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Chemisorption and Catalytic Properties of Supported Platinum

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The chemisorption of hydrogen on platinum deposited on two different supports, alumina and silica-alumina, has been investigated to determine the effect of the support on the degree of dispersion of the platinum. Measurements of the rate of dehydrogenation of cyclohexane were made to determine the corresponding effects on catalytic activity. The catalysts were prepared by impregnation of the supports with chloroplatinic acid and were reduced in hydrogen prior to both the chemisorption and catalytic activity measurements. The chemisorption results indicated that the platinum was dispersed to a much higher degree on alumina than on silica-alumina. The higher activity of the platinum on alumina for cyclohexane dehydrogenation is attributed to the greater platinum dispersion. For the platinum-on-alumina catalyst, the adsorption of hydrogen on platinum at moderately high surface coverage (70%) is estimated to be exothermic to the extent of 7–8 kcal/mole.

The chemisorption of hydrogen on supported platinum catalysts has been investigated recently by several groups of workers (*1–3*). In most of these investigations, the platinum was impregnated on alumina with an aqueous chloroplatinic acid solution, followed by calcination in air, and subsequent reduction in hydrogen at about 500°C. For catalysts prepared in this way with platinum concentrations less than 1.0 wt %, the results generally indicated that the ratio of hydrogen atoms adsorbed per platinum atom was close to unity, suggesting high dispersion of the platinum on the support. Relatively little information on hydrogen chemisorption has been reported for platinum deposited on other acidic supports such as silica-alumina. However, the data which are available suggest that the particular support used may have a substantial effect on the results (*4*). We have recently obtained some additional information in this regard and have investigated the effect on the catalytic properties of the platinum, using cyclohexane dehydrogenation as a test reaction. In addition, a rough estimate of the heat of adsorption of hydrogen was obtained at moderately high surface coverage on platinum supported on alumina.

EXPERIMENTAL

The apparatus used for the hydrogen chemisorption measurements was a conventional glass vacuum system described previously (*5*). The system had an 80 liter/sec oil diffusion pump. By means of a trap cooled in liquid nitrogen, ultimate dynamic vacua of 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 catalyst. The amount of sample charged to the adsorption cell was approximately 2 g. The samples were reduced in place in flowing hydrogen (500 cc/min) for 3 hr at 450°C, prior to evacuation at 450°C and subsequent cooling to the temperature at which the adsorption isotherm was to be obtained.

The cyclohexane dehydrogenation measurements were made in a stainless steel reactor tube with an approximate ID of 1.5 cm, employing a catalyst charge of 0.1 to 1.0 g diluted uniformly with quartz chips to a volume of 3 cc. The reaction conditions were 316°C, 1 atm total pressure, and a hydrogen-to-cyclohexane mole ratio of 5:1. The catalysts were reduced in place in the reactor for 3 hr at 450°C in flowing hydrogen. The extent of dehydrogenation to benzene was determined by chromatographic analysis, employing a 7,8-benzoquinoline column coupled directly to the reactor outlet. A sample of the reaction product was taken 15 min after the reactants were first introduced to the reactor.

The platinum catalysts used in this work were prepared by impregnation of alumina or silica-alumina with aqueous chloroplatinic acid solution, followed by drying and subsequent calcination in air for 1 hr at 540°C. The alumina was prepared by heating beta-alumina trihydrate, obtained from Davison Chemical Company, for 4 hr at 600°C. The surface area of the alumina was 295 m^2/g. The silica-alumina used as a support was Type DA-1 cracking catalyst (nominally 13% Al_2O_3, 87% SiO_2), also obtained from the Davison Chemical Company. The surface area was 450 m^2/g.

The cyclohexane used in this work was spectroscopic grade reagent and was obtained from Fisher Scientific Company. High-purity hydrogen was obtained from the Linde Company, 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 Dry Ice or by a molecular sieve dryer, the latter having been employed for the hydrogen used in the kinetic measurements.

RESULTS AND DISCUSSION

Adsorption isotherms for hydrogen on the platinum catalysts and supports are shown in Fig. 1. In obtaining the isotherms, approximately 30 min was allowed before an equilibrium pressure reading was taken. This procedure was similar to that adopted by Spenadel and Boudart (*1*), who indicated that more than 90% of the hydrogen adsorption on platinum supported on alumina was instantaneous and that the rate of uptake was negligible after about 30 min.

From the isotherms in Fig. 1, it can be seen that the adsorption on the alumina, at either 200° or 300°C, is small compared to the adsorption on the 2% platinum-on-alumina catalyst. The adsorption on the alumina is also seen to increase with increasing temperature. It appears that the adsorption on alumina, in contrast to adsorption on platinum, is slow and that the increase in adsorption at the higher temperature reflects a higher rate rather than an effect of temperature on adsorption equilibrium. In the case of the silica-alumina and platinum-on-silica-alumina samples, the adsorption on the former is only about 15% of that on the latter at a pressure of 2 cm, but increases to about 50% at a pressure of 20 cm.

When the adsorption isotherms for the platinum catalysts are corrected for adsorption on the supports, net isotherms for adsorption on the platinum itself are obtained. Adopting this procedure and expressing the results as atoms of hydrogen adsorbed per atom of platinum, we obtain the isotherms shown in Fig. 2. In the case of the platinum-on-alumina catalyst, the number of hydrogen atoms adsorbed per platinum atom is essentially unity, corresponding to a high degree of dispersion of platinum. This is similar to the result observed by Spenadel and Boudart for 0.6% platinum on alumina (*1*). The adsorption at 200° is higher than at 300°, indicating that the adsorption is exothermic. At the high coverage of platinum by hydrogen in these experiments ($\theta > 0.6$), the isosteric heat of adsorption is low, about 7–8 kcal/mole at $\theta = 0.7$. From experiments on the rate of desorption of hydrogen from platinum supported on alumina, Kubokawa and co-workers (*6*) determined a value of 10 kcal/mole for the activation energy of desorption at comparable high coverages.

In the case of the platinum-on-silica-alumina catalyst, the adsorption of hydrogen on the platinum is about an order of magnitude less than for the platinum-on-alumina catalyst. The dispersion of the platinum is therefore much poorer on silica-alumina than on alumina, i.e., the platinum surface area is about one-tenth as great on silica-alumina as on alumina. This difference in dispersion on the two supports is directionally similar to results reported previously for nickel (*7*),

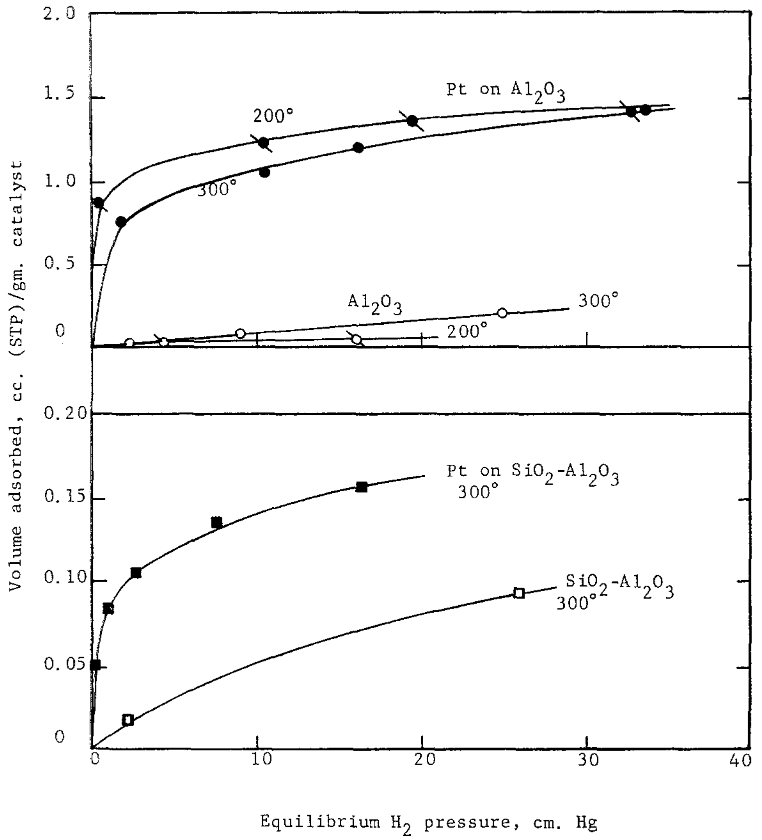

FIG. 1. Hydrogen chemisorption data on platinum catalysts and supports: ⊘, Al_2O_3 at 200°; ○, Al_2O_3 at 300°; ●̸, 2% Pt on Al_2O_3 at 200°; ●, 2% Pt on Al_2O_3 at 300°; □, SiO_2-Al_2O_3 at 300°; ■, 2% Pt on SiO_2-Al_2O_3 at 300°.

except that the magnitude of the difference is much greater in the present work on platinum. Perhaps this is due to the much lower concentration of metal employed in the case of platinum (2% vs. 10%).

From the hydrogen chemisorption data, an estimate of the average crystallite size of the platinum on the two different supports can be made. The determination of platinum crystallite size from adsorption data has been previously discussed in some detail by Spenadel and Boudart (*1*). In the case of the platinum-on-alumina catalyst employed in the present study, the crystallite size of the platinum is less than 10 Å. For the platinum-on-silica-alumina catalyst, the platinum crystallite size is 85 Å. In these calculations it is assumed that the platinum crystallites are cubes.

The effect of the difference in platinum dispersion on catalytic activity is shown by data on the rate of cyclohexane dehydrogenation to benzene over the two platinum catalysts. The data are given in Table 1.

TABLE 1
CATALYTIC ACTIVITY OF SUPPORTED PLATINUM FOR CYCLOHEXANE DEHYDROGENATION

Catalyst	F/W[a]	x, Conversion	Activity[b]
2% Pt on Al_2O_3[c]	17.9	0.033	0.59
2% Pt on SiO_2–Al_2O_3[d]	1.18	0.085	0.10

[a] Gram moles of cyclohexane fed per hr per gram of catalyst.

[b] Gram moles of benzene formed per hr per gram of catalyst; conditions: 315°C, 1 atm, mole ratio of hydrogen to cyclohexane, 5/1.

[c] 0.10-g catalyst charge.

[d] 1.0-g catalyst charge.

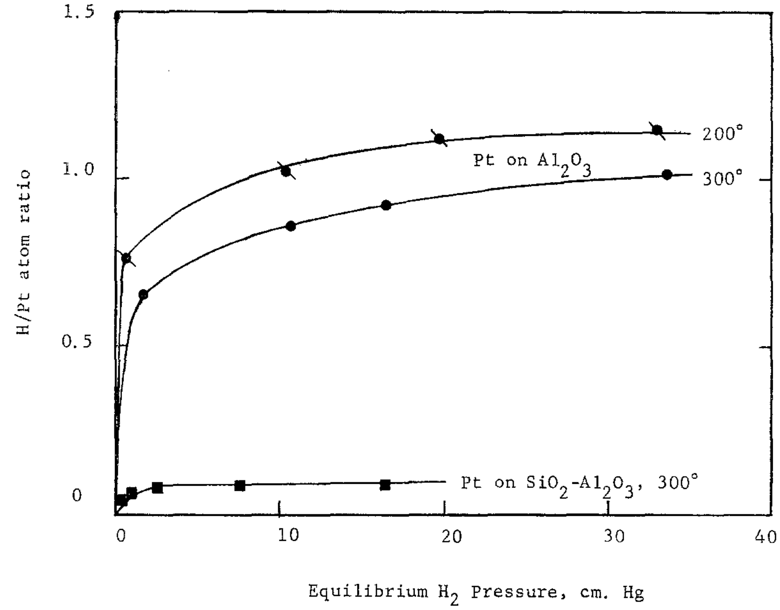

FIG. 2. Net adsorption of hydrogen on supported platinum: ⦸, 2% Pt on Al_2O_3 at 200°C; ●, 2% Pt on Al_2O_3 at 300°C; ■, 2% Pt on SiO_2-Al_2O_3 at 300°C.

The rates of dehydrogenation were determined at low conversion levels ($<10\%$), and were calculated as the product of the quantity, F/W, and the fractional conversion, x, where F represents the moles of cyclohexane charged per hour and W is the weight of catalyst in grams. The activity of the platinum-on-alumina catalyst was about six times as high as that of the platinum on silica-alumina. Interpreting the results in a strict manner, one would conclude that the difference in catalytic activity of the platinum on the two supports was smaller than the difference in platinum surface area, since the platinum surface area on alumina was about 10 times higher than on silica-alumina. However, it is possible that the more active platinum-on-alumina catalyst may have been limited to some degree by pore diffusion, so that the factor of 6 may be smaller than the true ratio of catalytic activities. In any case, there is little doubt that the major reason for the difference in catalytic activity is the difference in the platinum surface area on the two supports. In other words, the specific catalytic activity of the platinum (rate per unit platinum surface area) for cyclohexane dehydrogenation is essentially unaffected by the support.

The results of the present investigation indicate that the support did not exert any specific effect on the intrinsic catalytic properties of the platinum, but instead simply affected the degree of platinum dispersion. However, it should not be concluded that the role of the support is in general limited only to its effect on the surface area of the active catalytic component. Thus, it has been shown that the specific catalytic activity of nickel for ethane hydrogenolysis varies markedly with the support employed for the nickel (*7*), i.e., the catalytic activity of the nickel is affected to a much greater extent by the support than is the corresponding nickel surface area. It would therefore appear that the effect of the support can vary significantly, depending on the specific catalyst and reaction under study.

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