

Catalytic Hydrogenolysis of Ethane over the Noble Metals of Group VIII

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The kinetics of hydrogenolysis of ethane have been investigated over a series of noble metals of Group VIII of the Periodic Table. The metals used were ruthenium, rhodium, palladium, and iridium, all supported on silica at concentrations of 5-10 wt %. The surface areas of the metals were determined from measurements of the chemisorption of hydrogen and carbon monoxide. When the catalytic results are considered together with previously reported data on platinum, the order of catalytic activities is $Ru > Rh > Ir \gg Pd = Pt$. For all the metals studied the rate of hydrogenolysis was found to decrease strongly with increasing hydrogen pressure. It is concluded that extensive dissociation of carbon-hydrogen bonds in the ethane molecule occurs in the course of the initial chemisorption step. The pattern of catalytic activities of Group VIII noble metals is discussed in relation to that of the nonnoble metals of Group VIII, and points of contrast are emphasized.

I. INTRODUCTION

In a previous paper from this laboratory (1), results were presented of investigations of the catalytic hydrogenolysis of ethane over silica-supported metals, including nickel, cobalt, platinum, and copper. The experimental work included hydrogen chemisorption measurements to determine the surface areas of the metals. Limited data on carbon monoxide chemisorption were also obtained. One of the objectives of the work was to obtain information on the specific catalytic activities of the metals, i.e., the activity per unit of metal surface area. A large variation in catalytic activities was observed for the different metals, nickel being the most active. In addition, the kinetics disclosed marked differences in the apparent activation energies and in the dependence of rates on hydrogen partial pressure. The kinetics were interpreted in terms of a reaction scheme originally proposed by Cimino, Boudart, and Taylor (2). According to this scheme, the initial step in the reaction sequence is the dehydrogenation

of the ethane to an unsaturated surface residue. This step is followed by rupture of the carbon-carbon bond, with subsequent hydrogenation of the cracked fragments to produce methane. From an analysis of this type, it was concluded (1) that the composition of the surface species formed in the initial dehydrogenative chemisorption of ethane varied strikingly from one metal to another.

In view of the interesting results obtained with the previous series of metals, it was decided to extend the investigation to other Group VIII metals, including palladium, rhodium, ruthenium, and iridium. In this way it was hoped to establish some patterns of catalytic behavior of metals for hydrogenolysis reactions. As before, gas chemisorption techniques were employed to measure metal surface areas. In most cases, both hydrogen and carbon monoxide chemisorption isotherms were obtained. In line with the original objective, the investigation has resulted in a more comprehensive picture of catalytic hydrogenolysis over metals, both

from the point of view of the kinetic aspects and the classification of catalytic activities in relation to properties of the metals. With regard to catalyst activity patterns, in particular, the results tend to differentiate the noble metals of Group VIII as a class from the nonnoble metals.

II. EXPERIMENTAL

Apparatus and Procedure

The apparatus used for the chemisorption measurements was a conventional glass vacuum system with an 80 liters/sec oil diffusion pump. Using a trap cooled in liquid nitrogen, ultimate dynamic vacua of about 10^{-7} torr were obtained. The sample cells were made of Pyrex glass, and had two stopcocks to permit hydrogen to flow through the bed of material. The weight of sample used was approximately 1 g. Prior to measurement of an adsorption isotherm, the catalyst sample was reduced *in situ* in flowing hydrogen for 2 hr at 450°C. After evacuation at 450°C, the sample was cooled to room temperature for the adsorption measurement. Both hydrogen and carbon monoxide adsorption isotherms were obtained, except for palladium, where only carbon monoxide adsorption was measured. A period of 30 to 45 min was found to be sufficient to attain equilibrium in the determination of a point on an isotherm.

The ethane hydrogenolysis data were obtained in a flow reactor system at atmospheric pressure, using a vertically mounted stainless steel reactor tube 1.0 cm in diameter and 8.0 cm in length. Details of the reactor assembly, flow rate measurements, and the gas-chromatographic analysis of the reaction products have been reported previously (3). The ethane 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. By appropriate adjustment of the helium flow rate, it was possible to vary the partial pressures of ethane and hydrogen individually. The total gas flow was maintained at 1 liter/min throughout. In a typical run the reactant gases were passed over the catalyst for 3 min prior to sampling products for

analysis. The ethane was then cut out and the hydrogen flow continued for 10 min prior to another reaction period. As an insurance against possible complications due to changing catalyst activity, most of the reaction periods were bracketed by periods at a standard set of conditions, so that the kinetic data could be expressed as rates relative to the rate at the standard conditions. Detailed data illustrating the utility of this technique have been published previously (4). Prior to any reaction rate measurements, the catalysts were reduced in the reactor for 2 hr in flowing hydrogen at 450°C. This was done to duplicate the conditions used in the chemisorption experiments.

Materials

The supported metal catalysts used in this work contained 5% or 10% by weight of metal based on the combined weight of metal and support. The catalysts were prepared by individually impregnating silica with solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, PdCl_2 , and $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$. The solutions of the first three of these compounds were prepared by dissolving the salts in 38% hydrochloric acid solution. The rhodium trichloride was obtained from Fisher Scientific Company, Fair Lawn, New Jersey, while the ruthenium and palladium chlorides were obtained from Engelhard Industries, Inc., Newark, New Jersey. The chloroiridic acid was obtained from Alfa Inorganics, Inc., Beverly, Massachusetts. In the preparation of the catalysts, approximately 2 to 4 ml of impregnating solution of appropriate concentration were employed per gram of silica. One impregnation was used for the rhodium and iridium catalysts, while two impregnations were employed in the preparation of the palladium and ruthenium catalysts. The silica used as a support was Cabosil HS5 (300 m^2/g surface area), obtained from the Cabot Corp., Boston, Massachusetts. After impregnation, the catalysts were all dried overnight at 105°C. The dried catalysts were pressed at 8000 lb/sq inch into wafers which were subsequently crushed and screened to a size between 45 and 50 mesh.

The ethane used in this work was obtained from the Matheson Co. A chromatographic

analysis showed no detectable impurities. It is estimated that an impurity, e.g., methane, would have been detected by the chromatographic analysis if it were present at a concentration above 0.01 wt %. High-purity hydrogen was obtained from the Linde Co., Linden, New Jersey. It was further purified in a "Deoxo" unit containing palladium catalyst to remove trace amounts of oxygen. The water formed was then removed by a trap cooled in liquid nitrogen or by a molecular sieve dryer, the latter having been employed for the hydrogen used in the kinetic measurements.

III. RESULTS

The adsorption isotherms for hydrogen and carbon monoxide on the various metals at room temperature are shown in Figs. 1 and 2. An isotherm for hydrogen on the palladium catalyst was not determined because of the complication of solubility of hydrogen in palladium. Adsorption on the support is a negligible part of the total in all cases. The amount of gas adsorbed at 10 cm pressure was taken as the monolayer point. From the monolayer capacity a calculation can be made of the number of hydrogen atoms or carbon monoxide molecules adsorbed per atom of metal in the sample. The

results of such calculations are given in Table 1 under the headings, H/M and CO/M.

It is reasonable to expect that hydrogen is chemisorbed dissociatively on the metals investigated in this work, and that one hydrogen atom is adsorbed per metal surface atom at saturation. For carbon monoxide chemisorption, however, there is the complication that two different forms of adsorbed carbon monoxide exist, the linear structure and the bridged structure (5). In the case of the linear structure, each adsorbed carbon monoxide molecule is associated with one metal atom in the surface, whereas with the bridged structure each adsorbed molecule is bonded to two metal surface atoms.

Studies performed in this laboratory on the infrared spectra of adsorbed carbon monoxide (6) show that the linear structure predominates on the supported metal catalysts used in this study, except for palladium. In the latter case, there is a significant amount of the bridged structure present. Consistent with these observations, the quantities H/M and CO/M in Table 1 are essentially equal in the case of the rhodium and ruthenium catalysts. In the case of the iridium catalyst, the agreement between H/M and CO/M is less satisfactory, the

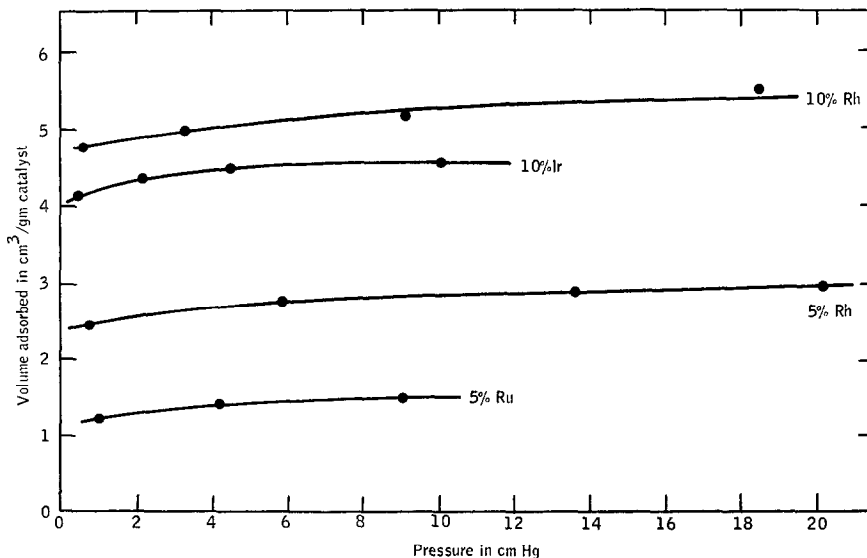


Fig. 1. Adsorption isotherms for hydrogen at room temperature on silica-supported noble metals of Group VIII.

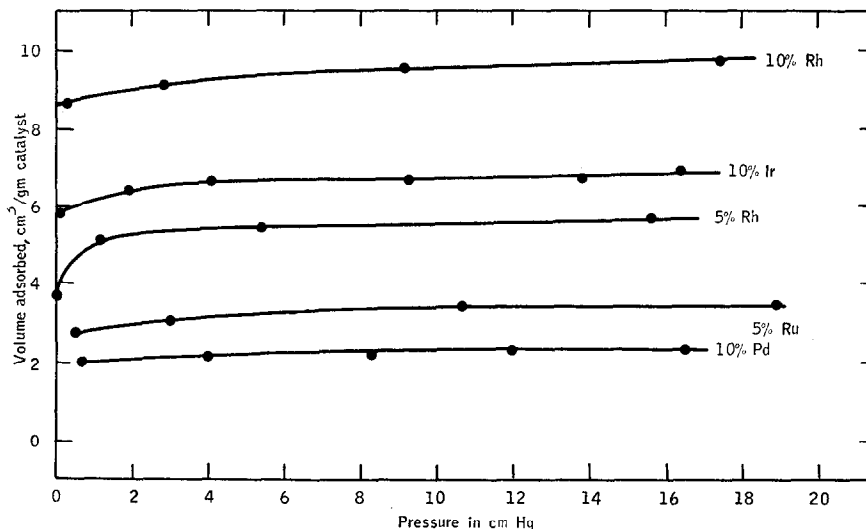


FIG. 2. Adsorption isotherms for carbon monoxide at room temperature on silica-supported noble metals of Group VIII.

values differing by a factor of about 1.3. At present we have no explanation why iridium should be different from rhodium and ruthenium in this regard.

The generally consistent nature of the results on adsorption of hydrogen and carbon monoxide is reassuring with regard to their

TABLE 1
SURFACE AREAS AND CRYSTALLITE SIZES
OF SILICA-SUPPORTED METALS

Catalyst ^a	H/M ^b	CO/M ^c	Surface area ^d (m ² /g metal)	Crystallite size, (Å)
10% Pd	—	0.11	47	106
10% Rh	0.48	0.44	214	23
5% Rh	0.53	0.52	237	20
5% Ru	0.27	0.31	121	42
10% Ir	0.78	0.58	186	14

^a All metals supported on Cabosil.

^b Atoms of hydrogen adsorbed (at 10 cm H₂ pressure) per metal atom.

^c Molecules of carbon monoxide adsorbed (at 10 cm pressure) per metal atom.

^d Calculated from the hydrogen adsorption data.

application in the determination of the surface areas of supported metals of the type considered here. Values of metal surface areas are given in Table 1. Where data on both hydrogen and carbon monoxide ad-

sorption were obtained, i.e., with rhodium, ruthenium, and iridium, the metal surface areas were calculated from the hydrogen adsorption data. The surface areas were calculated on the basis that each metal atom in the surface adsorbs one hydrogen atom or one carbon monoxide molecule. The area occupied by a metal atom in the surface was taken to be 7.6 Å². This represents an average value for the metals studied, and was obtained from a previously reported value of 6.5 Å² for nickel (?) by adjusting for the differences in atomic radii between the Group VIII noble metals and nickel. In the case of the palladium catalyst, where the surface area was obtained from carbon monoxide adsorption, the value may be low, in view of the evidence that part of the adsorbed carbon monoxide is the bridged configuration.

Crystallite sizes determined from the metal surface areas are also listed in Table 1. Assuming that the crystallites are cubes of length l , the crystallite size is calculated from the relation, $l = 6/Sd$, where d is the density of the metal and S is the surface area per gram of metal. In general, the crystallites are smaller than 50 Å, and the size cannot be determined by X-ray diffraction line-broadening. In the case of the palladium catalyst, however, the crystallites

are appreciably larger, and the X-ray method is applicable. Such a measurement gave a palladium crystallite size of 136 Å, which is in fair agreement with the value of 106 Å derived from the adsorption data.

The rate measurements on the hydrogenolysis of ethane to methane were made at low conversion levels (0.05% to 10%). Rates were calculated from the relation

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

where F represents the feed rate of ethane to the reactor in gram moles per hour, W represents the weight in grams of the metal in the catalyst, and x represents the fraction

of ethane converted to methane. The reaction rate r is thus expressed as gram moles of ethane converted to methane per hour per gram of metal.

In a run to measure reaction rates the catalyst was first prereduced with hydrogen using the identical conditions employed in the chemisorption measurements. This was done to ensure that the metal surface area of the freshly reduced catalysts would correspond exactly to that determined in the chemisorption measurements. Then the temperature was lowered and at a standard set of hydrogen and ethane partial pressures ($p_H = 0.20$ atm, $p_E = 0.030$ atm), the rates

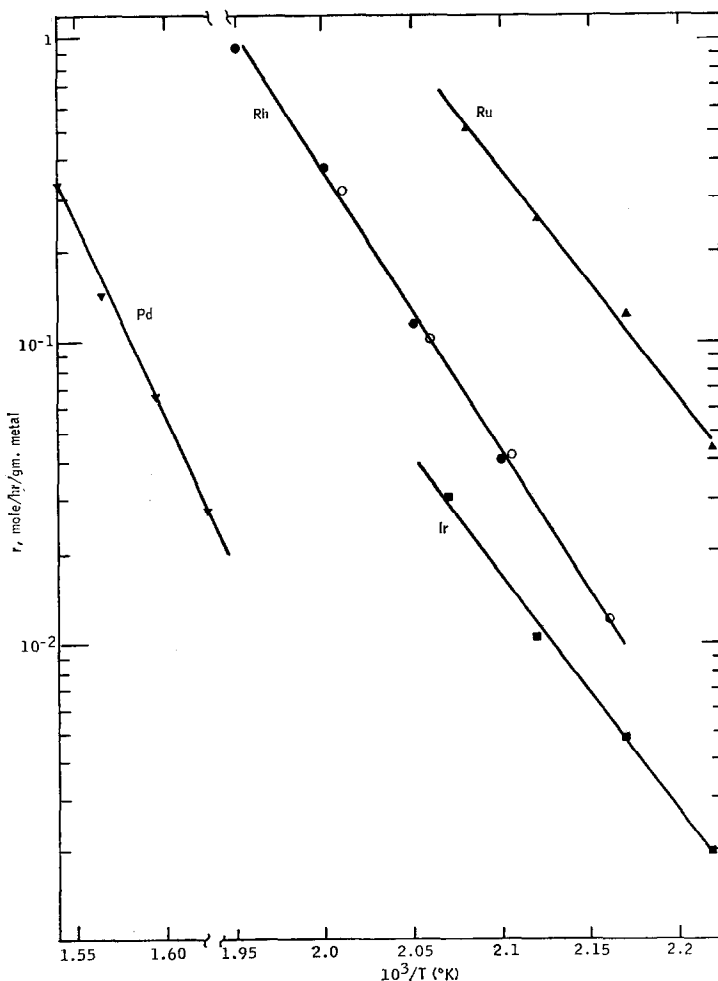


FIG. 3. Arrhenius plots for ethane hydrogenolysis over silica-supported Group VIII noble metals (at hydrogen and ethane pressures of 0.20 and 0.030 atm, respectively): ▼, 10% Pd; ○, 10% Rh; ●, 5% Rh; ▲, 5% Ru; ■, 10% Ir.

were measured at a series of temperatures in a rising temperature sequence. The data for all the catalysts are shown in the Arrhenius plots in Fig. 3. In the case of the rhodium catalyst, data are shown for two concentrations, 5 and 10 wt % rhodium. The rates per gram of rhodium fall along the same line for the two concentrations. With regard to the catalytic activities of the various metals, it is clear that ruthenium is the most active and that palladium is by far the least active over the range of temperature studied.

After the determination of the effect of temperature on rates, an intermediate temperature was selected in the range studied, and a series of measurements was made to determine the effects of the partial pressures of hydrogen p_H and ethane p_E on rates. As preliminary experiments had indicated that some variation of catalyst activity could occur in an extended set of rate measurements of this type, each reaction period was bracketed by periods at a standard set of conditions (3, 4). The rate r at any given set of conditions, relative to the rate r_0 at the standard conditions ($p_H = 0.20$ atm, $p_E = 0.030$ atm), is then given by the ratio r/r_0 . This procedure serves to minimize the effects of variations in catalyst activity. Data on the effects of hydrogen and ethane partial pressures on r/r_0 are given in Table 2.

For all catalysts the data in Table 2 show that the rate of ethane hydrogenolysis increases with increasing ethane partial pressure, but decreases with increasing hydrogen partial pressure. The dependence of the rate on the partial pressures of ethane and hydrogen can be expressed in the form of a simple power law, $r = kp_E^n p_H^m$. Approximate values of the exponents n and m as derived from the experimental data are summarized in Table 3. Values of the apparent activation energy E and the preexponential factor r' in the equation, $r = r' \exp(-E/RT)$, expressing the temperature dependence of the rate r at the standard conditions ($p_H = 0.20$ atm, $p_E = 0.030$ atm), are also given in Table 3. The preexponential factors were calculated per cm^2 of the supported metal, using the measured values of the metal surface areas given in Table 1. Kinetic parameters previously reported for

TABLE 2
EFFECT OF C_2H_6 AND H_2 PRESSURES ON RATES
OF C_2H_6 HYDROGENOLYSIS

Catalyst	p_H (atm)	p_E (atm)	r/r_0^a
Ru (188°C)	0.10	0.030	1.86
	0.20	0.030	1.00
	0.40	0.030	0.31
	0.20	0.010	0.37
	0.20	0.030	1.00
	0.20	0.100	2.15
Rh (214°C)	0.10	0.030	3.88
	0.20	0.030	1.00
	0.40	0.030	0.18
	0.20	0.010	0.35
	0.20	0.030	1.00
	0.20	0.100	2.20
Pd (354°C)	0.10	0.030	3.65
	0.20	0.030	1.00
	0.40	0.030	0.11
	0.20	0.010	0.25
	0.20	0.030	1.00
	0.20	0.100	2.06
Ir (210°C)	0.10	0.030	2.70
	0.20	0.030	1.00
	0.40	0.030	0.30
	0.20	0.010	0.44
	0.20	0.030	1.00
	0.20	0.100	2.05

^a Rate relative to the rate at standard conditions ($p_H = 0.20$ atm, $p_E = 0.030$ atm) for the particular catalyst and temperature in question.

platinum (1) are included in Table 3 for comparison.

Also included in Table 3 are specific catalytic activities of the various supported metals. The specific activity is defined as the reaction rate per unit surface area of metal at a given temperature. The purpose of determining specific activity is to allow for differences in catalytic activity arising solely from differences in surface area, and hence to put the comparison of activities on a fundamental basis. The specific activities listed in Table 3 refer to a temperature of 205°C. In the case of the palladium catalyst the value shown is an extrapolated value, since the activity of the palladium was too low to obtain data in the temperature range employed for the other catalysts. The extrapolation was made using the apparent activation energy listed for palladium in

TABLE 3
KINETIC PARAMETERS FOR ETHANE HYDROGENOLYSIS OVER GROUP VIII NOBLE METALS

	Catalyst				
	Ru	Rh	Pd	Ir	Pt ^a
Reaction orders					
C ₂ H ₆ (experimental), <i>n</i>	0.8	0.8	0.9	0.7	0.9
H ₂ (experimental), <i>m</i>	-1.3	-2.2	-2.5	-1.6	-2.5
H ₂ (calculated), ^b (1- <i>na</i>)	-1.4	-1.4	-1.7	-1.1	-1.7
Apparent activation energy, <i>E</i> (kcal/mole)	32	42	58	36	54
Pre-exponential factor, <i>r'</i> (molecules/sec cm ²) ^c	1.3 × 10 ²³	5.8 × 10 ³¹	3.7 × 10 ³³	5.2 × 10 ²⁸	5.9 × 10 ³¹
Specific catalytic activity (mole/hr m ² at 205°C) ^d	3.2 × 10 ⁻³	2.3 × 10 ⁻⁴	7 × 10 ⁻¹⁰	1.1 × 10 ⁻⁴	7 × 10 ⁻¹⁰

^a Detailed data are reported in ref. (1).

^b Calculated using a value of *a* equal to 3.

^c Defined by the equation, $r = r' \exp(-E/RT)$, expressing the temperature dependence of the rate *r* at standard conditions ($p_H = 0.20$ atm, $p_E = 0.030$ atm).

^d At $p_H = 0.20$ atm, $p_E = 0.030$ atm.

Table 3. A value for platinum extrapolated from previously published data (1) is also given. The order of catalytic activities is Ru > Rh > Ir ≫ Pd = Pt. Strictly speaking, the comparison of specific activities depends on the temperature, since the apparent activation energies are different for the various catalysts. However, the order of activities would be maintained over a reasonably wide range of conditions.

The general features of the kinetics of ethane hydrogenolysis over the catalysts employed in this study are conveniently discussed in terms of a reaction scheme originally proposed by Cimino, Boudart, and Taylor (2) to account for data on nickel and iron catalysts. These workers showed that the kinetics could be explained satisfactorily in terms of a mechanism involving a preliminary dehydrogenation of the ethane to an unsaturated radical C₂H_{*x*} on the surface, followed by attack of the surface radical by hydrogen,



where *a* is equal to (6 - *x*)/2. On the assumption that the first step was an equilibrated one, and that the rate was limited by the rate of rupture of carbon-carbon bonds by reaction of the surface species C₂H_{*x*} with H₂,

a rate law was derived which could be put in the form

$$r = kp_E^n p_H^{(1-na)} \quad (2)$$

From the experimental value of the exponent on ethane partial pressure *n*, the exponent (1 - *na*) on hydrogen pressure can be calculated for a given value of *a* and compared with the experimental value *m*. A simple and reasonable assumption is that *a* can have values of 1, 2, or 3, corresponding to ethylene, acetylene, or acetylenic residues on the surface (2). A comparison of observed and calculated values of the exponent on hydrogen pressure, for a value of *a* equal to 3, is given in Table 3. The agreement between observed and calculated values is fair. The value of *a* was chosen to give the best fit to the data. For all the catalysts except ruthenium, the calculated value indicates a smaller inverse effect of hydrogen than was actually observed. It may be that the additional effect is due to significant coverage of the surface by adsorbed hydrogen, not accounted for in the simplified kinetic analysis. In any case, the simple analysis is very useful in the interpretation of the results, and is consistent with much available information on the interaction of hydrocarbons with metal surfaces, as derived from chemisorption studies (8) or from companion studies of hydrogenolysis and exchange of

hydrocarbons with deuterium (9). The high degree of dissociation of carbon-hydrogen bonds in the chemisorption of ethane is particularly interesting. For the metals investigated in this study, it is concluded that the initial dehydrogenation step proceeds all the way to a completely hydrogen-deficient dicarbon surface residue. A similar conclusion was reached in previously reported studies on nickel catalysts (1, 2, 4).

IV. DISCUSSION

The results of this work present a clear pattern of the catalytic behavior of the Group VIII noble metals for the hydrogenolysis of ethane. If we consider the triad of ruthenium, rhodium, and palladium in the second long period of the Periodic Table, we note that the catalytic activity decreases as we proceed from left to right, i.e., Ru > Rh >> Pd. Furthermore, the decrease in catalytic activity is accompanied by an increase in the apparent activation energy. Exactly analogous behavior is observed with iridium and platinum from the triad of osmium, iridium, platinum in the fourth long period of the Periodic Table; i.e., iridium is more active than platinum, and the apparent activation energy is lower for iridium. The most striking observation is the extremely low activities of palladium and platinum compared with the activities of the other noble metals of Group VIII, the differences amounting to a factor of 10^5 to 10^6 .

In discussing the order of hydrogenolysis activities of the metals, it is of interest to consider the activities in relation to other properties of the metals. In Table 4 are listed the specific activities, percentage d character of the metal bond, and the atomic radii of the Group VIII metals. In addition to catalytic data on the metals investigated in the present study, Table 4 also includes previously reported data (1) on platinum, cobalt, and nickel. The use of percentage d character as a correlating variable was originally proposed by Boudart (10) and subsequently adopted by Beeck (11) in classifying the activities of metal films for the hydrogenation of ethylene. This type of correlation served to focus attention on the role of an electronic factor in catalysis, in

place of a purely geometric factor. However, there is the complication that geometric properties (such as atomic radii) are closely related to electronic structure, and hence it is not a simple matter to separate the effects of electronic and geometric factors.

TABLE 4
HYDROGENOLYSIS ACTIVITIES OF GROUP VIII
METALS IN RELATION TO OTHER
METALLIC PROPERTIES

Metal	Specific activity ^a	% d character ^b	Atomic radius, Å ^c
First triad			
Fe	—	39.7	1.24
Co	4×10^{-5d}	39.5	1.25
Ni	7.9×10^{-4d}	40	1.24
Second triad			
Ru	3.2×10^{-3}	50	1.32
Rh	2.3×10^{-4}	50	1.34
Pd	7×10^{-10}	46	1.37
Third triad			
Os	—	49	1.34
Ir	1.1×10^{-4}	49	1.35
Pt	7×10^{-10d}	44	1.38

^a Moles ethane converted per hour per sq. meter at 205°C; other conditions: $p_H = 0.20$ atm, $p_E = 0.030$ atm.

^b L. Pauling, *Proc. Roy. Soc. London* **A196**, 343 (1949).

^c W. Hume-Rothery and G. V. Raynor, "The Structure of Metals and Alloys," 4th ed., p. 95. The Institute of Metals, London, 1962.

^d From ref. (1).

In considering metals within a given triad in Group VIII, it is noted that the hydrogenolysis activity increases with increasing percentage d character. Furthermore, a satisfactory relation is observed when the metals of the second and third triads are considered together, as shown by Fig. 4. However, the data for the metals in the first triad do not fall on the same curve, indicating that percentage d character by itself is not sufficient to correlate all the data. In considering possible ways of differentiating the metals in the first triad from the others, it is noted that the atomic radii are significantly different from those in the second and third triads. It appears, therefore, that the relation

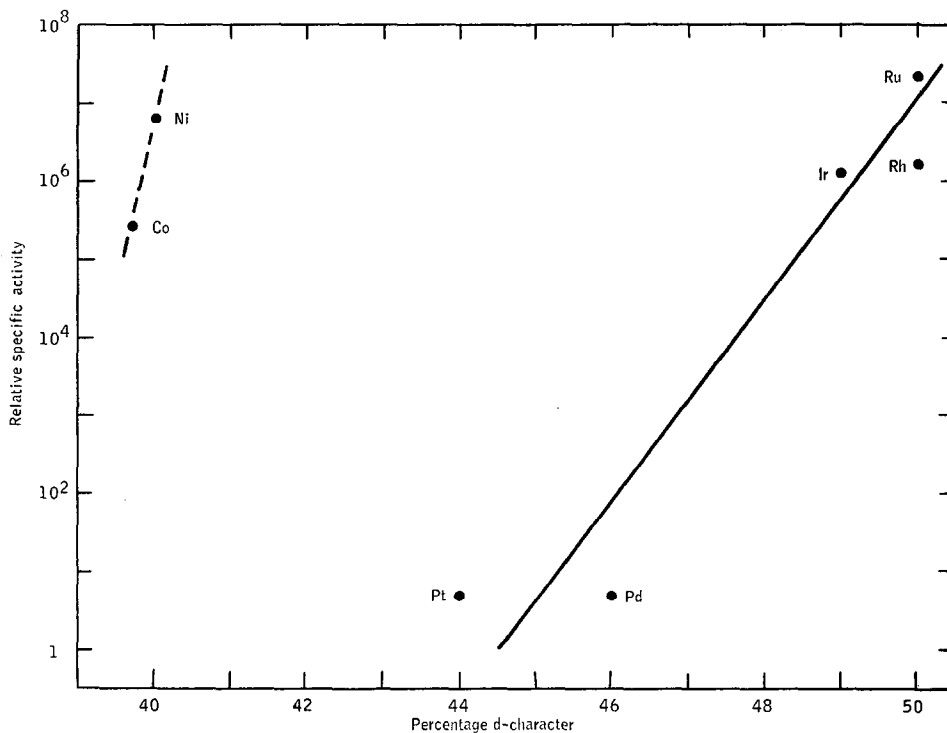


Fig. 4. Specific activity (at 205°C) of Group VIII metals for ethane hydrogenolysis as a function of % d character of the metal.

between percentage d character and catalytic activity holds satisfactorily for metals with approximately the same atomic spacing. This suggests that both electronic and geometric factors may play a role in determining the catalytic activities of metals for ethane hydrogenolysis, since the inclusion of a second parameter representative of a geometric factor (i.e., the atomic radius) gives a basis for separating the Group VIII metals into two groups when considering the effect of percentage d character on catalytic properties. It is not claimed that the foregoing considerations prove the existence of a critical geometric factor. Nevertheless, it is reasonable to expect that geometric considerations should play at least a secondary role in catalysis and should not be dismissed entirely when correlations of catalytic activity with electronic properties are attempted.

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