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# The Catalytic Activity of Rhodium in Relation to Its State of Dispersion

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The catalytic activity of rhodium for ethane hydrogenolysis has been investigated as a function of the state of dispersion of rhodium. The specific surface area of rhodium was varied by more than two orders of magnitude by including both supported and unsupported rhodium catalysts in the study and by sintering a rhodium catalyst in a controlled manner. The surface area of the rhodium was determined by measurements of hydrogen and carbon monoxide chemisorption. The specific catalytic activities of unsupported rhodium or of severely calcined rhodium on silica were substantially lower than those of highly dispersed rhodium crystallites of 40 Å size or smaller. The results also suggest that the catalytic activity ultimately decreases as the dispersion is increased to an extremely high degree, indicating that highest activity is associated with an intermediate level of dispersion.

## INTRODUCTION

A basis question in the subject of heterogeneous catalysis is the relation between catalytic activity and the state of dispersion of the active component of a catalyst. To obtain significant information on this question, it is necessary to determine the specific activity, i.e., the activity per unit surface area of the active component. In the case of a supported metal catalyst, in particular, an important problem is the determination of the surface area of the metal itself. The most satisfactory approach to this problem appears to be the selective chemisorption of gases, in which one uses a gas which adsorbs on the metal but not on the support. This approach to the measurement of specific catalytic activities of supported metals has been applied by several groups of investigators (*1–10*).

In the case of supported metals, several investigations on the specific activity of platinum catalysts have been reported (*1–4, 9, 10*). Boreskov (*2, 3*) has concluded that the specific activity of platinum for the oxidation of sulfur dioxide or hydrogen is largely independent of the form or crystallite size of the metal. Throughout this paper we will use the term crystallite, although it is recognized that for highly dispersed metals the concept of crystalline structure poses problems because examination of such systems is not possible by X-ray diffraction. Recently, Dorling and Moss (*9*) in studies of benzene hydrogenation over platinum-silica catalysts concluded that the specific activity of the platinum was essentially constant when the crystallite size was varied by calcining the catalyst in air at different temperatures up to 400°C. For samples calcined at still higher temperatures, however, there was an indication of decreased specific activity. In another recent study, Boudart and co-workers (*10*) concluded that the specific activity of platinum for the hydrogenation of cyclopropane was effectively independent of the degree of dispersion of the platinum over a very broad range of dispersion, in agreement with the results of the previous workers on platinum catalysts (*2, 3*). In view of the surprising nature of these results, and because of the potentially great significance to heterogeneous catalysis, it is of interest to determine how general the findings are. For example, one may inquire whether the same behavior would be found for other metals, or perhaps for a different type of reaction. With regard to these points, recent data on nickel catalysts (*7*) indicate that nickel behaves differently from platinum. The possibility that the particular reaction might be important has also been discussed recently (*10*).

In view of the above points, we have investigated the catalytic activity of another metal, rhodium, as a function of its state of dispersion, using the hydrogenolysis of ethane as a test reaction. The dispersion of the rhodium was varied by changing the concentration of rhodium on a silica support, by sintering rhodium on silica, and by including unsupported rhodium among the catalysts investigated. The degree of dispersion of the rhodium was determined by measurements of hydrogen and carbon monoxide chemisorption. The results of the study indicate that wide variations in the state of dispersion do indeed lead to significant variations in the catalytic properties of rhodium for ethane hydrogenolysis. These results are considered in relation to the available information on platinum catalysts of varying platinum dispersion.

## EXPERIMENTAL

**Apparatus and procedure.** The apparatus used for the adsorption measurements was a conventional glass vacuum system described previously (*5*). The catalyst samples were reduced *in situ* in flowing hydrogen for 2 hr at 450°C or for 16 hr at 400°C. After evacuation to $10^{-6}$ torr at the reduction temperature, the samples were cooled to room temperature for measurement of adsorption isotherms. In the measurement of an adsorption isotherm, the procedure adopted was to admit a known quantity of gas to the adsorption cell and then wait for a period of about 1 hr before reading the equilibrium pressure. A special feature of the adsorption apparatus was the use of a high-precision, fused quartz Bourdon pressure gauge manufactured by the Texas Instrument Co., Houston, Texas (*11*). The high precision of this instrument was very useful for determining the small uptakes of gas encountered with the low concentration and bulk rhodium samples. The smallest measurable pressure change was 0.004 cm (deflection 0.005°) with the particular 100° capsule in use. The gauge calibration (supplied by the manufacturers at 6° intervals) was interpolated every 0.01° with an IBM 1620 computer.

The apparatus employed for the catalytic studies has also been described previously (*12*). Briefly, it consisted of a flow reactor system at atmospheric pressure. The reactor was a stainless steel tube 1.0 cm in diameter and 8.0 cm in length. The reactants, ethane and hydrogen, were mixed with helium in measured proportions using appropriate metering devices and then 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 reaction period, the gases were passed over the catalyst for 3 min prior to sampling products for chromatographic analysis. The ethane flow was then stopped and the hydrogen flow continued for 10 min prior to another reaction period. Most of the reaction periods were bracketed by periods at a standard set of conditions to check catalyst activity. Prior to any reaction rate measurements, the catalysts were reduced *in situ* in hydrogen using the same conditions employed in the chemisorption measurements.

**Materials.** The supported rhodium catalysts were prepared by impregnating silica with an aqueous solution of $RhCl_3 \cdot 3H_2O$. The rhodium trichloride was obtained from Fisher Scientific Co., Fair Lawn, New Jersey. In the preparation of the catalysts, approximately 2 ml of impregnating solution of appropriate concentration was employed per gram of silica. 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 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. Two samples of 5% rhodium catalysts, after the drying step, were calcined in air for 4 hr at temperatures of 538° and 800°C to prepare samples which, after reduction, have larger rhodium crystallites than the noncalcined samples. An unsupported rhodium catalyst was prepared by direct reduction of $RhCl_3 \cdot 3H_2O$ in flowing hydrogen, and rhodium granules between 45 and 50 mesh were separated out for the catalytic studies.

The ethane used in the catalytic studies was obtained from the Matheson Co. Any impurities in the ethane were below the level of detection of the chromatographic analysis, which would have been about 0.01% for an impurity such as methane. High-purity hydrogen was obtained from the Linde Co. 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. The argon used was obtained from the Matheson Co., and was research grade of purity 99.9995%.

## Results

Adsorption isotherms determined at room temperature for hydrogen and carbon monoxide on the various rhodium catalysts are shown in Figs. 1 to 3. The amount adsorbed per gram of catalyst is expressed in terms of a gas volume corrected to the normal

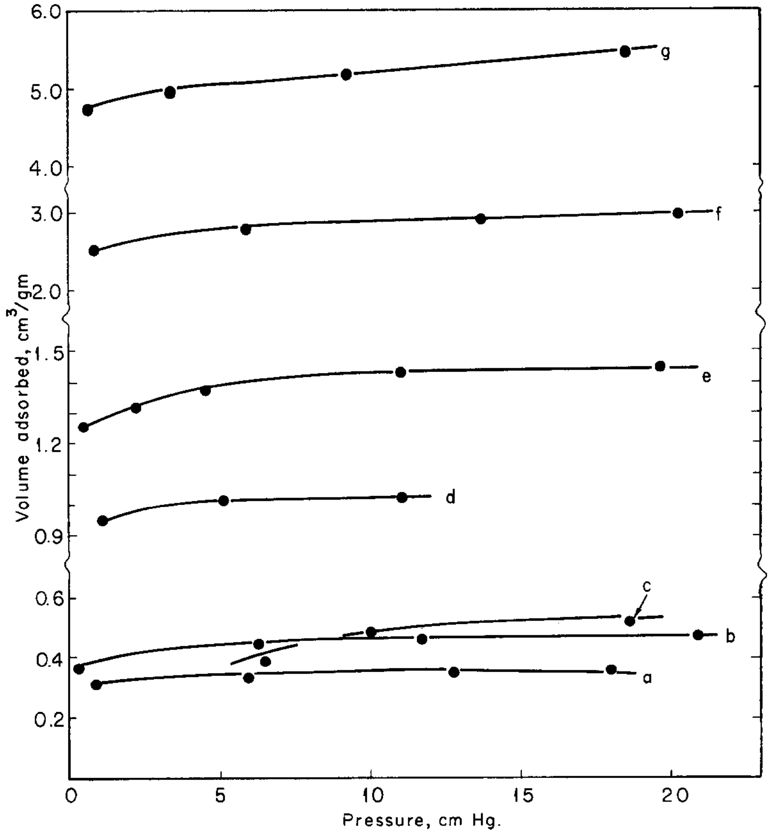

FIG. 1. Hydrogen adsorption isotherms at room temperature: a, 0.3% Rh; b, bulk Rh; c, 5% Rh (calcined at 800°C); d, 1% Rh; e, 5% Rh (calcined at 538°C); f, 5% Rh; g, 10% Rh (a, and c to g, supported on silica).

standard conditions of temperature and pressure, i.e., 0°C and 76 cm Hg. For the supported rhodium catalysts, adsorption on the support was in most cases negligible compared to the total adsorption. It represented a significant fraction of the total adsorption only in the case of carbon monoxide on the 0.1% rhodium catalyst. Isotherms for the 0.1% rhodium catalyst are shown in Fig. 3, which also includes data for the adsorption of carbon monoxide on the support. The net adsorption on rhodium is obtained by subtracting the support contribution from the total. No hydrogen adsorption could be detected at room temperature on the silica support after the sample had been pretreated using a procedure identical with that employed for the metal-containing samples.

The data in Fig. 3 show that accurate results can be obtained in chemisorption measurements on very low metal content (0.1% Rh) samples. It is of interest to note that carbon monoxide can be used for this low metal concentration, despite the fact that some physically adsorbed CO is present (curve b in Fig. 3). It should be noted that the correction isotherm in the figure was obtained by evacuating the sample for 1 min at the end of isotherm a, thus removing the weakly held CO, and then redetermining the isotherm. A correction isotherm identical to curve b in Fig. 3 was obtained on the pure silica support when the latter was pretreated by the same procedure used for the 0.1% rhodium sample prior to admitting the carbon monoxide at room temperature. This comparison shows that, at least for silica-supported rhodium, there is no cooperative effect in which the presence of metal promotes adsorption on the support. Such a possibility has been discussed in regard to measurement of platinum surface areas by carbon monoxide adsorption (*9*).

The amount of gas adsorbed at 10 cm pressure was taken as the monolayer point.

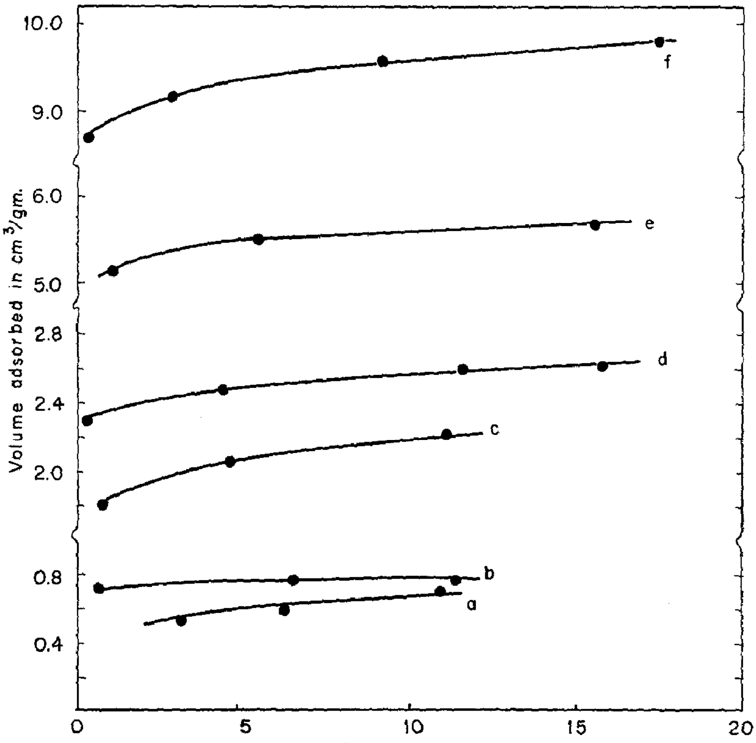

FIG. 2. Carbon monoxide adsorption isotherms at room temperature: a, 5% Rh (calcined at 800°C); b, bulk Rh; c, 1% Rh; d, 5% Rh (calcined at 538°C); e, 5% Rh; f, 10% Rh (a, and c to f, supported on silica).

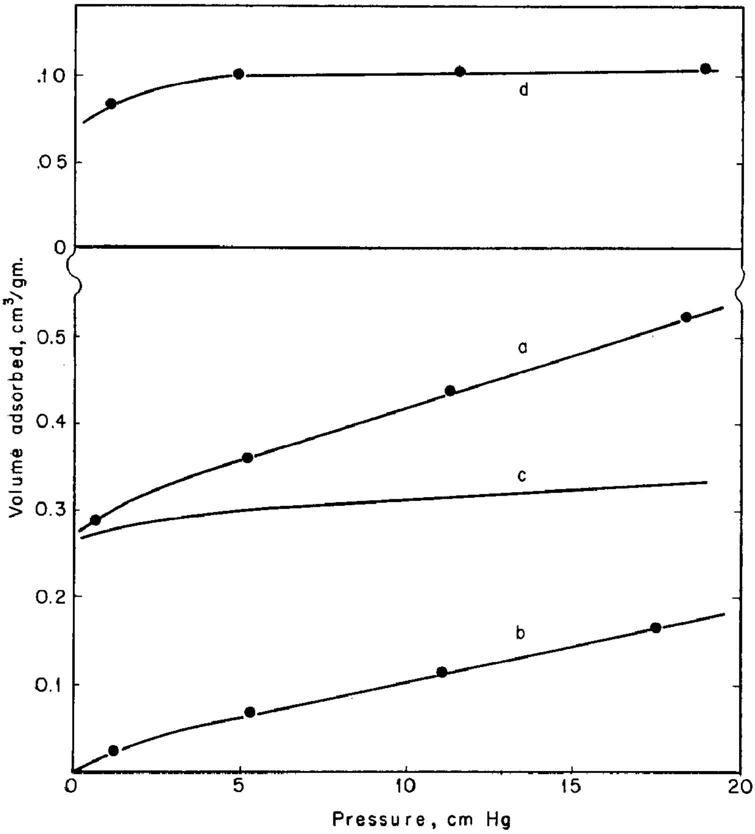

FIG. 3. Adsorption isotherms at room temperature on 0.1% Rh on silica: a, CO isotherm; b, CO isotherm after pumping out sample at end of isotherm a for 1 min; c, difference between a and b; d, hydrogen isotherm.

From the monolayer values a calculation can be made of the number of hydrogen atoms or carbon monoxide molecules adsorbed per atom of metal in the catalyst. In Table 1 the results of such calculations are listed under the headings, H/M and CO/M. In the calculation of rhodium surface areas, it is assumed that hydrogen is chemisorbed dissociatively on rhodium, and that one hydrogen atom is adsorbed per surface rhodium atom at saturation. In the case of carbon monoxide chemisorption, however, there is the complication that two different forms of adsorbed species exist, a linear structure and a bridged structure (*13*). In the case of the linear structure, each adsorbed carbon monoxide molecule is attached to one metal atom in the surface, whereas with the bridged structure each adsorbed molecule is considered to be attached to two surface atoms. For rhodium catalysts prepared by the procedures outlined in this paper, studies performed in this laboratory on the infrared spectra of adsorbed carbon monoxide indicate that the linear configuration predominates (*14*). The H/M and CO/M values in Table 1 are consistent with this.

It is of interest to note that, for most of the rhodium catalysts, the ratio of molecules of carbon monoxide adsorbed to atoms of hydrogen adsorbed is unity or lower (Table 1). Such data can be explained either by the CO being adsorbed entirely in the linear configuration, or in combination with the bridged species (*13*). However, ratios larger than unity are difficult to understand. With the 1.0% Rh sample, the number of molecules of adsorbed carbon monoxide is not much larger than the number of hydrogen atoms adsorbed, and the ratio may well be considered unity

TABLE 1
SURFACE AREAS AND SPECIFIC ACTIVITIES OF RHODIUM CATALYSTS

| Rh Conc. (wt %) | H/M[a] | CO/M[b] | Surface area[c] ($m^2$/g Rh) | Crystallite size (Å) | Specific[d] activity |
|---|---|---|---|---|---|
| 100 (unsupported) | 0.0042 | 0.0035 | 1.88 | 2560 | 0.79 |
| 10 | 0.48 | 0.44 | 213 | 23 | 13.5 |
| 5 | 0.53 | 0.52 | 237 | 20 | 12.2 |
| 5 (calcined at 538°C) | 0.26 | 0.24 | 118 | 41 | 8.1 |
| 5 (calcined at 800°C) | 0.086 | 0.066 | 38 | 127 | 0.41 |
| 1 | 0.94 | 1.01 | 416 | 12 | 16 |
| 0.3 | 0.98 | — | 438 | 11 | 4.3 |
| 0.1 | 0.95 | 1.40 | 421 | 11 | 4.4 |

[a] Atoms of hydrogen adsorbed per rhodium atom at 10 cm pressure.

[b] Molecules of carbon monoxide adsorbed per rhodium atom at 10 cm pressure.

[c] Calculated from hydrogen adsorption data.

[d] Millimoles ethane converted per hour per sq. meter of rhodium at 253°C; hydrogen and ethane pressures were 0.20 and 0.030 atm, respectively.

within the experimental error. With the 0.1% Rh sample, however, the number of carbon monoxide molecules adsorbed is considerably higher than the number of Rh atoms in the sample. It has previously been suggested that one of the infrared absorption bands of carbon monoxide on both supported (*15*) and unsupported (*16*) rhodium is due to sites where more than one carbon monoxide molecule is adsorbed on a given metal atom. Such a suggestion is consistent with our CO/H ratio being substantially larger than unity with the 0.1% Rh sample. However, in view of the very high Rh dispersion in this sample, and the low concentration, it is probable that it constitutes a rather special case. Certainly, for the higher concentration samples and for those with a lower degree of dispersion, there is no need to invoke such an assumption.

Rhodium surface areas calculated from the hydrogen adsorption data are listed in Table 1. A value of 7.6 $Å^2$ was taken for the area occupied by a metal atom in the surface. It was obtained from a previously reported value of 6.5 $Å^2$ for nickel (*17*) by adjusting for the differences in atomic radii between rhodium and nickel. Crystallite sizes determined from the rhodium surface areas are also included in Table 1. The values were calculated on the assumption of cubic crystallites of length $l$, using the relation, $l = 6/Sd$, where $d$ is the density of rhodium and $S$ is the surface area per gram of rhodium. The range of crystallite sizes is very broad, the values varying by several orders of magnitude. In the case of the 5% rhodium catalyst which was calcined at 800°C, the crystallites were sufficiently large so that an independent determination of crystallite size by X-ray diffraction line-broadening was possible. A value of 121 Å was obtained by this method, in excellent agreement with the value of 127 Å derived from the hydrogen adsorption measurement of rhodium surface area.

It is interesting to consider the surface area of rhodium as a function of its concentration in the catalyst. In Fig. 4 the variation of rhodium surface area with concentration is shown for those catalysts prepared and pretreated according to a common procedure. This series of catalysts includes all the samples of this study except the two which were calcined in air. The plot in Fig. 4 shows a good relationship between the logarithm of the surface area and the rhodium concentration over a 230-fold range of surface areas. The point at 100% rhodium concentration corresponds to the unsupported rhodium sample. The surface area of the rhodium increases smoothly with decreasing rhodium concentration, beginning with the unsupported rhodium sample and continuing with silica-supported samples of varying rhodium content. The surface area approaches the limiting value

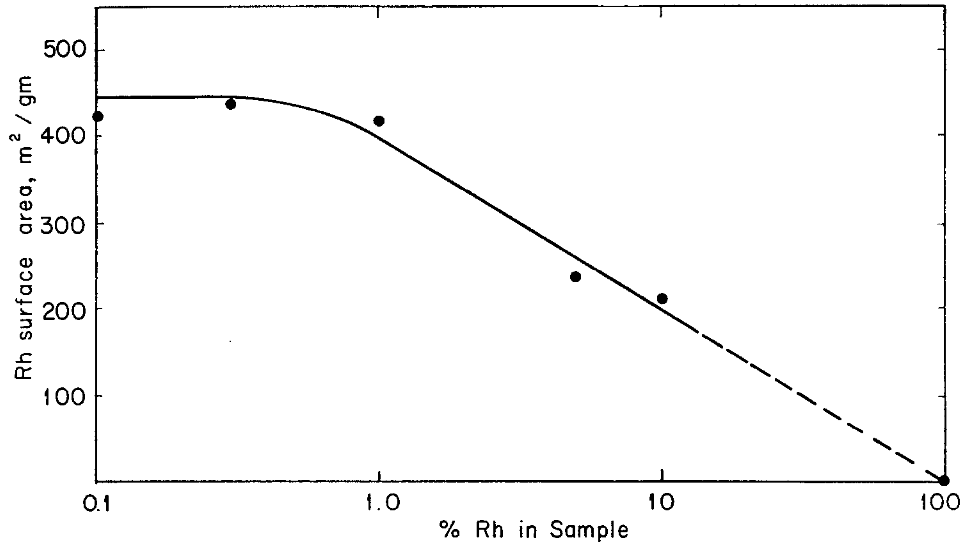

FIG. 4. Variation of the surface area of silica-supported rhodium as a function of metal concentration.

(corresponding to H/M equal to unity) at about 1% Rh concentration, below which it changes very little with further decrease in concentration. The general nature of the results is not surprising, since one would expect that crystal growth would be enhanced by increased concentration of metallic nucleii on the surface. Nevertheless, the general nature of the relation between surface area and concentration is gratifying from the points of view of reproducibility of catalyst preparation and of the overall consistency of the method of determining surface areas.

In the case of unsupported rhodium, the surface area was also measured by the adsorption of argon at 77°K, as a check on the area obtained by hydrogen chemisorption. Comparatively little work has been done on comparing metal areas by the two methods, except for evaporated films. Some work has been done on platinum black comparing chemisorption areas with BET areas using both nitrogen and argon for the latter (*18, 19, 20*) and hydrogen for the former, and a study has been reported for nickel powder (*21*). With a site area of 7.6 $Å^2$ per surface metal atom, the area of the rhodium by hydrogen chemisorption was found to be 1.88 $m^2/g$. Two argon isotherms were measured at 77°K, and gave an area of 1.97 $m^2/g$ with a variation of ±2.5%. The area was calculated assuming the argon atom occupies 14.6 $Å^2$ in a monolayer (*22*). The agreement between rhodium surface areas determined by adsorption of argon and hydrogen is within about 4%, which is about all that could be expected.

In the catalytic studies, rates of hydrogenolysis of ethane to methane were determined at low conversion levels, ranging approximately from 0.1% to 10%. The reaction rates per gram of rhodium for a given catalyst were determined from the relation

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

where $F$ represents the feed rate of ethane to the reactor in gram moles per hour, $W$ represents the weight in grams of rhodium in the catalyst charged to the reactor, and $x$ represents the fraction of ethane converted to methane.

In an actual run to determine reaction rates, the catalyst was first prereduced with flowing hydrogen, after which the reactor was cooled in flowing hydrogen to a convenient reaction temperature. At a standard set of conditions of hydrogen and ethane partial pressures, 0.20 and 0.030 atm, respectively, the activity of the freshly reduced catalyst was determined. Following this, reaction rates were measured at a series of temperatures in a rising tempera-

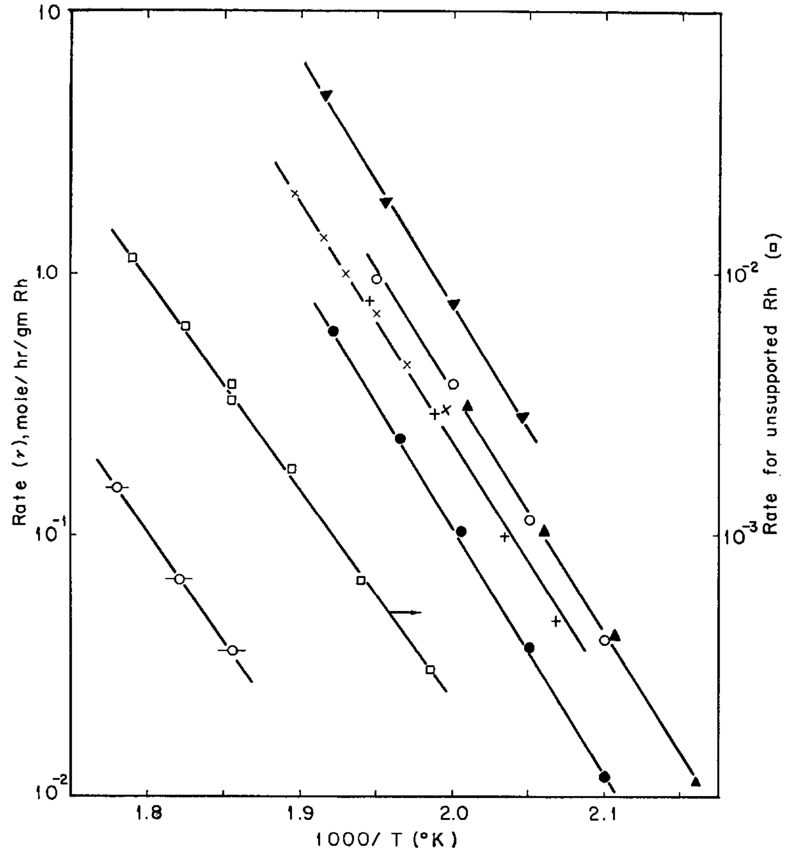

FIG. 5. Effect of temperature on the rate of ethane hydrogenolysis over rhodium catalysts at ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively: unsupported Rh, □; silica-supported Rh: ×, 0.1% Rh; +, 0.3% Rh; ▼, 1% Rh; ○, 5% Rh; ▲, 10% Rh; ●, 5% Rh calcined at 538°C; —○—, 5% Rh calcined at 800°C.

ture sequence. The data are shown in the Arrhenius plots in Fig. 5, where the rates per gram of rhodium are plotted for the various catalysts. There are clearly large differences in catalytic activity. To allow for differences in rhodium surface area, it is a simple matter to calculate rates per unit surface area of rhodium, using the surface areas given in Table 1. A comparison of specific catalytic activities determined in this way is given in the last column of Table 1. For a number of the supported rhodium catalysts of varying rhodium concentration, in which the degree of dispersion of the rhodium was high (crystallite sizes of 41 Å or lower), the specific activities did not vary by more than about fourfold. The 0.1% and 0.3% rhodium samples in this group have lower specific activity than the samples containing 1% or more rhodium. More striking, however, are the significantly lower specific activities of catalysts with large rhodium crystallites as compared to well-dispersed rhodium samples. Thus, the rhodium catalyst calcined at 800°C and the unsupported, bulk rhodium showed specific activities which were twenty to forty times lower than those of the highly dispersed rhodium catalysts.

With regard to kinetic parameters other than activity, Table 2 includes values of the apparent activation energy *E* and of *n* and *m*, the reaction orders with respect to ethane and hydrogen, respectively. For those catalysts with high rhodium dispersion, characterized by rhodium crystallite sizes of 41 Å or lower in Table 1, there are

TABLE 2
KINETIC PARAMETERS FOR ETHANE HYDROGENOLYSIS

| Catalyst | Crystallite size from Table 1 (Å) | Temp. range, (°C) | $E^a$ | $n^b$ | $m^c$ |
|---|---|---|---|---|---|
| Rh-SiO$_2$ (0.1–10% Rh) | ≤41 | 190–256° | 42 | 0.8 | −2.1 |
| 5% Rh on SiO$_2$ calcined at 800°C | 127 | 255–288° | 39 | 0.8 | −1.4 |
| Unsupported Rh | 2560 | 231–288° | 39 | 0.9 | −1.6 |

[a] Apparent activation energy, kcal/mole.

[b] Reaction order with respect to ethane; the ethane pressure was varied from 0.01 to 0.10 atm at a hydrogen pressure of 0.20 atm.

[c] Reaction order with respect to hydrogen; the hydrogen pressure was varied from 0.10 to 0.40 atm at an ethane pressure of 0.030 atm.

no significant differences in these parameters for catalysts varying in rhodium concentration from 0.1% to 10%. The apparent activation energy is 42 kcal/mole, and the reaction orders with respect to ethane and hydrogen are 0.8 and −2.1, respectively. In the case of the two catalysts with larger rhodium crystallites (127 and 2560 Å), the apparent activation energy is slightly lower, 39 kcal/mole. The reaction order with respect to hydrogen is also different, approximately −1.5 ± 0.1.

In considering kinetic parameters, it is of some interest to examine the dependence of rates on hydrogen pressure. The results on all of the rhodium catalysts can be interpreted satisfactorily in terms of a reaction scheme originally proposed by Cimino, Boudart, and Taylor (*23*). According to this scheme the initial step in ethane hydrogenolysis involves dehydrogenative chemisorption of ethane to form a surface residue $C_2H_x$,

$$C_2H_6 \rightleftharpoons C_2H_x + aH_2 \qquad (2)$$

where $a = (6 - x)/2$. This is followed by rupture of carbon–carbon bonds via reaction of $C_2H_x$ with hydrogen to form monocarbon fragments, $CH_y$ and $CH_z$, which are rapidly hydrogenated to methane

$$C_2H_x \xrightarrow{H_2} CH_y + CH_z \xrightarrow{H_2} CH_4 \qquad (3)$$

A kinetic analysis (*23*) leads to the rate expression

$$r = kp_E{}^n p_H{}^{(1-na)} \qquad (4)$$

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 rhodium catalysts, the best agreement with experiment is obtained for the highest possible value of $a$, i.e., for $a = 3$. From the experimental values of $n$, we can calculate values of the exponent $(1 - na)$ on hydrogen pressure in Eq. (4), and compare these with values of the experimental exponent $m$ listed in Table 2. For the well-dispersed rhodium catalysts, the experimental and calculated values of the exponent on hydrogen pressure are −2.1 and −1.4, respectively. For the less well dispersed rhodium catalysts, the agreement is better, −1.4 vs. −1.4 and −1.6 vs. −1.7. The conclusion that $a = 3$ means that the ethane undergoes extensive dissociation of carbon–hydrogen bonds during the chemisorption step to form a dicarbon fragment containing no hydrogen. This is similar to conclusions previously drawn for nickel (*6, 8, 23*) and platinum (*12*) catalysts.

## DISCUSSION

In discussing the catalytic properties of rhodium for ethane hydrogenolysis, it is convenient to distinguish between highly dispersed rhodium catalysts and those with much larger rhodium crystallites. The former are characterized by crystallite sizes too small to be measured by X-ray diffraction line-broadening, i.e., about 40 Å or lower, while the latter are characterized by crystallite sizes above about 125 Å. The specific activity of supported rhodium in the highly dispersed state varies by no more than fourfold over a broad range of concentrations from 0.1% to 10% rhodium. The data do indicate, however, that the specific activity is lower for the very low rhodium concentration catalysts. It is to be noted that the dispersion improves with decreasing rhodium concentration to a point where gas adsorption data indicate that the rhodium atoms are essentially all accessible to hydrogen. Below a certain nominal crystallite size (~10 Å), however, gas adsorption data cannot distinguish between different degrees of dispersion, since the rhodium atoms are then essentially all located in the surface of the crystallites, and the amount of gas adsorbed per metal atom in the sample is constant. For the rhodium-silica catalysts of the present study, this situation exists for rhodium concentrations of 1% or lower. In considering an extreme case, it is clear that the state of dispersion of isolated atoms on the surface is different from that of 10-Å crystallites, although these differences cannot be established by gas adsorption measurements. The detailed topography of highly dispersed, supported platinum has been discussed previously (*18*). However, catalytic measurements may well distinguish between states of dispersion intermediate between these extremes. It seems reasonable to conclude that the lower specific activity of the 0.1% and 0.3% rhodium catalysts is an indication that the properties of rhodium in an extremely high state of dispersion are different from those of rhodium in larger aggregates (which, however, are still characterized by an H/M ratio of unity). To return to the extreme situation just mentioned, one would expect a transition in the properties of rhodium in proceeding from isolated rhodium atoms to a state in which rhodium atoms are bonded together. Such a transition could take place under conditions where each rhodium atom can adsorb a hydrogen atom.

Although the specific activity of rhodium on silica appears to decline as the concentration is decreased to very low levels, a more striking effect is observed on moving in the opposite direction, i.e., from highly dispersed rhodium to less well dispersed forms. The specific activities of the massive, unsupported rhodium and of the 5% rhodium catalyst calcined at 800°C are 20 to 40 times lower than that of well-dispersed rhodium catalysts containing from 1% to 10% of the metal. Thus, when the dispersion is varied markedly in either direction from that encountered in catalysts which are reasonably typical of those employed in actual practice, the specific activity declines. High catalytic activity thus appears to be associated with an intermediate state of dispersion of the metal.

The results of the present study on rhodium are in agreement with the studies of Dorling and Moss (*9*) on platinum, insofar as severe calcination of the catalyst to grow large metal crystallites decreases the specific activity of the metal. The present results on rhodium also tend to parallel those of Boudart and co-workers on platinum (*10*) with regard to the effect of metal concentration on specific activity. However, the results of the present study, in contrast to the findings of the latter workers, show that the specific activity is substantially lower for the metal in the massive form. It should be noted, however, that the ethane hydrogenolysis reaction investigated here is a much more difficult and demanding one than the hydrogenation of cyclopropane employed by Boudart *et al.* (*10*). As recognized by these investigators (*10*), certain reactions may not be sensitive to differences in surface topography which would become important under more demanding circumstances. Here it is noted that the work of McKee (*24*) on propane cracking showed a strong decrease in the specific activity of platinum black on sintering. In general, there would appear to be little *a priori* reason to expect that the specific activity of a metal should remain invariant as the dispersion is varied over extreme ranges.

In assessing the catalytic activity of metals in relation to their state of dispersion, it seems to us that the matter should be considered from two different points of view. On the one hand, the relation between catalytic activity and dispersion is of fundamental interest in understanding the nature of "active centers," and in this respect differences in the catalytic properties of such diverse forms as the massive metal and extremely small crystallites are clearly important. On the other hand, it is important to consider the relevance of such differences to the large body of catalytic investigations, since these differences present another complicating factor to be added to the extensive list of variables which are already present in catalysis. In this latter respect, it is encouraging that for metals such as platinum and rhodium, the effects of dispersion on catalytic properties only become important when extreme conditions of dispersion are considered. The generality of the findings to date, however, is still to be established and further investigations with other metal catalysts would be helpful.

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