

Catalytic Hydrogenation of Cyclohexene

VI. Turnover Rate of the Gas-Phase Reaction on Unsupported Platinum Powders

D. J. O'REAR, D. G. LÖFFLER, AND M. BOUDART

Department of Chemical Engineering, Stanford University, Stanford, California 94305

Received March 19, 1984; revised February 12, 1985

A platinum powder, suitable for conventional studies of adsorption and catalysis, was prepared by washing a potassium-contaminated commercial platinum black in nitric acid. The acid-washed powder was potassium free, as shown by Auger electron spectroscopy. Surface areas were measured by the BET method with dinitrogen and argon. On the acid-washed platinum powder, the turnover rate for hydrogenation of cyclohexene under standard conditions was practically the same as on supported samples of platinum and a large clean single crystal, as determined by others. On that evidence, it is concluded that the surface of the acid-washed powder can be considered a clean surface for studies of adsorption and catalysis. © 1985 Academic Press, Inc.

INTRODUCTION

Platinum powders, most commonly called blacks, have long been used in fundamental studies of adsorption and catalysis because they present relatively large specific surface areas that can be measured by the BET method. Here are a few examples. Back in 1926, Benton (1) measured the uptake of dihydrogen, dioxygen, and carbon monoxide by a platinum black and reviewed the literature available at the time. More recently, Vannice *et al.* (2) studied the adsorption of dihydrogen and dioxygen and the reaction of dihydrogen with oxygen adsorbed on platinum black, while Menon and Froment (3) compared the performance of platinum black with that of alumina-supported platinum for *n*-pentane hydrogenolysis. Bond and Mallát (4) used an electrochemical technique to measure hydrogen spillover from platinum black to carbon powder.

In spite of a clean surface being a prerequisite to any study of adsorption and catalysis, we know of only one reported investigation of surface composition of platinum powders (5). In the present work, we show that platinum black can be seriously con-

taminated with a potassium impurity, difficult to eliminate by water washing, but easily removed by nitric acid. A clean, convenient platinum powder can thus be readily prepared. Evidence for surface cleanliness is provided by Auger electron spectroscopy and measurements of turnover rates for hydrogenation of cyclohexene.

EXPERIMENTAL

Materials. Portions of three lots of platinum powder obtained from Engelhard Industries have been used. The powder from Lot 11379 will be referred to as the *untreated* powder, while the powder from Lot 10272, which had been previously reduced in dihydrogen at 398 K by Vannice *et al.* (2), will be referred to as the *dihydrogen-sintered* powder. Finally, a third powder was heated at 828 K in air and will be referred to as the *air-sintered* powder. From atomic absorption analysis the potassium contents of the untreated, dihydrogen-sintered, and air-sintered powders were 0.48, 0.33, and 0.011 wt%, respectively. It should be noted that potassium was not listed in the chemical analysis supplied by the manufacturer of the powder. The carbon con-

tent of the untreated powder was 350 ppm by weight as determined by combustion analysis.

All gases used were Matheson research grade except for the dihydrogen and carbon dioxide, which were Liquid Carbonic Hi-Purity grade. Dihydrogen was purified by diffusion through a Milton-Roy palladium thimble, while carbon dioxide was passed through a molecular sieve trap cooled to 198 K. The other gases were used without further purification.

Apparatus. A conventional volumetric adsorption apparatus was used to measure BET areas, to reduce the powders, and to study chemisorption of carbon dioxide. This is a fixed-volume glass system fitted with a Texas Instruments pressure gauge (6). The adsorption cell used in the present study had a side arm of capillary tubing which was cooled to 195 K to condense the water formed during reduction.

The Varian ultrahigh vacuum system used to perform the AES study of the powders has been described elsewhere (7). All three powders were separately mounted on a molybdenum mesh by pressing to 17 MPa between steel dies. The molybdenum mesh could be heated by passage of an electric current.

Reduced powders were prepared in the volumetric adsorption apparatus by evacuating the sample at room temperature for 30 min at 10^{-3} Pa, heating for another 30 min at the same pressure, and then admitting dihydrogen into the cell. This initial reduction is highly exothermic, causing a temperature rise and, in consequence, sintering of the powder. The extent of sintering depends on the rate of admission of dihydrogen into the cell. Reduced powders with different surface areas can be obtained for different flow rates of dihydrogen. The final reduction conditions involved static dihydrogen at 20 to 50 kPa for 0.5 h at 398 K, followed by evacuation at 10^{-3} Pa for 16 h at 398 K.

The vapor-phase hydrogenation of cyclohexene was studied in a glass recirculating

TABLE 1

Comparison of the Measurements of the Total Surface Area of the Untreated Powder with Dinitrogen and Argon

Pretreatment	Value of S_g , m^2g^{-1}	
	With N_2	With Ar
Nonreduced	28.0 \pm 0.9	26.9 \pm 0.8
Reduced		
Portion 1	11.8 \pm 0.1	10.8 \pm 0.1
Portion 2	7.61 \pm 0.15	7.06 \pm 0.06

Note. BET surface area, S_g , of the untreated powder with 0.162 and 0.169 nm^2 as cross-sectional areas of N_2 and Ar, respectively.

batch reactor following the experimental procedures described elsewhere (8). Portions of the powder samples were reduced and characterized in the adsorption apparatus, then diluted with Superbrite glass beads (Type 120-5005, previously washed in aqua regia) and loaded into the reactor. The diluted powders were further reduced for 30 min at 398 K, cooled to room temperature, and evacuated for 5 min. This procedure was repeated before each run.

RESULTS

Surface Areas

The BET method (9) was used to measure the surface areas of platinum powders. Both dinitrogen and argon were used. The measurements of total surface area on several samples of untreated powder are summarized in Table 1. The cross-sectional areas of dinitrogen and argon were assumed to be 0.162 and 0.169 nm^2 , respectively. The results obtained using argon are close enough (less than 10% difference) to those obtained using dinitrogen that either gas can be used in measuring surface areas of unsupported platinum.

Potassium Impurity

The presence of potassium at the surface of the platinum powder was demonstrated by AES. The Auger electron spectra of the

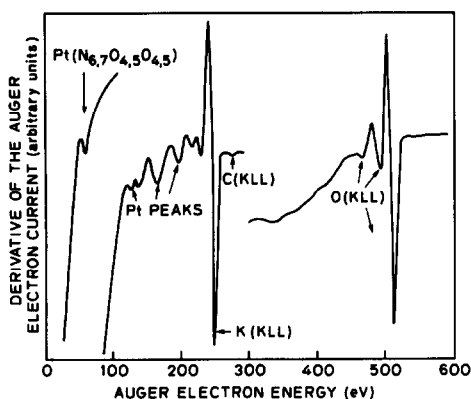


FIG. 1. Auger electron spectrum of the untreated powder. Correction factors are 1.25, 0.139, and 0.0138 for the ranges 30–100, 100–300, and 300–600 eV, respectively. Note that no peaks are evident for the main Si and Ca transitions at 91 and 287 eV, respectively.

three powders showed peaks corresponding to only four elements: platinum, potassium, oxygen, and carbon. No calcium or silicon peaks were evident in the spectra, as shown in Fig. 1. The peak-to-peak heights for the transitions 66, 250, 270, and 517 eV corresponding to platinum, potassium, carbon, and oxygen were corrected as described elsewhere (10) and referred to as I_{Pt} , I_K , I_C , and I_O , respectively.

Heating the samples at temperatures between ambient and 1200 K resulted in similar changes in peak heights for the three powders. Values of I_K and I_O decreased with increasing temperature above 800 K, and both peaks disappeared at 1200 K, while the value of I_{Pt} increased continuously, and I_C presented an irregular pattern at temperatures below 900 K, then increased sharply as I_O and I_K dwindled.

Hydrogenation of Cyclohexene

The turnover rate was measured at temperatures between 273 and 303 K on portions of three reduced untreated powders which had surface areas of 9.72, 8.01, and 2.51 m²g⁻¹.¹ A slight deactivation of the cat-

alyst was observed in the course of the reaction. This process followed a first-order rate law with a small decay constant. The apparent activation energy for the hydrogenation reaction was found to be 34 kJ mol⁻¹ on all powders. The cyclohexene pressure did not affect the rates on the 2.51-m²g⁻¹ powder, but the order in dihydrogen pressure was 0.71 and 0.77 Pa for the 2.51- and 9.72-m²g⁻¹ powders, respectively. Details are given elsewhere (10).

Washing of the Untreated Powder

The potassium impurity in the untreated powder was removed by washing the powder with nitric acid. A 5.03-g portion of the untreated powder was mixed with 200 cm³ of Baker reagent grade concentrated nitric acid at room temperature. The suspension was stirred with a Pyrex rod for 600 s and allowed to settle for 1 h. The platinum powder was rinsed five times in 200 cm³ of distilled water at room temperature. Following the last rinse, the powder was dried in a preheated vacuum oven at 358 K for 1 h. A check of the dry weight of the powder indicated that 97.4% of the original material had been recovered.

The potassium content of the acid washed powder was below the limit of detection by atomic absorption, 1 ppm. The carbon content of this powder was 70 ppm, as determined by combustion analysis. The X-ray diffraction patterns showed only the presence of platinum metal.

An attempt was made to remove the potassium impurity from three portions of the untreated powder, two of them reduced as described above, by washing with water only. The water-washing procedure simulated the acid-washing procedure. After washing and drying, the potassium contained in the unreduced powder was 0.22%; therefore, the water wash had removed only 54% of the potassium in the untreated powder.

The two reduced powders had surface areas of 11.80 and 2.51 m²g⁻¹. After washing and drying, these powders contained 0.014

¹ Reactant partial pressures varied between 0.8 and 3.5 Pa for cyclohexene, and between 6.1 and 27.8 Pa for H₂.

TABLE 2
Rates of Turnover for Hydrogenation of
Cyclohexene on Platinum Catalysts

Catalyst	Rate of turnover at $T = 295$ K, $P_{\text{H}_2} = 9.9$ kPa ^a	Author
Untreated powder	0.64	This work
Acid-washed powder	2.0	This work
Pt/SiO ₂	2.53–2.75	Segal <i>et al.</i> (8)
Pt/SiO ₂ and Pt/Al ₂ O ₃	1.99 ^b	Leclercq and Boudart (11)
(223) Single-crystal plane	2.8	Davis and Somorjai (12)

^a Order with respect to cyclohexene pressure is equal to zero (10).

^b Rate extrapolated from $T = 273$ K assuming an apparent activation energy $E = 34$ kJ mol⁻¹.

and 0.0049% potassium, respectively. Apparently, the potassium can be removed by water much more readily from the reduced than from the nonreduced powders.²

The Auger electron spectrum of the acid-washed powder was dominated by a large peak at 270 eV due to amorphous carbon, the probable origin of which will be discussed below. After heating for 0.5 h at 1075 K in 6×10^{-4} Pa dioxygen, only the Auger transitions from platinum were observed.

Samples of the acid washed-powder were reduced under different dihydrogen admission rates, resulting in different degrees of sintering. Two reduced powders, with BET surface areas of 11.30 and 2.52 m²g⁻¹, were used as catalysts for the hydrogenation of cyclohexene. The activation energy and the reaction order in dihydrogen partial pressure were found to be 34 kJ mol⁻¹ and 0.77, respectively, on both powders.

DISCUSSION AND CONCLUSION

Important questions raised in any study of catalytic reactions on unsupported pow-

² This suggests that the hydrogen treatment may induce segregation of the potassium impurity to the surface.

ders concern the cleanliness of the surface and the degree of sintering. We have shown that commercial platinum black can be severely contaminated by potassium, but that this impurity can be readily removed by washing the powder in concentrated nitric acid. The BET area of the samples can be easily measured by means of either dinitrogen or argon.

Potassium or other alkali metals are used in four common methods of preparation of platinum powders (13). A solution of potassium hydroxide and formaldehyde is used to reduce chloroplatinic acid in Loew's method (14). In Adams' method (15), chloroplatinic acid is fused with potassium nitrate to form platinum dioxide. Platinum dioxide is reduced to the platinum powder. Platinum powders have also been made by reduction of chloroplatinic acid with sodium borohydride in solution (16). Finally, Raney platinum has been made by treating a platinum alloy with potassium hydroxide (17). Potassium or sodium may be present in any of these powders if they are not cleaned properly.

Water is a much less efficient cleaning agent than nitric acid. We found that water removed half the potassium in the powder after a 1-h wash. Paál *et al.* (5) found no potassium in a platinum black prepared by Loew's method after washing it for 2 weeks in distilled water; however, they found traces of silicon in their powders.

The gas-phase hydrogenation of cyclohexene provides a convincing demonstration of the cleanliness of the acid-washed powder. The rates of turnover measured on the acid-washed powder are very close to those reported by other authors, as shown in Table 2. This suggests that the cleanliness of our powder was similar to the cleanliness of supported platinum (8, 11) or of platinum single-crystal surfaces (12). In particular, the surface carbon detected by AES on the acid-washed powder must be largely the result of contamination by residual gases in the UHV chamber. By contrast, the rate of turnover on the untreated

powder is more than three times lower than on the clean powder.

Finally, it was observed that carbon dioxide is readily adsorbed on the untreated powder, while it is not adsorbed on the acid-washed powder (10). Since it is well known that carbon dioxide is adsorbed on K_2O (17), this result suggests that the potassium is probably associated with oxygen on the platinum surface. Furthermore, both potassium and oxygen were observed by AES on the untreated powder.

ACKNOWLEDGMENTS

This work was supported by NSF continuing grants, including the current NSF CPE 8219066. One of us (D.G.L.), on leave from the University of Mar del Plata (Argentina), acknowledges support of CONICET.

REFERENCES

1. Benton, A. F., *J. Amer. Chem. Soc.* **48**, 1850 (1926).
2. Vannice, M. A., Benson, J. E., and Boudart, M., *J. Catal.* **16**, 348 (1970).
3. Menon, P. G., and Froment, G. F., *J. Catal.* **59**, 138 (1979).
4. Bond, G. C., and Mallát, T., *J. Chem. Soc., Faraday Trans. 1* **77**, 1743 (1981).
5. Paál, Z., Tétényi, P., Prigge, D., Wang, X. Zh., and Ertl, G., *Appl. Surf. Sci.* **14**, 307 (1982-83).
6. Hanson, F. V., Ph.D. dissertation. Stanford University, 1975.
7. Williams, F. L., Ph.D. dissertation. Stanford University, 1972.
8. Segal, E., Madon, R. J., and Boudart, M., *J. Catal.* **52**, 45 (1978).
9. Anderson, J. R., "Structure of Metallic Catalysts," p. 293. Academic Press, New York, 1975.
10. O'Rear, D. J., Ph.D. dissertation. Stanford University, 1980.
11. Leclercq, G., and Boudart, M., *J. Catal.* **71**, 127 (1981).
12. Davis, S. M., and Somorjai, G. A., *J. Catal.* **65**, 78 (1980).
13. Anderson, J. R., "Structure of Metallic Catalysts," p. 451. Academic Press, New York, 1975.
14. Loew, O., *Ber. Dtsch. Chem. Ges.* **23**, 289 (1980).
15. Adams, R., and Shriner, R. L., *J. Amer. Chem. Soc.* **45**, 2171 (1923).
16. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **20**, 223 (1971).
17. Emmett, P. H., and Brunauer, S., *J. Amer. Chem. Soc.* **59**, 310 (1937).