JOURNAL OF CATALYSIS 20, 223–229 (1971)

Hydrogenolysis of *n*-Heptane over Unsupported Metals

J. L. CARTER, J. A. CUSUMANO, AND J. H. SINFELT

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

Received June 9, 1970

The catalytic hydrogenolysis of *n*-heptane was investigated on a series of noble metal catalysts in the form of powders. The metals studied were palladium, rhodium, ruthenium, platinum, and iridium. Hydrogenolysis was the predominant reaction on all the metals except platinum, on which extensive isomerization and dehydrocyclization were observed. The hydrogenolysis activity of palladium was very much lower than that of rhodium and ruthenium, and the activity of platinum was in turn very much lower than that of iridium. This order of hydrogenolysis activities corresponds closely to the pattern of variation of the percentage *d*-character of the metallic bond. The distribution of hydrogenolysis products showed striking differences among the metals. Palladium and rhodium cracked the terminal C–C bond almost exclusively, while the other metals, especially platinum and iridium, showed a much less selective type of cracking. The isomerization reaction on platinum appears to involve several reaction paths, with some contribution from a path involving a cyclic intermediate on the surface.

INTRODUCTION

Previous studies on the hydrogenolysis of ethane over supported metals have established the order of catalytic activities for a considerable number of metals, including all the metals of Group VIII of the periodic table (*1–4*). Within a given period of the periodic table, the hydrogenolysis activity varied in the same manner as the percentage *d*-character of the metallic bond. In the case of the noble metals of Group VIII, the activity within a given period decreased markedly from left to right in the direction of increasing atomic number, i.e., from ruthenium to palladium or from osmium to platinum.

Recently we have investigated the hydrogenolysis of *n*-heptane over most of the Group VIII noble metals. The studies have been conducted with unsupported metals to eliminate any possible support effects. The purpose of the work was severalfold: (a) to obtain additional data on the order of hydrogenolysis activities of metals to confirm the previous results on ethane, (b) to compare hydrogenolysis product distributions ("cracking patterns") on the various metals, and (c) to investigate the occurrence of other reactions such as isomerization and dehydrocyclization.

EXPERIMENTAL

Apparatus and Procedure

The catalytic studies were conducted in a flow reactor system at atmospheric pressure. The reactor was a vertically mounted stainless steel tube about 18 cm long and 1 cm in diameter, and was surrounded by an electrical heater. The catalyst was supported on a fritted stainless steel disk located about 6 cm from the bottom of the tube. The catalyst was employed in the form of fine metal powders diluted with inert alundum granules in all the runs. The catalyst bed depth was approximately 6 cm. A 6-cm layer of inert alundum granules was placed on top of the catalyst bed to serve as a preheat section. Reaction temperatures were measured with an iron-constantan thermocouple housed in a 3-mm axial thermowell extending upward through the fritted steel disk to the center of the catalyst charge. The reactants, *n*-heptane and hydrogen, were passed downflow through the catalyst bed. The hydrogen flow rate was determined with a rotameter. A measured flow of *n*-heptane was delivered to the reactor with a motor-driven syringe. The syringe was connected to the reactor inlet by a section of teflon tubing. On entering the preheat section of the reactor, the *n*-heptane was vaporized and brought to reaction temperature in admixture with hydrogen prior to passage through the catalyst bed.

Reaction products were analyzed by a Perkin-Elmer Model 226 gas chromatograph containing a 300-ft squalane capillary column with a flame ionization detector. The chromatographic unit was connected directly to the outlet of the reactor.

Gas adsorption measurements of metal surface areas were made in a conventional high vacuum adsorption system described previously (*5*).

Materials

The *n*-heptane was obtained from Phillips Petroleum Co. A chromatographic analysis indicated less than 0.1% of hydrocarbon impurities. High purity hydrogen obtained from the Linde Co. was further purified by passing it through a Deoxo unit containing palladium catalyst to remove trace amounts of oxygen as water and then drying with a molecular sieve. The trans-1,2-dimethylcyclopentane was obtained from Chemical Samples Co., Columbus, Ohio, and had a minimum purity of 99%.

The metal catalysts were prepared in most cases by the reduction of aqueous solutions of salts of the metals with sodium borohydride at room temperature (*6*). For the preparation of the palladium, rhodium, ruthenium, and platinum, aqueous solutions of the following were employed: $(NH_4)_2PdCl_4$, $RhCl_3$, $RuCl_3 \cdot xH_2O$, and $H_2PtCl_6 \cdot 6H_2O$. The iridium catalyst was obtained by reduction of IrO_2 in flowing hydrogen at 300°C. The iridium oxide was obtained as a powder from Alfa Inorganics, Inc., Beverly, Massachusetts. The metals prepared by the borohydride reduction procedure were thoroughly washed to remove sodium and boron impurities to a level less than 10 ppm. After being charged to the reactor or to an adsorption cell, the metals were treated in flowing hydrogen at 300°C to assure complete reduction. The specific surface areas in m^2g^{-1} after this reduction procedure were: palladium, 12.8; rhodium, 30.5; ruthenium, 26.4; platinum, 3.7; iridium, 1.1. The surface areas were determined by the physical adsorption of argon at 77°K, i.e., by the BET method (7).

RESULTS

Three types of reactions of *n*-heptane were observed over the various metals: (a) hydrogenolysis to lower molecular weight paraffins, (b) isomerization to methylhexanes and dimethylpentanes, and (c) dehydrocyclization to dimethylcyclopentanes, methylcyclohexane and toluene. The reactions occur to varying degrees on the different metals, as shown by the data in Table 1, which were obtained at low conversion levels. Over palladium, rhodium, ruthenium, and iridium, hydrogenolysis predominates, accounting for virtually all of the reaction. On platinum, however, the situation is markedly different, in that extensive isomerization and dehydrocyclization are observed. In Table 1 it is seen that the data on the various metals were obtained at widely different temperatures, as necessitated by the huge differences in their catalytic activities. However, the unique isomerization and dehydrocyclization properties of platinum are not simply a consequence of the temperature at which the data were obtained, since palladium at about the same temperature gives almost all hydrogenolysis.

Arrhenius plots of the rate of hydrogenolysis of *n*-heptane as a function of temperature are given in Fig. 1. The rate represents the total number of moles of *n*-heptane converted to lower carbon number products per hour per square meter of metal surface area. The method of determining reaction rates from the data has been described

TABLE 1

REACTIONS OF n-HEPTANE OVER METALS IN THE PRESENCE OF HYDROGEN[a]

Metal	Temp, °C	F/W[b]	% Hydrogenolysis	% Isomerization	% Dehydrocyclization	Total Conversion, %
Pd	300	0.010	5.8	0.4	0.2	6.4
Rh	113	0.010	2.7	0.2	—	2.9
Ru	88	0.010	3.7	0.3	—	4.0
Pt	275	0.10	0.6	0.7	1.0	2.3
		0.025	3.4	3.8	2.2	9.4
		0.010	8.0	10.0	3.4	21.4
Ir	125	0.010	1.3	0.2	—	1.5

[a] Conditions: 1 atm, $H_2/n\text{-}C_7$ mole ratio = 5.

[b] Moles n-heptane hr^{-1} g^{-1} *catalyst.*

previously (*1*, *2*). The rates all refer to a total pressure of 1 atm, and a hydrogen to n-heptane mole ratio of 5/1. The rate data in Fig. 1 represent a broad range of temperatures, 74–350°C, which attests to the wide range of catalytic activities of the various metals. The order of activities of the metals for the hydrogenolysis of n-heptane is $\text{Pd} < \text{Pt} \ll \text{Rh} < \text{Ir} < \text{Ru}$.

The distribution of hydrogenolysis products varies markedly among the different metals. Palladium and rhodium crack the terminal C–C bond in n-heptane almost exclusively, while the other metals, particularly platinum and iridium, exhibit a much less selective type of cracking. Data on the distribution of hydrogenolysis products at low conversion levels are given in Table 2. There is no simple relation between the level of hydrogenolysis activity and the type of "cracking pattern" observed. Thus platinum and palladium, which have comparable low hydrogenolysis activities, show greatly different distributions of hydrogenolysis products. The product distributions are also very different for iridium and rhodium, which have comparable high hydrogenolysis activities.

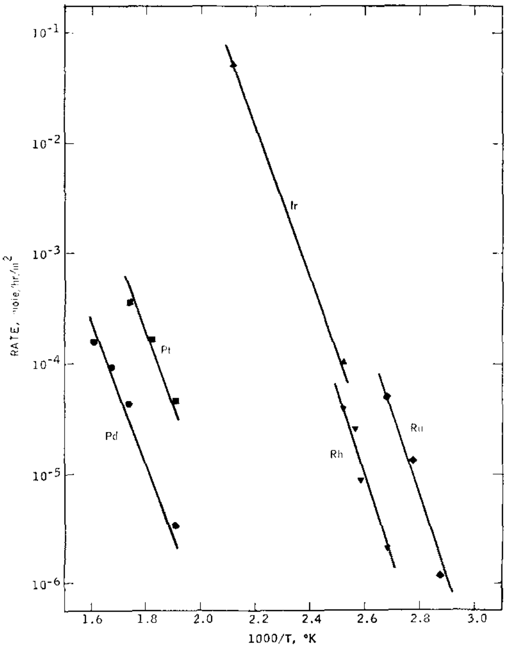


FIG. 1. Arrhenius plots for n-heptane hydrogenolysis over various Group VIII metals (at 1 atm. and a $H_2/n\text{-}C_7$ mole ratio of 5/1): ●, Pd; ■, Pt; ▼, Rh; ▲, Ir; ◆, Ru.

The isomerization of n-heptane to methylhexanes and dimethylpentanes, and the dehydrocyclization to dimethylcyclopentanes, methylcyclohexane, and toluene on platinum are shown by the data in Figs. 2 and 3. In both of these figures, the percentage conversion to a particular product is plotted as a function of the quantity W/F, which is the weight of catalyst in grams divided by the number of moles per hour of n-heptane fed to the reactor. The slope of such a plot at any point gives the rate of conversion of n-heptane to a particular product in moles per hour per gram of catalyst at that point in the course of the reaction. In the case of methylhexanes and dimethylpentanes, the slope of the curve increases initially with increasing W/F, i.e., with increasing conversion. Similar behavior is observed for *trans*-1,3-di-

TABLE 2
Distribution of *n*-Heptane Hydrogenolysis Products over Metals[a]

Metal	Temp, °C	% Total Conversion	Distribution of Hydrogenolysis Products, Mole %[b]					
			C_1	C_2	C_3	n-C_4	n-C_5	n-C_6
Pd	300	6.4	46	4	—	—	4	46
Rh	113	2.9	42	5	4	3	5	41
Ru	88	4.0	28	12	13	12	10	25
Pt	275	2.3	31	13	17	16	9	14
Ir	125	1.5	21	21	15	14	14	15

[a] Conditions: 1 atm, H_2/n-C_7 mole ratio = 5.
[b] All products are *n*-paraffins.

methylcyclopentane. On the other hand, this is not observed for *trans*-1,2- and *cis*-1,2-dimethylcyclopentanes, for which the slope has its highest value at the origin and decreases continuously with increasing conversion. In the case of the methylcyclohexane and toluene products, the exact shape of the curve at very low conversions is more difficult to ascertain. The amounts of *trans*-1,2- and *cis*-1,2-dimethylcyclopentanes formed, and also methylcyclohexane, approach constant, limiting values in the range of W/F of 50–100, corresponding to *n*-heptane conversion levels of 10–20%. The ratio of the *trans*-1,2- to the *cis*-1,2-dimethylcyclopentane corresponds closely to the expected equilibrium value (*8*) over the whole range of conversions studied. The initial high ratio of methylcyclohexane to toluene in the product, and its subsequent decrease with increasing *n*-heptane conversion, indicates that the methylcyclohexane behaves like an intermediate in the formation of toluene. The dehydrogenation of methylcyclohexane to

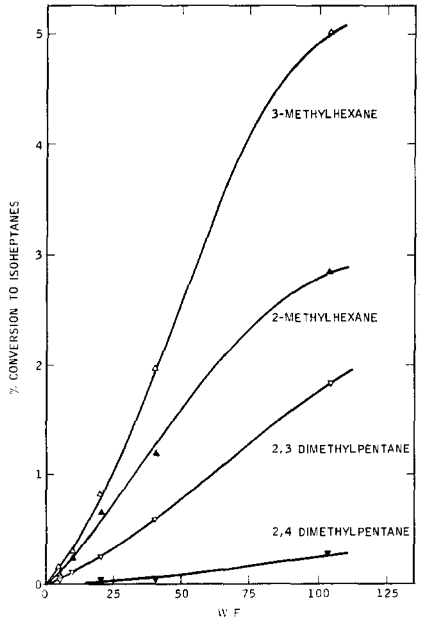


Fig. 2. Isomerization of *n*-heptane to methylhexanes and dimethylpentanes on platinum at 275°C. Other conditions are 1 atm and a H_2/n-C_7 mole ratio of 5/1. The quantity W/F is the weight (grams) of catalyst divided by the number of moles of *n*-heptane fed per hour.

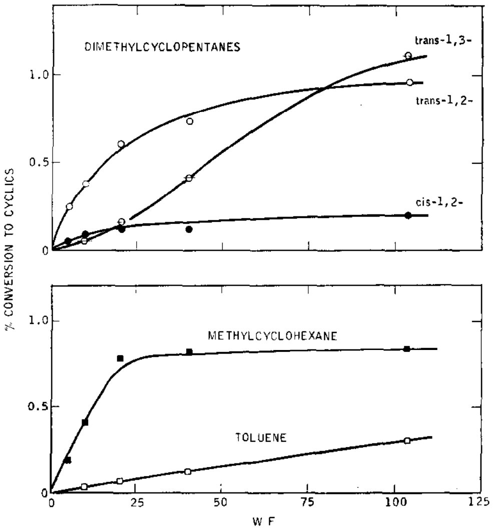


Fig. 3. Dehydrocyclization of *n*-heptane to dimethylcyclopentanes, methylcyclohexane, and toluene on platinum at 275°C. Other conditions are 1 atm and a H_2/n-C_7 mole ratio of 5/1. The quantity W/F is the weight (grams) of catalyst/the number of moles of *n*-heptane fed per hour.

TABLE 3
REACTIONS OF *trans*-1,2-DIMETHYLCYCLOPENTANE ON PLATINUM

% Conversion to:[a]	
cis-1,2-dimethylcyclopentane	19.4
trans-1,3-dimethylcyclopentane	0.4
2-methylhexane	<0.1
3-methylhexane	1.0
2,4-dimethylpentane	0.1
2,3-dimethylpentane	3.4
n-heptane	0.5
methylcyclohexane	0.2
C_6 and lower carbon number products	1.3

[a] Conditions: 275°C, 1 atm., mole ratio of hydrogen to *trans*-1,2-dimethylcyclopentane = 5/1, F/W = 0.025 moles of *trans*-1,2-dimethylcyclopentane fed per hour per gram of platinum.

toluene over platinum catalysts is a well-known reaction (*9*).

The results of auxiliary experiments on *trans*-1,2-dimethylcyclopentane on platinum are of interest in relation to the *n*-heptane results. Data on the conversions of *trans*-1,2-dimethylcyclopentane on platinum at 275°C are given in Table 3. The main product was *cis*-1,2-dimethylcyclopentane. The ratio of *cis*-1,2-dimethylcyclopentane to *trans*-1,2-dimethylcyclopentane in the reactor effluent was close to the expected equilibrium value (*8*). Another experiment at a much higher reactant flow rate (F/W = 0.20) than was used in obtaining the data in Table 3 gave the same ratio of *cis* to *trans* isomers, confirming that equilibrium was established between the *cis*-1,2- and *trans*-1,2-dimethylcyclopentanes. This cis-trans isomerization is clearly much faster than any of the other reactions which occur. Among the other reactions, some isomerization to *trans*-1,3-dimethylcyclopentane and methylcyclohexane occurred, but hydrogenolysis to C_7 paraffins and lower carbon number products was more extensive. The 2,3-dimethylpentane, 3-methylhexane, and *n*-heptane can be formed directly by rupture of a single carbon–carbon bond in the 1,2-dimethylcyclopentane structure, followed by hydrogenation. The predominance of the first of these hydrogenolysis products indicates that carbon–carbon bond rupture occurs preferentially at the bonds most remote from the point of substitution on the ring. This has been observed by other investigators (*10*). The formation of 2-methylhexane and 2,4-dimethylpentane is small compared to the other C_7 paraffins, which is attributable to the need for a molecular rearrangement in the formation of these products. Of particular interest is the fact that the ratio of 3-methylhexane to 2-methylhexane is much higher than is obtained from *n*-heptane. Furthermore, the rate of formation of the methylhexanes, especially the 2-methylhexane, is substantially lower than is observed from *n*-heptane. These data indicate that *n*-heptane isomerization does not require the formation of a dimethylcyclopentane type of surface intermediate, although part of the reaction seems to occur via this path. The initial increase in the slopes of the curves in Fig. 2 with increasing W/F possibly arises through an increasing contribution of dimethylcyclopentane intermediates as the *n*-heptane conversion increases. It is possible that dimethylcyclopentane intermediates may be relatively more important for the formation of the dimethylpentanes than for the methylhexanes.

DISCUSSION

The order of activities of Group VIII noble metals for *n*-heptane hydrogenolysis is the same as that reported for ethane hydrogenolysis in previous work from this laboratory (*2–4*). The hydrogenolysis activity decreases markedly across Group VIII in the direction of increasing atomic number; i.e., Ru > Rh ≫ Pd, and Ir ≫ Pt. This is shown in the lower field of Fig. 4, which is a plot of rates at a common temperature of 205°C as a function of the position of the metal in the periodic table. The rates at 205°C were determined by extrapolation of the Arrhenius plots in Fig. 1. The temperature of 205°C was chosen as an intermediate temperature in the range of temperatures studied to decrease any uncertainties due to extrapolation. In the upper field of Fig. 4 the percentage *d*-character of the metallic bond (*11*) is plotted for each of the metals. The patterns of

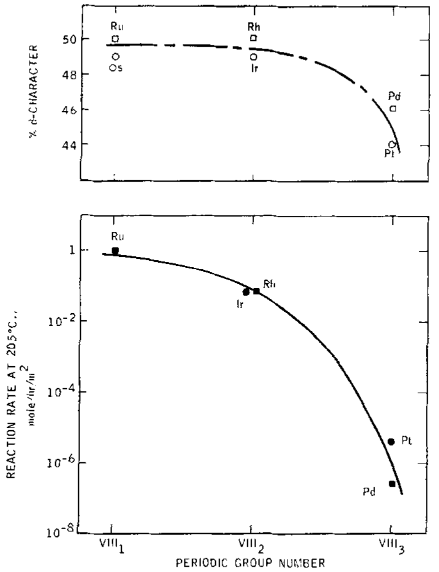
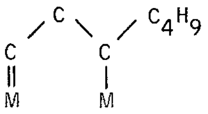


FIG. 4. Catalytic activities of metals for n-heptane hydrogenolysis and the relation to % d-character of the metallic bond. The activities are compared at a temperature of 205°C at 1 atm and a $H_2/n\text{-}C_7$ mole ratio of 5/1.

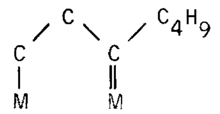
variation of percentage d-character and hydrogenolysis activity are clearly similar, as pointed out in previous studies on ethane hydrogenolysis on supported metals (*2–4*). It is significant that the same conclusions regarding hydrogenolysis activity patterns have emerged from studies with two different hydrocarbons on two different forms of metal catalysts.

The rates of hydrogenolysis of n-heptane on the unsupported metals in this work are higher than the previously reported rates of ethane hydrogenolysis on silica-supported metals (*2–4*) by about two orders of magnitude or more. This comparison is intended only to give a rough indication of the effect of molecular size on the rate of hydrogenolysis of n-paraffins, since metal dispersion and carrier effects could influence such a comparison. The higher rates of hydrogenolysis of n-heptane are attributable, at least in part, to the lower dissociation energies of carbon–carbon bonds in n-heptane relative to ethane.

The differences in the distribution of the primary products of n-heptane hydrogenolysis over the various metals are striking, ranging from a very selective rupture of the terminal carbon–carbon bond on palladium and rhodium to a nonselective rupture of all carbon–carbon bonds in the case of platinum and iridium. Ruthenium appears to offer an intermediate type of behavior. In considering possible ways to rationalize these results, we speculate that the ability of certain metals to undergo shifts in the valency of surface atoms may be important. This suggestion is prompted by the previous suggestion of Boudart and Ptak (*12*) that the ability of platinum and iridium to catalyze the isomerization of neopentane to isopentane may be related to the phenomenon of a variable surface valency originally proposed by Plummer and Rhodin (*13*). In considering how this idea may have a bearing on the "cracking patterns" observed over the various metals, we make use of the ideas of Anderson and Avery (*14*) regarding the nature of the chemisorbed species involved in the isomerization and hydrogenolysis of simple aliphatic hydrocarbons. These workers proposed a 1,3-diadsorbed intermediate with one of the carbon atoms forming a double bond with a metal surface atom. In the case of n-heptane we might envision the species shown below, where the letter M refers to a surface metal atom:

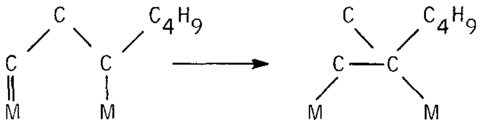


and

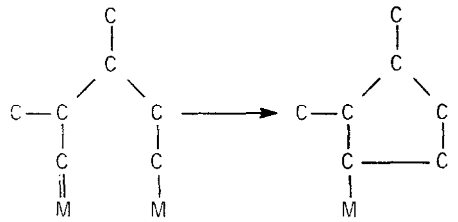


We assume that the C–C bond adjacent to the carbon–metal double bond cracks preferentially, and that in the case of metals such as palladium and rhodium the carbon–metal double bond is located primarily at the terminal carbon atom. Hence the cracking occurs selectively at the end of the molecule. With metals such as platinum and iridium, which can exhibit variable surface valencies, we suggest that the position of the double bond could shift readily from the terminal carbon atom to other carbon atoms along the hydrocarbon chain to give a species such as the second one shown above. Hence, rupture of carbon–carbon bonds in the central part of the molecule could then occur readily, leading to a nonselective "cracking pattern."

With regard to isomerization reactions of *n*-heptane, platinum clearly distinguishes itself from the other metals in its ability to catalyze these reactions to a degree at least roughly comparable to hydrogenolysis. Again it is tempting to relate this unique behavior to the capability of the metal to exhibit variable surface valencies. The difference between platinum and iridium is then rationalized on the basis that the very high hydrogenolysis activity of iridium tends to obscure the intrinsic capability of iridium to catalyze isomerization. The isomerization reaction on platinum can be visualized as involving a transformation of the type:



The change from a carbon–metal double bond to a single bond is attributed to the ability of the metal atom to undergo a shift in valency, as emphasized by Boudart and Ptak (*12*) for neopentane isomerization. In the case of dehydrocyclization, we might consider that the reaction involves a transformation of the type:



Again it is suggested that variable surface valency would aid in the change from a carbon–metal double bond to a carbon–metal single bond in the transformation. The mechanism of dehydrocyclization shown has been proposed previously (*15*). It has been proposed also that cyclic intermediates are involved in isomerization of hexanes on platinum catalysts, at least in part (*16*). The present work on *n*-heptane indicates that cyclic intermediates are probably a contributing factor in isomerization, but it appears that a mechanism involving alkyl shifts is more important.

References

1. Sinfelt, J. H., Taylor, W. F., and Yates, D. J. C., *J. Phys. Chem.* **69,** 95 (1965).

2. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8,** 82 (1967).

3. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **10,** 362 (1968).

4. Sinfelt, J. H., *Catal. Rev.* **3**(2), 175 (1969).

5. Yates, D. J. C., Taylor, W. F., and Sinfelt, J. H., *J. Amer. Chem. Soc.* **86,** 2996 (1964).

6. Brown, H. C., and Brown, C. A., *J. Amer. Chem. Soc.* **84,** 2827 (1962).

7. Brunauer, S., Emmett, P. H., and Teller, E., *J. Amer. Chem. Soc.* **60,** 309 (1938).

8. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Inc., New York, 1953.

9. Sinfelt, J. H., Hurwitz, H., and Shulman, R. A., *J. Phys. Chem.* **64,** 1559 (1960).

10. Newham, J., *Chem. Rev.* **63,** 123 (1963).

11. Pauling, L., *Proc. Roy. Soc. Ser. A.* **196,** 343 (1949).

12. Boudart, M., and Ptak, L., *J. Catal.* **16,** 90 (1970).

13. Plummer, E. W., and Rhodin, T. N., *J. Phys. Chem.* **49,** 3479 (1968).

14. Anderson, J. R., and Avery, N. R., *J. Catal.* **7,** 315 (1967).

15. Muller, J. M., Ph.D. Thesis, University of Caen, 1969.

16. Barron, Y., Maire, G., Muller, J. M., and Gault, F. G., *J. Catal.* **5,** 428 (1966).