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Studies of Ethane Hydrogenolysis over Group VIII Metals: Supported Osmium and Iron

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The hydrogenolysis of ethane has been investigated over silica-supported osmium and iron. The surface areas of the metals were determined by hydrogen and carbon monoxide chemisorption. The osmium was much more active than the iron, and there was a marked difference in the dependence of reaction rates on hydrogen pressure. For osmium the rate was a strong inverse function of hydrogen pressure, while for iron the rate increased with increasing hydrogen pressure. When considered together with earlier data on the other Group VIII metals, the results strengthen the conclusion that the noble and nonnoble metals show different patterns of catalytic behavior.

INTRODUCTION

In an earlier paper we compared the specific activities of most of the Group VIII metals for ethane hydrogenolysis (*1*). The metals were all supported on silica. From their patterns of catalytic behavior, it appeared that the metals could be separated into two groups, the noble metals and the nonnoble metals. For the five noble metals for which data were then available (Pd, Rh, Ru, Pt, Ir), the activity within a given period increased substantially in proceeding from right to left across the Periodic Table, e.g., from Pd to Rh to Ru, or from Pt to Ir. Correspondingly, the apparent activation energy of the reaction decreased. In the case of two of the nonnoble metals of Group VIII (Ni and Co), the pattern of catalytic activities was considerably different. In the first place, the difference in activity between Ni and Co was much smaller than that between Pd and Rh and between Pt and Ir. Second, the direction of variation with position in the Periodic Table was different, as cobalt was less active than nickel. When the catalytic activity was related to the percentage of *d* character of the metal bond, it was found that the noble metals gave a satisfactory correlation, the activity increasing with increasing *d* character. However, the data on cobalt and nickel did not fit the same correlation line. In view of these interesting catalytic activity patterns, we decided to investigate the two remaining metals of Group VIII for which specific activities for ethane hydrogenolysis were not available, i.e., osmium and iron.

EXPERIMENTAL

Apparatus and Procedure. The apparatus for both the catalytic reaction studies and the gas chemisorption measurements has been described in detail elsewhere (*2–4*). The catalytic studies were made in a flow reactor system at low conversion levels (0.05% to 4%), and adsorption measurements were made with a conventional high-vacuum apparatus.

Materials. The supported catalysts used in this work contained 10% by weight of metal, and were prepared by impregnating silica with solutions of either chloroosmic acid or ferrous nitrate. Chloroosmic acid was obtained from Alfa Inorganics, Inc., Beverly, Massachusetts, and ferrous nitrate from Baker Chemical Co., Phillipsburg, New Jersey. The silica used was

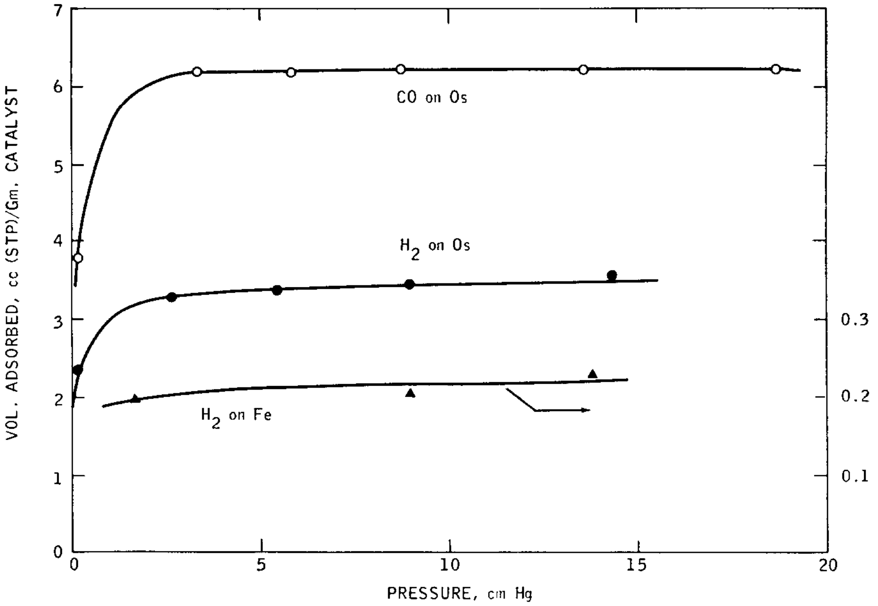

FIG. 1. Adsorption isotherms at room temperature on silica-supported osmium and iron.

Cabosil HS5 (300 m^2/g surface area), obtained from the Cabot Corp., Boston, Massachusetts. After impregnation, the catalysts were dried overnight at 105°C. They were then pressed at 8000 lb/sq inch into wafers which were subsequently crushed and screened to a size between 45 and 50 mesh. Reproducibility is good for osmium catalyst preparations (adsorption measurements agree within 10%), but is poorer for iron (within 20%).

The ethane and hydrogen used in this work were obtained from the Matheson Co. and the Linde Co., respectively. Details of the purification methods used have been given elsewhere (*1*, *4*).

RESULTS

Adsorption isotherms at room temperature for hydrogen on both the osmium and iron catalysts, and for carbon monoxide on the osmium catalyst, are shown in Fig. 1. Adsorption on the support was negligible for both catalysts. Prior to the adsorption measurements, the catalysts were reduced in flowing hydrogen for 2 hr, the osmium catalyst at 450°C and the iron catalyst at 550°C. After this, the catalysts were evacuated to approximately 10^{-7} torr before cooling to room temperature for the adsorption measurements. It is well known that chlorides of the noble metals, commonly employed in acidic solution for catalyst preparation (*5*), are not difficult to reduce (*6*). After reduction in hydrogen at 450°C, the supported osmium should therefore be present entirely in the metallic state. However, it is most probable that the iron catalyst does not show the same behavior, as iron catalysts are notoriously difficult to reduce (*7*, *8*). Despite this problem, it still appears feasible to estimate the amount of reduced iron in the surface by hydrogen chemisorption. This is supported by supplementary adsorption experiments we have performed on unsupported iron samples which were pretreated in flowing hydrogen at varying temperatures and times to alter the degree of reduction of the surface. Both argon adsorption at 77°K and hydrogen chemisorption at room temperature were measured after each reduction period. As the reduction conditions were made more severe (higher temperatures and/or longer times), an increase was found in the ratio of the volume of hydrogen adsorbed (at 10 cm pressure) to the volume of argon adsorbed at the monolayer point. For example, after reduction at 450°C for several hours in flowing hydrogen, the ratio was typically 0.3. On reducing at higher temperatures (550° to 600°C), still higher values of this ratio were obtained, up to 0.6. The physical adsorption of argon at 77°K gives a measure of the total surface, while hydrogen adsorption at room temperature is more specific and is a measure of the metal surface area.

The amount of gas adsorbed at 10 cm pressure was taken as the monolayer point for the chemisorption isotherms. A calculation can then be made of the number of hydrogen atoms or carbon monoxide molecules adsorbed per atom of metal in the sample, and these values are given in Table 1 under the headings, H/M and CO/M. In determining metal surface areas, it is assumed that hydrogen is chemisorbed dissociatively on the metal, and that one hydrogen atom is adsorbed per surface metal atom at saturation. With carbon monoxide chemisorption, however, there is the possibility of two different forms of adsorbed species, a linear structure bonded to one metal atom and a bridged structure bonded to two metal atoms (ref. *8*, p. 13). The H/M and CO/M values for osmium in Table 1 indicate that the linear form predominates. This conclusion is also supported by some unpublished infrared studies on osmium by one of us (D.J.C.Y.).

TABLE 1
SUMMARY OF ADSORPTION DATA AND KINETIC PARAMETERS FOR ETHANE HYDROGENOLYSIS ON IRON AND OSMIUM CATALYSTS

	Catalyst[a]	
	Fe	Os
Adsorption data		
H/M[b]	0.011	0.59
CO/M[c]	—	0.53
Metal surface area[d] (m²/g catalyst)	0.8	14.1
Ethane hydrogenolysis parameters		
Apparent activation energy (kcal/mole)	—	35
Reaction order, ethane	0.6[e]	0.6[f]
Reaction order, hydrogen	+0.5[e]	−1.2[f]
Specific activity[g] (mmoles/hr per sq. meter of metal at 205°C)	0.012	42

[a] Metals supported on Cabosil at 10 wt % concentration.

[b] Atoms of hydrogen adsorbed (at 10 cm H_2 pressure) per metal atom.

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

[d] Calculated from the hydrogen adsorption data.

[e] Determined at 270°C.

[f] Determined at 152°C.

[g] At ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively.

Metal surface areas calculated from hydrogen adsorption isotherms are given in Table 1. Values of 7.6 Å² and 6.5 Å² were taken as the areas occupied by osmium and iron atoms, respectively, in the metal surface. The value for osmium was taken to be the same as that previously used for the other platinum metals in Group VIII, while the value for iron was assumed to be the same as that of nickel (*1*, *3*).

In the ethane hydrogenolysis studies, reaction rates for the conversion of ethane to methane were determined at low conversion levels (0.05% to 4%) over a range of temperatures and partial pressures of ethane and hydrogen. Arrhenius plots for the catalysts are shown in Fig. 2. With the iron catalyst, the Arrhenius plot is not linear, but decreases in slope at higher temperatures. The behavior is not attributed to pore diffusion effects, as we find effectiveness factors (*9*) close to unity throughout. For the osmium catalyst the apparent activation energy is 35 kcal/mole. Because of the curved Arrhenius plot for the iron catalyst, no apparent activation energy is given in Table 1, but at the lowest temperatures a value of about 25 kcal/mole is estimated. From the reaction rates in Fig. 2 and the metal surface areas in Table 1, the specific catalytic activities of the osmium and iron can be calculated, and they are given in Table 1. The temperature of 205°C was chosen for reporting specific activities because it is intermediate between the temperature ranges employed for the two catalysts and so minimizes the extrapolation of the Arrhenius plots required for a comparison. Also, it permits a ready comparison with the other catalysts for which specific activities at 205°C have been reported previously (*1*). Evidently, osmium is much more active than iron for ethane hydrogenolysis.

Data on reaction orders with respect to ethane and hydrogen are listed in Table 1. The order in ethane was determined over a range of ethane pressures from 0.01 to 0.10 atm, at a constant hydrogen pressure of 0.20 atm. The order in hydrogen was determined for hydrogen pressures ranging from 0.10 to 0.40 atm, at a constant ethane pressure of 0.030 atm. The main difference between osmium and iron is in the hydrogen order, where for osmium it is —1.2 and for iron +0.5. The osmium data can be interpreted satisfactorily in terms of the reaction scheme of Cimino, Boudart, and Taylor (*10*), according to which the initial step in ethane hydrogenolysis involves dehydrogenative chemisorption of ethane to form a surface residue C_2H_x,

$$C_2H_6 \rightleftarrows C_2H_x + aH_2 \qquad (1)$$

where $a = (6 - x)/2$. Rupture of carbon–carbon bonds takes place subsequently by reaction of C_2H_x with hydrogen to form monocarbon fragments which are rapidly hydrogenated to methane. Assuming the rupture of carbon–carbon bonds to be rate-limiting, a kinetic analysis leads to the rate expression

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

where p_E and p_H are the partial pressures of ethane and hydrogen, respectively, and n is the reaction order with respect to ethane. For osmium, as with the other

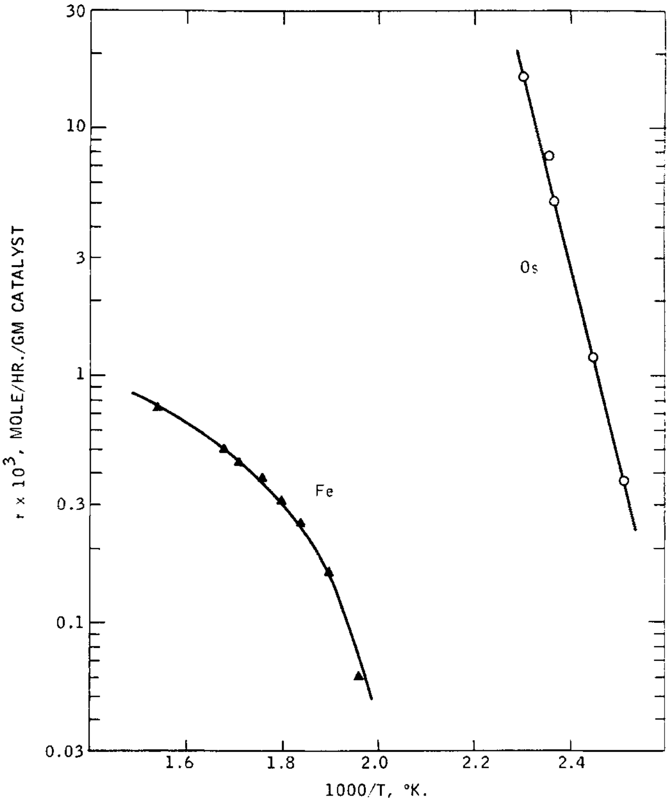

FIG. 2. Arrhenius plots for ethane hydrogenolysis over silica-supported osmium and iron. The data were obtained at ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

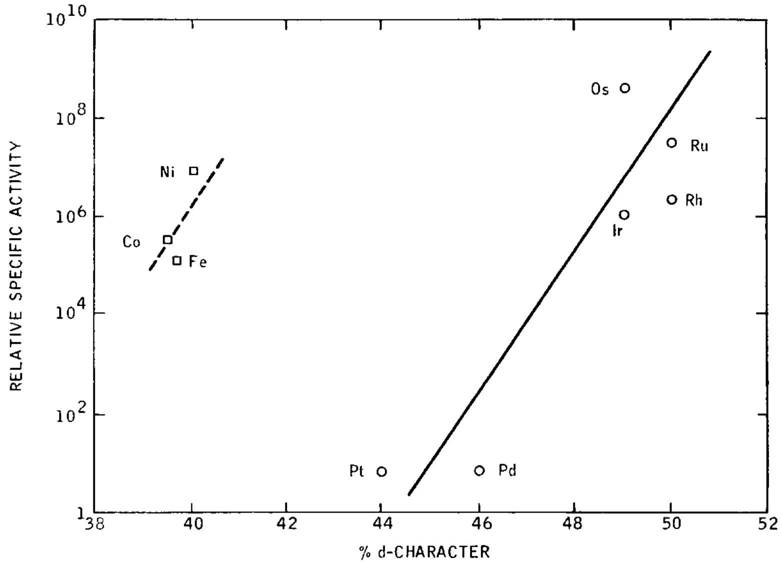

FIG. 3. Specific activity (at 205°C) of Group VIII metals for ethane hydrogenolysis as a function of % *d* character of the metal. The activities are for ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

Group VIII noble metals (*1*), the best agreement with experiment is obtained for the highest possible value of a, i.e., for $a = 3$. From the experimental value of n, we can calculate the exponent $(1 - na)$ on hydrogen pressure in Eq. (2) and compare it with the experimental value in Table 1. Taking $a = 3$ for osmium, and noting from Table 1 that the experimental order in ethane (n) is 0.6, the calculated order in hydrogen is -0.8, compared to an experimental value of -1.2. If we treat the data on the iron catalyst in the same way, the best value of a is found to be 1, giving a calculated hydrogen order of 0.4, compared with the experimental value of 0.5. However, there is some question whether the kinetic analysis leading to Eq. (2) is applicable to iron. One of the key reasons for the assumption that the carbon–carbon bond rupture is rate-limiting is the observation that the rate of exchange of ethane with deuterium is much higher than the rate of hydrogenolysis, as originally shown for nickel (*11*). This, of course, indicates that C—H bonds are more rapidly broken than C—C bonds. In the case of iron films, however, Anderson and Kemball (*12*) have shown that the exchange to form deuteroethanes does not take place even at temperatures at which hydrogenolysis occurs.

DISCUSSION

It is interesting to consider the activities of supported osmium and iron for ethane hydrogenolysis in relation to our previous results (*1*) on the other Group VIII metals. With regard to patterns of variation of catalytic properties from one metal to another, the new data on osmium and iron are consistent with the previously published work. In the case of the noble metals within a given period in Group VIII, the hydrogenolysis activity increases markedly as we proceed in the direction of decreasing atomic number across the various subgroups, i.e., from Pd to Rh to Ru, and from Pt to Ir to Os. In the period containing the nonnoble metals (Fe, Co, Ni), however, the order of catalytic activities is reversed, decreasing as we proceed from Ni to Co to Fe. Furthermore, the variation in activity of the nonnoble metals is much smaller than that of the noble metals. These points can be seen from Fig. 3, which summarizes the specific activities of the Group VIII metals for ethane hydrogenolysis. In addition, Fig. 3 shows how the activities relate to the % *d* character (*13*) of the metallic bond. The distinction between the noble and nonnoble metals is again evident. The activities of these two classes do not fit the same correlation line at all. Within each class, however, % *d* character is at least an approximate criterion of catalytic activity. For example, in the case of the noble metals, it is clear that platinum and palladium, with the lowest values of % *d* character, are much less active than the metals (Os, Ir, Ru, Rh) of highest % *d* character. Furthermore, for the nonnoble metals, where the range of variation in % *d* character is much smaller than for the noble metals, the variation in catalytic activity is also much smaller. In considering an explanation for the separation of the metals into two groups, it has previously been noted that the lattice spacings of the nonnoble metals of Group VIII are significantly smaller than those of the noble metals (*1*). This suggests the possibility of a secondary geometric factor influencing the catalytic activity, in addition to the electronic factor.

In a comparison of the activities of a series of metals, a question arises concerning the effect of the state of dispersion of a metal on its specific activity. From gas chemisorption data (*1, 3*) on the supported metal catalysts included in Fig. 3, excluding the iron catalyst, we estimate metal crystallite sizes ranging from 14 Å for iridium to 106 Å for palladium. From the hydrogen chemisorption data on the iron catalyst, it would appear that the crystallite size of the iron is much larger than for any of the other metals. However, the possibility that hydrogen does not chemisorb on a substantial part of the iron, due to incomplete reduction of the surface, makes inadvisable such an estimate of crystallite size. While crystallite size effects of the type we have reported previously (*4*) could conceivably affect the activity of a given metal by as much as one order of magnitude, or slightly more, the conclusions on the patterns of variation of catalytic activities should not be affected significantly. In the case of the noble metals, for example, the range of variation of catalytic activity is so large that crystallite size effects of the magnitude indicated are of minor importance by comparison. In the case of the nonnoble metals, where the range of activities is small compared to that observed for the noble metals, allowance for a substantially higher crystallite size for iron relative to nickel and cobalt would make the range even smaller, and would not have an important bearing on the conclusions.

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