

## Cyclopropane-Hydrogen Reaction Over the Group VIII Noble Metals

R. A. DALLA BETTA, J. A. CUSUMANO, AND J. H. SINFELT

*Corporate Research Laboratories, Esso Research and Engineering Company,  
Linden, New Jersey 07036*

Received April 23, 1970

The specific catalytic activities of the Group VIII noble metals have been determined for the hydrogenation of cyclopropane to propane. Metal surface areas required for the determination of specific activities were measured by chemisorption of hydrogen or carbon monoxide at room temperature. On two of the metals, ruthenium and osmium, a fragmentation reaction yielding methane and ethane was observed in addition to the hydrogenation reaction. For the two triads of metals comprising osmium, iridium, and platinum in one case, and ruthenium, rhodium, and palladium in the other, the orders of variation of cyclopropane hydrogenation activities are  $Pt > Ir > Os$  and  $Pd < Rh > Ru$ , which are very different from previously reported results for ethane hydrogenolysis. In addition, the range of activities of the metals is much smaller for cyclopropane hydrogenation than for ethane hydrogenolysis, suggesting that the former is much less sensitive than the latter to the electronic structure of the metal.

### INTRODUCTION

The reaction of cyclopropane with hydrogen over metal catalysts has been studied by several groups of investigators (1-6). The studies have disclosed the general features of the kinetics of the reaction and have contributed to the understanding of the reaction mechanism. The studies also give some idea of the general level of catalytic activities of various metals for the reaction, but very little attempt appears to have been made to determine the specific catalytic activities of the metals (7, 8), i.e., activities referred to unit area of metal surface. The principal reason for this has been the absence of information on the surface areas of the metal component in the supported metal catalysts commonly used. The recent development of selective chemisorption techniques for the determination of the surface areas of highly dispersed, supported metals (9-18) has made it possible to conduct meaningful investigations of this kind.

In previous reports from this laboratory (11-15) the specific catalytic activities of

a number of metals, including all the Group VIII metals, have been compared for the ethane hydrogenolysis reaction. The studies showed an extremely large variation in the activities, amounting to eight orders of magnitude difference between platinum or palladium at one extreme and osmium at the other, and showed a good correspondence between the patterns of variation of catalytic activity and % *d*-character of the metallic bond (12, 14, 19). More recent work on the hydrogenolysis of neopentane (20) has confirmed this. The hydrogenolysis of hydrocarbons is thus a reaction which is highly sensitive to the particular metal employed as a catalyst. The results of this work pose an interesting question of how such a comparison of metal activities would be affected by the nature of the reaction. Preliminary studies on cyclopropane hydrogenation in this laboratory had indicated that the reaction might be quite different from ethane hydrogenolysis in the way catalytic activity varies from metal to metal, and that the range of variation of

catalytic activity among the metals may be much smaller. Consequently, we decided to determine the specific activities of the Group VIII noble metals for the hydrogenation of cyclopropane to propane. The metals were all supported on silica, and the surface areas of the metals were determined by the selective chemisorption of hydrogen or carbon monoxide. The results of the work point to some marked differences between cyclopropane hydrogenation and ethane hydrogenolysis in the dependence of catalytic activity on the metal. Another point of interest in the work is the aspect of selectivity, as cyclopropane has been found to undergo a fragmentation reaction with hydrogen to yield methane and ethane (7, 8). The present work serves to distinguish the metals which promote very selectively the hydrogenation reaction to propane from those which catalyze also the formation of fragmentation products.

#### EXPERIMENTAL METHODS

##### *Apparatus and Procedure*

The reaction kinetic data were obtained in a flow reactor system at atmospheric pressure, using a vertically mounted Pyrex glass reactor 1.2 cm in diameter and 16 cm long. The inlet to the reactor was preceded by a glass tube preheater section. The catalyst was supported on a coarse fritted glass disk. Details of the flow rate measurements and gas chromatographic analysis of reaction products are similar to those previously reported elsewhere (21), the only difference being the use of high precision "Vari-Vac" valves (22) to regulate the reactant flows. The cyclopropane and hydrogen were mixed with helium and passed downflow through a bed containing 0.20 g of catalyst diluted uniformly with 0.50 g of ground Vycor glass. Both the catalyst and diluent were of 45-60 mesh size. By appropriate adjustment of the helium flow rate, it was possible to vary the partial pressures of cyclopropane and hydrogen individually. The total gas flow was maintained at 1 liter/min in all experiments. In a typical run the reactant gases were passed over the catalyst for 3 min prior to sampling prod-

ucts for analyses. The cyclopropane was then cut out and the hydrogen and helium flows continued until the next reaction period. The catalyst was usually "flash reduced" at 365°C for about 30 min between reaction periods so that reproducible activity could be obtained. Such a procedure was especially necessary for the more active catalysts run at temperatures below 0°C. The temperature of the catalyst could be varied continuously from -100 to 25°C  $\pm$  0.2° by means of a specially designed cooling system. The system consisted mainly of a Dewar containing a heat transfer fluid (e.g., isopropanol), the temperature of which was controlled by cooling coils containing liquid nitrogen. Above 25°C the temperature was controlled to  $\pm$ 0.5°C by a fluidized solids bath (23). Prior to any rate measurements, the catalyst was reduced for 16 hr in flowing hydrogen (50 ml/min) at 450°C in the reactor.

The surface areas of the supported metals used in this study were obtained by hydrogen chemisorption, or carbon monoxide chemisorption in the case of the palladium catalyst. Details of the chemisorption technique used to estimate the metal surface areas have been given previously (10-15). The surface areas were determined after the catalyst had been reduced at the same conditions which were employed in the catalytic studies.

##### *Materials*

The supported palladium, iridium, osmium, and ruthenium catalysts used in this work contained 10 wt % of metal and were prepared by impregnation of silica (Cabosil) with a solution of an appropriate compound of the metal. The platinum and rhodium catalysts were prepared in a similar manner, but because of their higher activity, contained only 0.6 and 0.3 wt % metal, respectively. The details of preparation of these catalysts are given in Table 1.

The research grade cyclopropane used in this work was obtained from the Lif-O-Gen Co. This gas was very pure, containing about 500 ppm impurities, most of which were propane and propylene. Under the conditions at which the present catalysts

TABLE 1  
PREPARATION AND PROPERTIES OF CATALYSTS

Catalyst <sup>a</sup>	Preparation of catalyst		Metal surface area <sup>c</sup> (m <sup>2</sup> /g of catalyst)
	Impregnating solution	Procedure <sup>b</sup>	
10% Pd	(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub>	A	5.0
0.3% Rh	RhCl <sub>3</sub>	A	1.3
10% Ru	RuCl <sub>3</sub> · xH <sub>2</sub> O	A	10.0
0.6% Pt	H <sub>2</sub> PtCl <sub>6</sub>	B	1.2
10% Ir	H <sub>2</sub> IrCl <sub>6</sub>	A	18.1
10% Os	H <sub>2</sub> OsCl <sub>6</sub>	A	12.7

<sup>a</sup> All metals were supported on silica (Cabosil HS5, surface area = 300 m<sup>2</sup>/g).

<sup>b</sup> Procedure: A. Cabosil was impregnated with an aqueous solution of the appropriate metal compound in the amount of 2 ml of solution/g of Cabosil. The resulting material was mixed thoroughly and dried at 60°C. B. H<sub>2</sub>PtCl<sub>6</sub> was dissolved in a solution comprising 1 ml of concentrated NH<sub>4</sub>OH per 10 ml of water. The resulting solution was then mixed with Cabosil in the amount of 2.2 ml/g. The impregnated Cabosil was washed with water (20 ml/g), and finally dried at 60°C.

<sup>c</sup> The metal surface areas were determined by hydrogen chemisorption, except for the palladium catalyst, in which case carbon monoxide chemisorption was used.

were run, the propylene impurity readily hydrogenated to propane. A small correction was made for this. High purity hydrogen was obtained from the Linde Co., Linden, N. J. It was further purified in a Deoxo unit containing a palladium catalyst to remove trace amounts of oxygen. The water formed was then removed by a molecular sieve dryer.

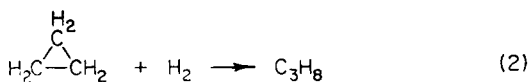
## RESULTS

The metal surface areas of the catalysts used in this study are given in Table 1. They were obtained using previously described techniques (10-15).

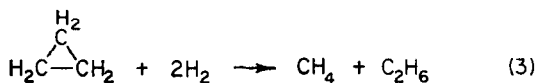
The reaction of cyclopropane with hydrogen was studied at low conversion levels (0.05 to 5.0%). Rates were calculated from the relation

$$r = (F/W)x, \quad (1)$$

where  $F$  is the feed rate to the reactor in moles of cyclopropane per hour,  $W$  the weight in grams of the catalyst, and  $x$  represents the fraction of cyclopropane converted. In calculating the rate of the hydrogenation reaction,



$x$  is the fraction of cyclopropane converted to propane, and in the case of the fragmentation reaction,



$x$  is the conversion to methane and ethane. Under the present experimental conditions equimolar quantities of methane and ethane were formed. The methane and ethane appear to be primary products (8). Reaction rates in moles of cyclopropane converted per hour per gram of catalyst to propane, or to methane plus ethane, were readily converted to molecules/sec cm<sup>2</sup>, since the metal surface areas were known.

In a typical experiment to obtain the temperature dependence, the catalyst was first reduced for about 16 hr at 450°C in 50 ml/min of hydrogen. The reactor was then usually cooled in flowing hydrogen to the first reaction temperature. The rate of reaction was then measured as a function of temperature in a rising temperature sequence at a standard set of hydrogen and cyclopropane pressures of 0.20 and 0.030 atm, respectively. For most of the catalysts, it was necessary to "flash reduce" the catalyst at 365°C for 30 min between reaction periods to maintain reproducible catalytic

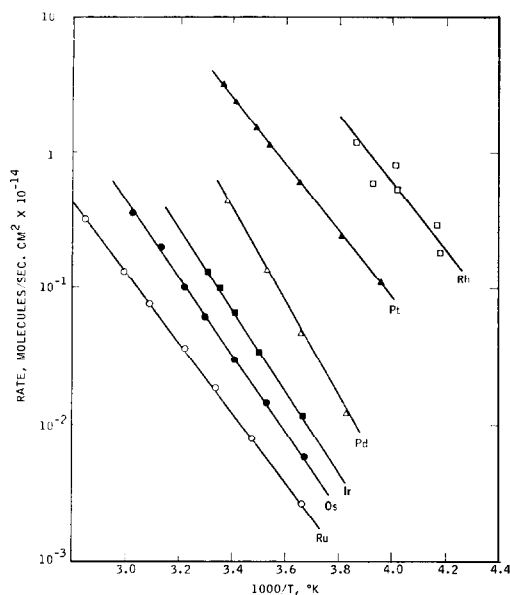


Fig. 1. The effect of temperature on the rate of hydrogenation of cyclopropane to propane over the Group VIII noble metals supported on silica: ○, Ru; ●, Os; □, Rh; ■, Ir; △, Pd; ▲, Pt. The data were obtained at hydrogen and cyclopropane pressures of 0.20 and 0.030 atm, respectively.

activity. Arrhenius plots of the rate of hydrogenation of cyclopropane are given in Fig. 1 for the various Group VIII noble metal catalysts. The order of activities of

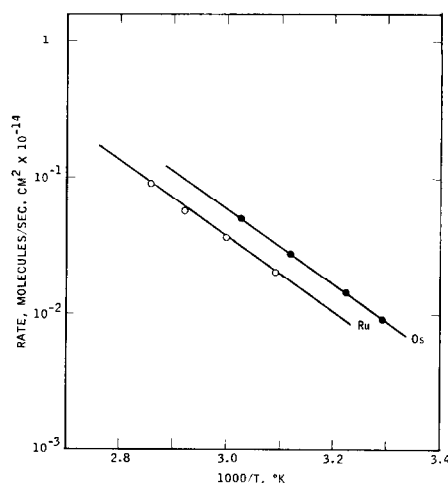


Fig. 2. The effect of temperature on the rate of fragmentation of cyclopropane to methane and ethane over silica-supported osmium and ruthenium: ○, Ru; ●, Os. The data were obtained at hydrogen and cyclopropane pressures of 0.20 and 0.030 atm, respectively.

the metals is  $Rh > Pt > Pd > Ir > Os > Ru$ . Arrhenius plots for the cyclopropane fragmentation reaction to methane and ethane are given in Fig. 2 for the osmium and ruthenium catalysts, which were the only catalysts to show the reaction. Previous work (7) has shown that nickel and cobalt also give the fragmentation reaction. The osmium catalyst is slightly more active

TABLE 2  
SUMMARY OF KINETIC PARAMETERS FOR THE REACTIONS OF CYCLOPROPANE WITH HYDROGEN OVER SILICA-SUPPORTED GROUP VIII NOBLE METALS

Catalyst	Temp (range; °C)	Reaction <sup>a</sup>	$E^b$	$r'^c$	Specific activity <sup>d</sup>
10% Pd	-10 to 25	Hydrogenation	16	$3.0 \times 10^{25}$	$1.6 \times 10^{12}$
0.3% Rh	-35 to -10	Hydrogenation	11	$2.4 \times 10^{23}$	$1.8 \times 10^{14}$
10% Ru	0 to 80	Hydrogenation	12	$1.1 \times 10^{21}$	$1.2 \times 10^{11}$
		Fragmentation	12	$2.0 \times 10^{20}$	$2.3 \times 10^{10}$
0.6% Pt	-20 to 30	Hydrogenation	11	$3.7 \times 10^{22}$	$2.7 \times 10^{13}$
10% Ir	0 to 30	Hydrogenation	13	$2.8 \times 10^{22}$	$4.5 \times 10^{11}$
10% Os	0 to 60	Hydrogenation	13	$1.6 \times 10^{22}$	$2.5 \times 10^{11}$
		Fragmentation	13	$2.3 \times 10^{21}$	$3.6 \times 10^{10}$

<sup>a</sup> Hydrogenation of cyclopropane to propane, or fragmentation of cyclopropane to methane and ethane.

<sup>b</sup> Apparent activation energy (kcal/mole).

<sup>c</sup> Pre-exponential factor in the expression,  $r = r' \exp(-E/RT)$ , which expresses the temperature dependence of the reaction rate at standard conditions (hydrogen and cyclopropane pressures of 0.20 and 0.030 atm, respectively). The units of  $r'$  are molecules/sec cm<sup>2</sup>.

<sup>d</sup> Reaction rate (molecules/sec cm<sup>2</sup>) at -10°C and hydrogen and cyclopropane pressures of 0.20 and 0.030 atm, respectively.

than the ruthenium catalyst for the fragmentation reaction. Kinetic parameters, including apparent activation energies and pre-exponential factors, are given in Table 2, which also lists specific activities of the metals for the hydrogenation and fragmentation reactions. A temperature of  $-10^{\circ}\text{C}$  was chosen for comparison of specific activities.

It should be noted that the activity data for the platinum catalyst used in the present study do not agree with previous data from our laboratory (7) on a platinum catalyst prepared from  $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ . The previous data indicated much lower activity, suggesting that the catalyst was probably poisoned. Our present results on platinum have been rechecked several times, and have been found to be reproducible. Another point of interest in the present work is the observation that the palladium catalyst was more active (about twofold) when it was purged in helium after reduction and cooled to reaction temperature in flowing helium. Perhaps the normal procedure of cooling in hydrogen results in the palladium containing dissolved hydrogen which may inhibit catalysis.

### DISCUSSION

The present work on the reaction of cyclopropane with hydrogen over Group VIII noble metal catalysts permits us to draw some conclusions regarding both activity and selectivity patterns of these metals for the reaction. In considering activity patterns first, it is convenient to refer to a plot of specific catalytic activity as a function of the position of the metal in the Periodic Table, as shown in Fig. 3. In the case of the triad of metals comprising osmium, iridium, and platinum in the third transition series, the activity for hydrogenation of cyclopropane to propane increases in the direction of increasing atomic number from osmium to platinum. This contrasts markedly with the previously reported activity pattern for ethane hydrogenolysis (19), in which the activity decreases precipitously from osmium to platinum. For the metals osmium, iridium, and platinum, we note that the range of variation of catalytic activities is much smaller

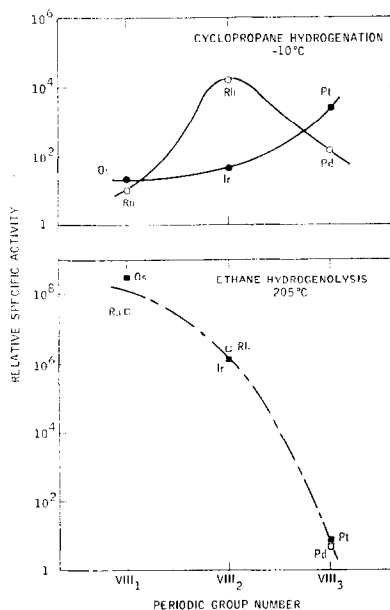


FIG. 3. Activity patterns of the Group VIII noble metals for cyclopropane hydrogenation and ethane hydrogenolysis. The ethane hydrogenolysis data were taken from Ref. (19). All points are for hydrogen and hydrocarbon (cyclopropane or ethane) pressures of 0.20 and 0.030 atm, respectively.

for cyclopropane hydrogenation than for ethane hydrogenolysis, suggesting that the former reaction is much less sensitive to the electronic structure of the metal. In the case of the triad of metals comprising ruthenium, rhodium, and palladium in the second transition series, the catalytic activity for cyclopropane hydrogenation passes through a maximum at rhodium; whereas for ethane hydrogenolysis the activity decreases continuously from ruthenium to palladium. Again the variation of activities is much smaller for the cyclopropane hydrogenation reaction. Also, as shown in Fig. 4, the apparent activation energy of the latter reaction is much lower and shows very little variation from one metal to another.

In a study of the hydrogenation of cyclopropane on platinum catalysts, Boudart *et al.* (24) observed that the specific activity of the platinum was essentially independent of the form of the catalysts, of the nature of the carrier, or of the state of dispersion of the platinum. They proposed that cyclopropane hydrogenation on

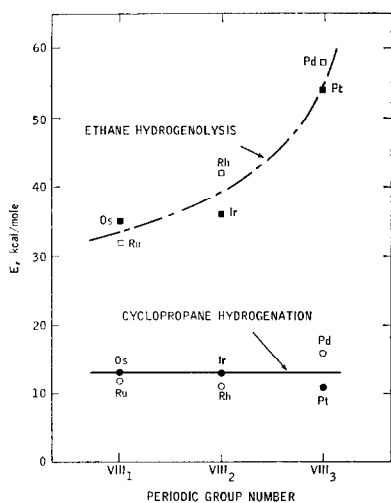


Fig. 4. Apparent activation energies of the cyclopropane hydrogenation and ethane hydrogenolysis reactions over the Group VIII noble metals. The values for ethane hydrogenolysis were taken from Ref. (19). The apparent activation energies were determined for hydrogen and hydrocarbon (cyclopropane or ethane) pressures of 0.20 and 0.030 atm, respectively.

platinum be termed a "facile" reaction to reflect the insensitivity of the catalytic activity to structural features of the platinum related to the method of preparation of the catalyst. By contrast, this group of workers proposed that neopentane hydrogenolysis on platinum is a "demanding" reaction, in the sense that the specific activity of the platinum is sensitive to catalyst preparation variables which influence the surface structure of the metal (25). The specific activities of metals for ethane hydrogenolysis are also a function of catalyst preparation variables such as the state of metal dispersion and the nature of the carrier (19). Consequently, we consider ethane hydrogenolysis on metals to be a demanding reaction, and attribute this to the involvement of dissociatively chemisorbed hydrocarbon intermediates (19, 26) which are multiply-bonded to the surface.

The classification into "facile" and "demanding" reactions just discussed is based on differences in the sensitivity of reactions to surface structure, as influenced by variables such as metal dispersion, carrier prop-

erties, and reduction or sintering temperatures employed in the preparation of the catalyst. However, the distinction between the two types of reactions may not be limited to differences in sensitivity to surface structure. Thus, if one reaction is much less sensitive than another to surface structure, it may well show much lower variation in rate from one metal to another. This is illustrated by the present comparison of cyclopropane hydrogenation and ethane hydrogenolysis over the Group VIII noble metals. The range of activities of the metals for these two reactions differs by about five orders of magnitude or more. Furthermore, the activation energy of the cyclopropane hydrogenation reaction is much lower than that of ethane hydrogenolysis, and is virtually invariant from one metal to another. Similarly, the activation energies for hydrogenation of olefins, and of aromatics, have often been observed to vary little from metal to metal (27), and this in itself is one basis for classifying such reactions as facile. Correspondingly, the huge variation in activation energy for ethane hydrogenolysis on different metals is a basis for classifying it as a demanding reaction.

In the choice of a test reaction for systematic studies of the catalytic activities of a series of metals, it has been suggested that facile reactions would be preferred (25). According to this view, the use of facile reactions would avoid complicating effects due to the involvement of special types of active centers. However, while a reaction such as the hydrogenolysis of ethane may depend somewhat on details of catalyst preparation, including differences in metal dispersion and properties of the carrier, it is highly sensitive to the particular metal employed as a catalyst. Fortunately, the effects of catalyst structural or preparative details, while they are far from being negligible for this latter reaction, are small compared with the effect of varying the metal itself, and hence do not obscure the patterns of variation of catalytic activity from one metal to another. The hydrogenolysis of ethane is therefore a very effective reaction for differentiating

among various metals with regard to their catalytic properties.

As pointed out above, hydrogenolysis reactions are generally considered to involve dissociatively chemisorbed hydrocarbon intermediates (19, 26) which are presumably multiply bonded to the surface via carbon-metal sigma bonds. Hydrogenation reactions, on the other hand, including the hydrogenation of cyclopropane, olefins, or aromatics, do not require the formation of dissociatively chemisorbed hydrocarbon intermediates, and the suggestion has been made that such reactions proceed via pi-bonded intermediates (28). It is interesting that a number of metal-catalyzed hydrogenation reactions of hydrocarbons have been classified as facile reactions (25). The possibility thus suggests itself that reactions which may involve intermediates of the pi-bonded type are facile, while those involving multiply-bound chemisorbed species are more likely to be demanding.

In returning to other aspects of the present study on the reaction of cyclopropane with hydrogen, we note that ruthenium and osmium are the only noble metals of Group VIII which promote significant fragmentation of cyclopropane to methane and ethane. Interestingly, these are the two metals which are most active for the hydrogenolysis of ethane (14, 19). The "noblest" four (Pt, Pd, Ir, Rh) catalyze the hydrogenation reaction to propane very cleanly. Previous studies (7, 8) have shown that nickel and cobalt also catalyze the fragmentation reaction [termed hydrogenolysis in Ref. (7 and 8)], and we have recently observed the reaction on iron. In agreement with these results, other workers (29, 30) have reported that the fragmentation reaction occurs on evaporated nickel and iron films.

#### REFERENCES

1. BOND, G. C., AND SHERIDAN, J., *Trans. Faraday Soc.* **48**, 713 (1952).
2. ADDY, J., AND BOND, G. C., *Trans. Faraday Soc.* **53**, 368 (1957).
3. ADDY, J., AND BOND, G. C., *Trans. Faraday Soc.* **53**, 383 (1957).
4. ADDY, J., AND BOND, G. C., *Trans. Faraday Soc.* **53**, 388 (1957).
5. BOND, G. C., AND NEWHAM, J., *Trans. Faraday Soc.* **56**, 1501 (1960).
6. BENSON, J. E., AND KWAN, T., *J. Phys. Chem.* **60**, 1601 (1956).
7. SINFELT, J. H., YATES, D. J. C., AND TAYLOR, W. F., *J. Phys. Chem.* **69**, 1877 (1965).
8. TAYLOR, W. F., YATES, D. J. C., AND SINFELT, J. H., *J. Catal.* **4**, 374 (1965).
9. SPENADEL, L., AND BOUDART, M., *J. Phys. Chem.* **64**, 204 (1960).
10. YATES, D. J. C., TAYLOR, W. F., AND SINFELT, J. H., *J. Amer. Chem. Soc.* **86**, 2996 (1964).
11. SINFELT, J. H., TAYLOR, W. F., AND YATES, D. J. C., *J. Phys. Chem.* **69**, 95 (1965).
12. SINFELT, J. H., AND YATES, D. J. C., *J. Catal.* **8**, 82 (1967).
13. YATES, D. J. C., AND SINFELT, J. H., *J. Catal.* **8**, 348 (1967).
14. SINFELT, J. H., AND YATES, D. J. C., *J. Catal.* **10**, 362 (1968).
15. YATES, D. J. C., AND SINFELT, J. H., *J. Catal.* **14**, 182 (1969).
16. ADLER, S. F., AND KEAVNEY, J. J., *J. Phys. Chem.* **64**, 208 (1960).
17. GRUBER, H. L., *J. Phys. Chem.* **66**, 48 (1962).
18. BENSON, J. E., AND BOUDART, M., *J. Catal.* **4**, 703 (1965).
19. SINFELT, J. H., *Catal. Rev.* **3**(2), 175 (1969).
20. BOUDART, M., AND PTAK, L. D., *J. Catal.* **16**, 90 (1970).
21. SINFELT, J. H., *J. Phys. Chem.* **68**, 344 (1964).
22. Vactronic Lab Equipment, Inc., East Northport, N. Y.
23. Techne Inc., Princeton, N. J.
24. BOUDART, M., ALDAG, A., BENSON, J. E., DOUGHARTY, N. A., AND HARKINS, C. G., *J. Catal.* **6**, 92 (1966).
25. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
26. CIMINO, A., BOUDART, M., AND TAYLOR, H. S., *J. Phys. Chem.* **58**, 796 (1954).
27. BOND, G. C., "Catalysis by Metals," pp. 241-242, 315, Academic Press, New York, 1962.
28. ROONEY, J. J., AND WEBB, G., *J. Catal.* **3**, 488 (1964).
29. KNOR, Z., PONEC, V., HERMAN, Z., DOLEJSEK, Z., AND CERNY, S., *J. Catal.* **2**, 299 (1963).
30. ANDERSON, J. R., AND AVERY, N. R., *J. Catal.* **8**, 48 (1967).