

An Investigation of the Dispersion and Catalytic Properties of Supported Rhenium

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The state of dispersion and catalytic properties of supported rhenium have been investigated using a rhenium-silica catalyst containing 10% rhenium. The chemisorption of hydrogen or carbon monoxide at room temperature is satisfactory for determining the rhenium surface area, as judged by the good agreement on crystallite size between these measurements and an X-ray line-broadening determination. The catalytic properties of rhenium for ethane hydrogenolysis were investigated for comparison with our earlier studies on the noble metals of Group VIII of the periodic table. Some significant differences from the Group VIII noble metals were observed in the kinetics, particularly with regard to the dependence of the reaction rate on hydrogen pressure. When the activity of rhenium is considered together with the activities of the Group VIII noble metals of the same period, a pattern of variation of catalytic activity is observed which is similar to the variation in percent *d* character of the metallic bond.

INTRODUCTION

In recent years there has been increased interest in rhenium catalysts (1). While the general catalytic behavior of rhenium is reasonably well known by now, there appears to be little quantitative information on its specific catalytic activity relative to the activities of other metals. Some data of this type on ammonia decomposition are available from studies on rhenium powders (2) and films (3). In the case of supported rhenium catalysts, no information of this kind seems to have been reported. The state of dispersion of rhenium on a carrier appears not to have been investigated previously, with the consequence that the data on metal surface area have not been available for the determination of specific activity.

We have for some time been investigating the state of dispersion and catalytic properties of supported metals (4-7). Much of this work has been done using ethane hydrogenolysis as a test reaction, and the studies to date have encompassed all of the metals of Group VIII of the periodic table. A major objective of the work is to establish patterns

of variation in catalytic behavior among the metals. To extend the studies beyond Group VIII, we have investigated the catalytic properties of supported rhenium for ethane hydrogenolysis, using a rhenium-silica catalyst containing 10% rhenium. As part of the study, selective chemisorption methods to determine the state of dispersion of the rhenium have also been investigated. With such data, the specific activity of supported rhenium for the ethane hydrogenolysis reaction can be determined readily. The results, including a comparison of rhenium with the platinum metals of Group VIII, are reported in this paper.

EXPERIMENTAL

Apparatus and procedure. The apparatus for both the catalytic reaction studies and the chemisorption measurements has been described in detail elsewhere (4-8). The catalytic studies were made in a flow reactor system at atmospheric pressure, and adsorption measurements were made in a high-vacuum apparatus. The catalyst was reduced in flowing hydrogen at 500°C prior to adsorption or catalytic measurements.

Materials. The supported rhenium catalyst used in this work contained 10% by weight of rhenium, and was prepared by impregnating silica with a solution of perrhenic acid. The silica used was Cabosil HS5 (300 m²/g surface area), obtained from the Cabot Corp., Boston, Massachusetts. The perrhenic acid was obtained from Cleveland Refractory Metals, Solon, Ohio, and had a rhenium purity of 99.99%. 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.

The ethane and carbon monoxide used in this work were obtained from the Matheson Co., and hydrogen from the Linde Co. Details of the purification procedures employed have been given elsewhere (6).

RESULTS

Isotherms for the room-temperature adsorption of hydrogen and carbon monoxide on the rhenium catalyst are shown in Fig. 1. Adsorption on the silica support was a negligible part of the total in these experiments, as shown also in previous work on other supported metals (6). Prior to the

adsorption measurements, the catalyst was reduced in flowing hydrogen (500 cm³/min) at 500°C and outgassed to approximately 10⁻⁶ torr before being cooled to room temperature. Some effect of time of reduction on the isotherms was noted, as will be seen by comparing the open and closed points in Fig. 1. With increasing time of reduction, the isotherms become less pressure-dependent, a characteristic which is indicative of improved reduction of the metal. A reduction period of 6 hr at 500°C was finally adopted in the present investigation.

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

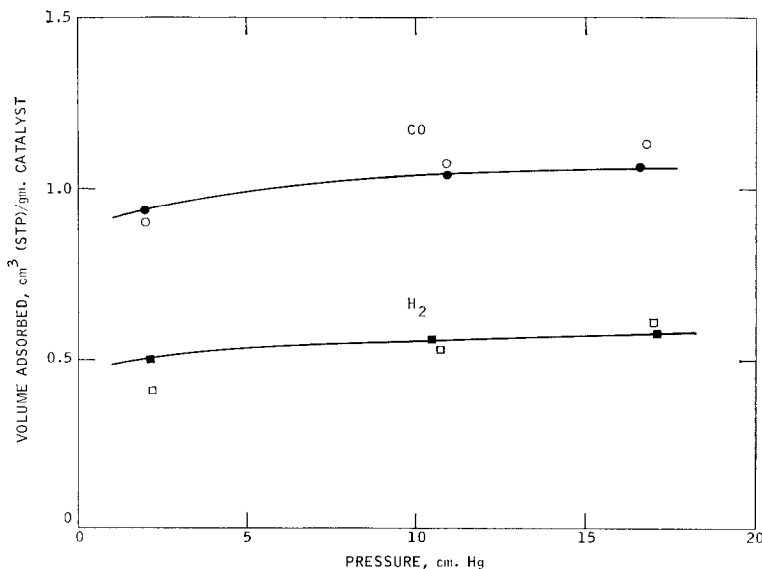


FIG. 1. Adsorption isotherms at room temperature for hydrogen and carbon monoxide on silica-supported rhenium: ○, ●, CO; □, ■, H₂. The open points are for a sample reduced at 500°C in flowing hydrogen for 3 hr, while the closed points are for the same sample reduced for 6 hr.

TABLE 1
SUMMARY OF ADSORPTION DATA AND KINETIC
PARAMETERS FOR ETHANE HYDROGENOLYSIS
OVER SUPPORTED RHENIUM

<i>Adsorption results</i>	
H/M ^a	0.093
CO/M ^b	0.086
Re surface area (m ² /g Re) ^c	23
Re crystallite size (Å) ^c	122
<i>Ethane hydrogenolysis parameters</i>	
Apparent activation energy (kcal/mole)	31
Reaction order, ethane ^d	0.5
Reaction order, hydrogen ^d	0.3
Specific activity (mmoles/hr m ² Re at 205°C) ^e	0.070

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

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

^c Calculated from the hydrogen adsorption data.

^d Determined at 250°C.

^e At ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively.

metal atom and a bridged structure bonded to two metal atoms (9). The good agreement between the H/M and CO/M values in Table 1 indicates that the linear form predominates. This conclusion is also supported by some unpublished infrared studies by one of us (D. J. C. Y.) of carbon monoxide chemisorbed on rhenium. The infrared studies did not show a band in the vicinity of 1800 to 1900 cm⁻¹, and hence no evidence was found for a bridged structure. Another observation of interest in the infrared work is the absence of a band in the vicinity of 2180 cm⁻¹, which has been often observed on oxide surfaces (10, 11) and on poorly reduced (12) or oxidized (9, 13) metal surfaces. This shows that the rhenium surface is well reduced.

The rhenium surface area given in Table 1 was calculated from the hydrogen chemisorption data by taking a value of 7.6 Å² for the area associated with each rhenium atom in the surface. This is the same as the value previously adopted for the Group VIII noble metals (6). The small differences in metallic radii among these metals and rhenium have been ignored here. The crystallite size of the

rhenium (122 Å) was calculated from the rhenium surface area by a method previously discussed (6). This value agrees very well with data obtained by X-ray diffraction line-broadening, which gave an average value of 130 ± 10 Å. An average value is reported, since there was a variation of about 20 Å in the value depending on the particular diffraction line which was used for the determination of crystallite size. The X-ray measurements were made with a Phillips diffractometer employing copper K α radiation. The rhenium crystallite size was calculated from the width of the diffraction line in the usual manner (14), with a correction for instrumental broadening. The particular rhenium catalyst used in this work was ideal for a comparison of results from gas adsorption and X-ray line-broadening measurements, since the crystallite size was in a range where both methods have satisfactory accuracy. It is well known that very highly dispersed metals present a problem for X-ray studies, as the lines are broad and weak.

In the ethane hydrogenolysis studies, reaction rates for the conversion of ethane to methane were determined at low conversion levels (0.2% to 1.4%) over a range of temperatures and partial pressures of ethane and hydrogen. The effect of temperature on the rate is shown in the Arrhenius plot in Fig. 2, giving an apparent activation energy of 31 kcal/mole. From the reaction rate data in Fig. 2 and the rhenium surface area given in Table 1, the specific catalytic activity of the rhenium can be calculated, and is given in Table 1. A temperature of 205°C was chosen for reporting the specific activity to simplify the comparison with other catalysts for which we have reported specific activities (6, 7) at 205°C. To do this, it was necessary to extrapolate the Arrhenius plot some 25°.

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 reaction orders

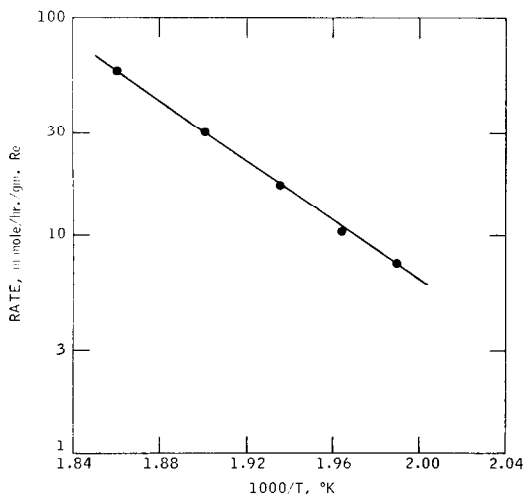


FIG. 2. Arrhenius plot for ethane hydrogenolysis over silica-supported rhenium. The data were obtained at ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively. The catalyst was reduced in flowing hydrogen for 6 hr at 500°C prior to the rate measurements.

with respect to ethane and hydrogen are, respectively, 0.5 and 0.3.

DISCUSSION

The results of this work indicate that the chemisorption of hydrogen and carbon monoxide can be applied satisfactorily to determine the state of dispersion of supported rhenium, as the agreement between the room-temperature chemisorption measurements and X-ray line-broadening measurements of crystallite size is good. On the basis of these results, one can now proceed more confidently in applying these chemisorption methods for characterizing the state of dispersion of rhenium in samples where the crystallites are too small to obtain information by X-ray line-broadening. The present work has also shown, as expected, that supported rhenium is more difficult to reduce than supported Group VIII noble metals. Nevertheless, the reduction can be effected satisfactorily at 500°C in flowing hydrogen without employing prohibitively long reduction times.

Having obtained information on the surface area of supported rhenium, it is interesting to compare the specific catalytic

activity of rhenium with that of other metals, e.g., the Group VIII noble metals. A comparison with platinum, iridium, and osmium, which are in the same period as rhenium, is of particular interest. When this is done for the ethane hydrogenolysis reaction, by comparing previously reported data on platinum, iridium, and osmium (6, 7) with the present data on rhenium, an interesting pattern of variation of catalytic activity emerges. Proceeding in the direction of increasing atomic number from rhenium to platinum, one finds that the catalytic activity passes through a maximum at osmium. It is interesting to note that the percentage *d* character of the metallic bond, a quantity introduced by Pauling in 1949 (15), shows precisely the same behavior. A relationship between hydrogenolysis activity and percent *d* character has been noted previously by us in studies on the Group VIII metals (6, 7) and the present data on rhenium tend to make such a correlation more convincing. The observation of corresponding maxima in activity and percent *d* character at osmium would seem to fulfill a rather stringent test.

With regard to the kinetics of ethane hydrogenolysis over rhenium, there is clearly one significant difference from the Group VIII noble metals. For rhenium, the reaction order in hydrogen pressure is slightly positive, whereas for the Group VIII noble metals the order is strongly negative, ranging from -1.2 to -2.5 (6, 7). The strong inverse dependence on hydrogen pressure observed with the Group VIII noble metals can be rationalized satisfactorily (6, 7) in terms of a simple kinetic scheme originally proposed to account for results on nickel catalysts (16). According to this analysis, the hydrogenolysis reaction involves an initial dehydrogenation step leading to a highly unsaturated surface C_2 species which is in equilibrium with ethane and hydrogen in the gas phase. The strong inverse dependence of the rate on hydrogen pressure is then attributed to suppression of this step. Applying this type of analysis to rhenium, one would conclude that the C_2 intermediate on the surface is not highly unsaturated, since the reaction rate does

not decrease with increasing hydrogen pressure. However, it is not clear why rhenium should be so different from the Group VIII noble metals in this regard. This may reflect a limitation in the applicability of the kinetic analysis to rhenium. Perhaps the situation is similar to that previously noted for supported iron (γ), in which it was suggested that equilibrium may not be established in the initial dehydrogenative chemisorption step. Experiments on the exchange of ethane with deuterium on rhenium would be informative, since the existence of such an equilibrium would require that the formation of deuterioethanes occur more readily than the hydrogenolysis reaction.

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