed on platinum are mobile at temperatures of 7°C and higher. Hydrogen atoms are also well known to be mobile in both  $\alpha$ - and  $\beta$ -palladium-hydrogen solutions over a very wide range of temperatures, and it is not unreasonable for them to be mobile at the surface as well. Therefore it is likely that hydrogen atoms form on the surfaces of these metals and then diffuse to adjacent nickel oxide particles, where they react to form nickel metal and water.

Reduction of nickel oxide particles not in contact with precious metal is also possible due to diffusion of activated hydrogen over the alumina support. Such surface diffusion of hydrogen has been inferred in a recent report (15) of platinum-catalyzed hydrogen-deuterium exchange with hydroxyl groups on alumina. Very low concentrations of platinum were shown to substantially increase the rate of exchange of deuterium for hydrogen in surface OH groups, as monitored by infrared spectroscopy. Similarly, then, it may be possible for activated hydrogen produced on precious metal particles to diffuse over the alumina support to nearby nickel oxide particles, where the reduction takes place.

There is an alternate model for metal-catalyzed reduction of metal oxides which is worthy of some consideration. This model also involves two simultaneous rate phenomena, in analogy with the previously described rate model of Bandrowski, Bickling, Yang, and Hougen (10). One rate process is nucleation of nickel metal crystallites on nickel oxide. This rate should be proportional to nickel oxide area and corresponds to the monotonically decreasing rate of the previous model. The other rate process is crystal growth at the metal-metal

oxide phase boundary. The role of the metal at the boundary may be twofold: to supply copious quantities of atomic hydrogen and also to provide a substrate for rapid growth of the metallic nickel phase without a high activation barrier to nucleation. The rate of this second process should show a maximum during the reduction, being a function of both nickel oxide and metal areas just as in the previous model. Platinum or palladium, initially present in the form of small crystallites, would act as nuclei for the rapid growth of metallic nickel crystals.

To distinguish between these models is difficult, but the authors prefer the former model which invokes the catalyzed activation of hydrogen. This preference gains support from experimental results recently reported by Verhoeven and Delmon (16), who measured rates of hydrogen reduction of NiO powders containing small amounts of finely divided foreign metals. It is significant that the metals which accelerated the reduction reaction (Pt, Pd, Cu) are also well known to activate hydrogen, while those which did not accelerate the reaction (Ag, Au, Cd) also do not activate hydrogen. Although the lack of effect with Ag, Au, and Cd does not completely rule out the nucleation model, it does substantially increase the likelihood that metal-catalyzed activation of hydrogen has a significant influence on the reduction rate.

#### ACKNOWLEDGMENTS

We wish to thank Mr. R. Nichols for assistance in the experimental work, Prof. M. Boudart, Mr. J. E. Hofmann, and Dr. J. H. Sinfelt for helpful discussions, and Esso Research and Engineering Company for permission to publish this paper.

#### REFERENCES

1. French Patent 1,372,516, August 10, 1964 (Imperial Chemical Industries Ltd.).
2. SAKAIDA, R. R., Ph.D. Thesis, Calif. Inst. Technology, Pasadena, California, 1960.
3. SAKAIDA, R. R., RINKER, R. G., WANG, Y. L., AND CORCORAN, W. H., *A.I.Ch.E. J.* 7, 658 (1961).
4. YATES, D. J. C., unpublished results.
5. HAENSEL, V., AND IPATIEFF, V. N., *J. Am. Chem. Soc.* 68, 345 (1946).

6. HAENSEL, V., AND IPATIEFF, V. N., *Ind. Eng. Chem.* **39**, 853 (1947).
7. HEINEMANN, H., MILLS, G. A., HATTMAN, J. B., AND KIRSCH, F. W., *Ind. Eng. Chem.* **45**, 130 (1953).
8. BENTON, A. F., AND EMMETT, P. H., *J. Am. Chem. Soc.* **46**, 2728 (1924).
9. PEASE, R. N., AND TAYLOR, H. S., *J. Am. Chem. Soc.* **43**, 2179 (1921).
10. BANDROWSKI, J., BICKLING, C. R., YANG, K. H., AND HOUGEN, O. A., *Chem. Eng. Sci.* **17**, 379 (1962).
11. BENSON, J. E., KOHN, H. W., AND BOUDART, M., *J. Catalysis* **5**, 307 (1966).
12. HILL, F. N., AND SELWOOD, P. W., *J. Am. Chem. Soc.* **71**, 2522 (1949).
13. SONDAG, P., KIM, D. Q., AND MARION, F., *Compt. Rend.* **259**, 4704 (1964).
14. ASTON, J. G., *J. Phys. Chem.* **67**, 2042 (1963).
15. CARTER, J. L., LUCCHESI, P. J., CORNEIL, P., YATES, D. J. C., AND SINFELT, J. H., *J. Phys. Chem.* **69**, 3070 (1965).
16. VERHOEVEN, W., AND DELMON, B., *Compt. Rend., Sec. C*, **262**, 33 (1966).