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# The Surface Area of the Annealed Palladium Foil Catalyst as Determined by a Novel Method of Measuring a Small Surface Area

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In order to measure the small surface area of metal foils down to a few ten square centimeters by making use of gas adsorption, an apparatus was developed, which made it possible to estimate the amount of adsorbed xenon at 77.5°K from the desorption of the gas on the surface by moving the foil from the adsorbing bulb into the hot furnace; the change in the surface area of palladium foil catalysts which had been annealed at various temperatures was followed by the use of this method. The roughness factor, the ratio of the real surface area to the geometrical one, of the palladium foil decreased from 1.7 to 1.1 with the progress of annealing at 150—300°C, but it increased to 1.9 after heating at 400°C and then decreased again under treatment at high temperatures to 1.0 for 800°C. The chemisorption of carbon monoxide on the same foil catalyst, which is often used for the surface-area determination, was also studied, and the difference between the adsorbed states of the respective molecule on the palladium surface was briefly discussed in order to compare these methods.

In the study of the heterogeneous catalysis, the central problem has been to ascertain the relationship between the surface structure of a solid and its catalytic activity. Especially for the metal catalysts, it has been disputed by many researchers whether the catalytic reaction proceeds all over the surface of the catalyst or at special surface points, the so-called "active sites." In order to make the situation clear, the surface structure of foil or wire catalyst was changed by cold-working or by ion bombardments, and the effects of these treatments and of the successive annealing on the catalytic activities were studied.¹⁾ It was then found that the catalytic activity decreased rapidly with annealing in the temperature range where the lattice defects in metals would disappear; these defects were, therefore, supposed to be responsible for the catalytic activity as the active centers.²⁾ There is, however, an ambiguity in this proposition because of our little information on the real surface area of annealed foil; it is necessary to confirm the change in the surface area of metal in relation to the annealing temperature.

The use of the physical adsorption of nitrogen for determining the surface area of solids was established by Brunauer, Emmett, and Teller in 1938.³⁾ Recently this method has been extended to the measurement of a small surface area, such as a few hundred square centimeters, by making use of the low equilibrium pressures of krypton and xenon as adsorbates,⁴⁾ but the surface area of metal foils has only been estimated by a gravimetric method using the nitrogen adsorption.⁵⁾

Two essential difficulties in the measurement of the small surface area are that, when any volumetric method is used, the surface area of the adsorbing bulb is comparable to that of the metal foils, and that the area of the glass wall may change markedly with the thermal treatment.⁶⁾ To avoid these difficulties, the present authors have

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1) H. E. Farnsworth and R. F. Woodcock, *Advances in Catalysis*, **9**, 123 (1957).

2) I. Uhara, S. Kishimoto, T. Hikino, Y. Kageyama, H. Hamada and Y. Numata, *J. Phys. Chem.*, **67**, 996 (1963).

3) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

4) a) A. J. Rosenberg, *ibid.*, **78**, 2929 (1956). b) D. W. Aylmore and W. B. Jepson, *J. Sci. Instr.*, **38**, 156 (1961). c) P. Chenébault and A. Schürenkämper, *J. Phys. Chem.*, **69**, 2300 (1965).

5) T. N. Rhodin, *J. Am. Chem. Soc.*, **72**, 4343, 5691 (1953); **73**, 3143 (1951).

6) J. R. H. Ross and M. W. Roberts, *J. Catalysis*, **4**, 620 (1965).

developed an apparatus in which the amount of adsorbed gas can be measured from the desorption of the gas on the surface by transfer of the foil adsorbent from the adsorbing bulb to the hot furnace; the character and the accuracy of the method were studied by using a sample with a known surface area.

By the use of this apparatus, the surface area of the palladium foil catalyst, which is active for the acetylene hydrogenation and which had been annealed at various temperatures, was measured. The adsorbed state of the molecule on the surface will also be briefly discussed in comparison with the results of carbon monoxide chemisorption on the same foil catalyst.

## Experimental

**Apparatus.** A sketch of the apparatus used for the surface area measurements is shown in Fig. 1. It includes a high vacuum system, connections for introducing xenon, an adsorption system, and a McLeod gauge for purposes of calibration. Mercury vapor was cut off by the A trap, maintained at the temperature of liquid nitrogen; the adsorption system was protected from grease vapor by another trap, B, at the same temperature, and by a greaseless valve, and the pressure of the system was measured with pirani and ionization gauges.

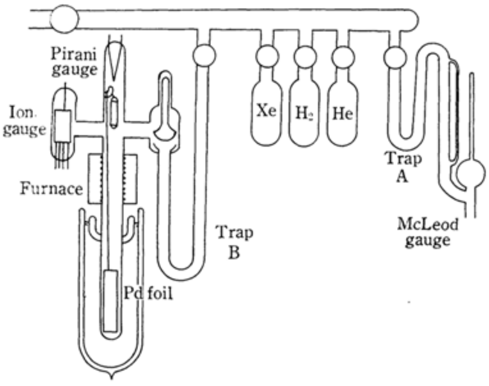

Fig. 1. Apparatus for surface area measurement.

The palladium foils were hung by quartz fibre (0.2 mm in diameter), which was then connected with tungsten wire (0.02 mm in diameter), and a piece of iron sealed in glass was attached to the other end of the wire, so that the foils could be moved by a magnet outside the apparatus. The adsorbing bulb, C, was designed to have a vacuum jacket, E, so that the temperature gradient on the wall where the adsorption occurs may not be sensitive to variations in the level of liquid nitrogen. The total geometrical area of the glass wall maintained at 77.5°K was estimated to be about 30 cm$^2$.

**Specimens.** The palladium foils obtained from Johnson, Matthey and Co., Ltd., 0.2 mm thick and more than 99.99% pure, were used in the form of stripes 0.7 cm wide and 9 cm long, with a total geometrical surface area of 44.6 cm$^2$. These foils were treated with hot concentrated nitric acid and then washed thoroughly. Prior to the measurement, the foils were reduced with 50 mmHg of hydrogen at 100°C and then annealed in a vacuum at various temperatures for 1 hr.

High-purity xenon, hydrogen, and helium, contained in glass cylinders, purchased from the Takachiho Chemical Co., were used without further purification.

**Procedure.** Prior to the adsorption study, the adsorption system, traps, and connecting glass tubing were baked at 400°C for several days unitl the residual pressure could be maintained below $1\times10^{-7}$ mmHg. First, the area of the glass wall cooled at 77.5°K was measured. In this case, xenon was introduced to a small ($10^{-3}$ mmHg) portion, and then the change in pressure was measured when the cold part was warmed to 100°C. For the measurement of the palladium foil, the foils were at first hung in an adsorbing bulb maintained at 77.5°K, and helium (about 2 mmHg) was introduced in order to accelerate the cooling of the palladium foil. After the foils had attained the equilibrium temperature, the helium was evacuated; then xenon was carefully introduced at the pressure of about $10^{-3}$ mmHg, as read with both the ionization and the pirani gauges. After a constant pressure had been achieved, the palladium foils were lifted up to a place inside the furnace maintained at 100°C, and the pressure increase was read with the pirani gauge. From this increase in the pressure, the amount of adsorbed xenon was evaluated, with the increase in adsorption on the wall due to the pressure change being corrected. This procedure was repeated several times at various xenon pressures in order to obtain adsorption isotherms.

**Calibrations.** The dead-space volumes of the whole apparatus and the adsorbing bulb maintained at the temperature of liquid nitrogen were $133.3\pm0.1$ cc and $11.0\pm0.1$ cc at 26°C. On the assumption that the average cubical expansion coefficient of molybden glass is $4.0\times10^{-6}$, the volume was reduced by only 0.1% as the adsorbing bulb was cooled at 77.5°K.

The ionization and the pirani gauges were calibrated with the McLeod gauge. In the former calibration, the effect of the diffusion due to the stream of mercury vapor coming from the McLeod gauge to the A trap was corrected by the use of Ishii and Nakayama's formula,[7] but the correction was not done for the latter because the pirani gauge was used in the high pressure range of $10^{-2}$ mmHg. The pumping action by the ionization gauge was found to cause no appreciable error in the measurement of the equillibrium pressure or, therefore, in the estimation of the adsorbed amount.

**Corrections for Thermal Transpiration.** Since the adsorbing bulb and the gauges were maintained at widely different temperatures and since the diameter of the adsorbing bulb (10 mm) was of the same order as the mean free path of xenon, corrections for the thermal transpiration were needed. The general empirical equation for the correction of thermal transpiration across a single connection has been obtained by Takaishi and Sensui.[8] Moreover, the corrections

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7) H. Ishii and K. Nakayama, *Shinkuu*, **4**, 414 (1961).

8) T. Takaishi and Y. Sensui, *Trans. Faraday Soc.*, **59**, 2503 (1963).

9) H. H. Podgruski and F. N. Davis, *J. Phys. Chem.*, **65**, 1343 (1961).

for the thermal transpiration of xenon were estimated in detail by Podgruski and Davis.⁹⁾ Those results were used in the present corrections for xenon pressures.

## Results and Discussion

**Adsorption Isotherms.** The adsorption isotherm for the glass wall of the adsorbing bulb was determined first by plotting the volume of the adsorbed xenon, $V$, at S. T. P. as a function of the equilibrium pressure, $P$, as is shown in Fig. 2. The adsorption on the quartz bulb was also measured; it was found that the surface of quartz is more porous than that of molybden glass, and that the surface area changed greatly with evacuation at high temperatures. Therefore, in order to measure a surface area of the order of a few square centimeters, it was necessary to avoid heating the foils in the adsorbing bulb, and the foils were annealed in a place just above the bulb, by pulling up the foils with a magnet.

The surface area of $\alpha$-alumina was estimated by applying the B. E. T. method of both nitrogen and xenon adsorption. Figure 2 shows the isotherm of xenon obtained for $\alpha$-alumina.

**Evaluation of the Surface Area.** The surface area was evaluated by the use of the current B. E. T. method.

Since the B. E. T. equation is applicable in the range of relative pressures ($P/P_0$) from 0.05 to 0.35, the present experimental conditions were chosen.

The B. E. T. plots obtained from the xenon adsorption isotherms of Fig. 2 are shown in Fig. 3. By taking the value for the xenon area at the temperature of liquid nitrogen as $\sigma_{Xe}=25$ Å$^2$ (the average value proposed in the literature¹⁰⁾), the surface area is given by the relation $S=6.7\times 10^4 V_m$, when $S$ is expressed as cm$^2$ and $V_m$, the monolayer volume, as cm$^3$ (S. T. P.). The values of the B. E. T. parameters $C$ and $V_m$, the surface area obtained from Fig. 3, and the results from the nitrogen adsorption at 77.5°K on $\alpha$-alumina are summarized in Table 1. In these evaluations, $\sigma_{N_2}$ is assumed to be approximately the same on all adsobents 15.4 Å$^2$ at 77.5°K¹¹⁾ which is the best value on both experimental and theoretical grounds. As Table 1 shows, the surface areas of $\alpha$-alumina obtained from nitrogen and xenon

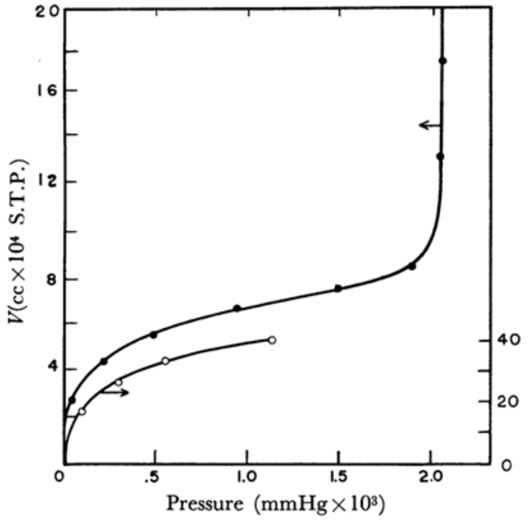

Fig. 2. Adsorption isotherms for the bulb wall (●) and $\alpha$-alumina (○) at 77.5°K.

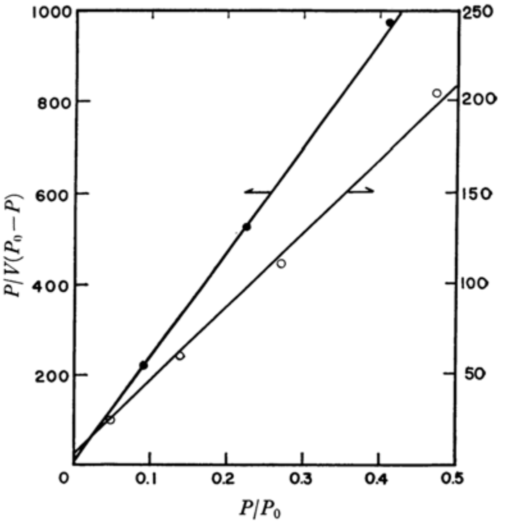

Fig. 3. B. E. T. plots for xenon adsorption. ● the bulb wall, ○ $\alpha$-alumina

Table 1. Results of surface area measurements on glass, $\alpha$-alumina and palladium foil

| Adsorbent | $C$ | $V_m$(STP) cm$^3$ | Surface area cm$^2$ | Geometrical surface area cm$^2$ |
|---|---|---|---|---|
| Adsorbing bulb (Xe) | 41 | $4.88\times10^{-4}$ | 32.6 | 30.1 |
| $\alpha$-Alumina (Xe) | 46 | $2.78\times10^{-3}$ | 186 | — |
| $\alpha$-Alumina ($N_2$) | 81 | $5.25\times10^{-3}$ | 197 | — |
| Pd foil* (Xe) | | $7.18\times10^{-4}$ | 48.0 | 44.6 |
| Pd foil* (CO) | | $5.3\ \times10^{-4}$ | 17.0 | 44.6 |

*. Annealed at 800°C.

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10) W. A. Cannon, *Nature*, **197**, 1000 (1963).

11) H. K. Livingston, *J. Colloid Sci.*, **4**, 447 (1949).

adsorptions are 197 cm²/g and 186 cm²/g respectively. Since the volume of the adsorption system can be measured within an error of 1%, and since pressure measurements with a precision of 5% are quite feasible in the $10^{-3}$—$10^{-4}$ mmHg range, the error in the calculated value of surface area was estimated to be within 6% for areas of several tens of square centimeters, and less than 10% even for that of only a ten square centimeters. Therefore, those values are in agreement within the range of experimental error, and we can safely use this method with the same order of accuracy as the current B. E. T. method.

In comparison with the method of Chenébault and Schürenkämper, in which the adsorbate molecule is labelled by the radioactive isotope, the present method is advantageous in that it uses only the conventional technique at low pressures.

**The Surface Area of the Palladium Foil Catalyst.** The adsorption isotherms of xenon for palladium foil catalysts annealed at 150, 200, and 300°C are shown in Fig. 4. The figure shows that about 90% of the amount of xenon required to form a monolayer has been adsorbed at $P/P_0$ 0.05. This compares with a $P/P_0$ value of 0.005 for complete coverage with xenon on tungsten films.[12] The $C$ value in the B. E. T. equation decreased from 286 to 147 when the annealed sample at 150°C was heat-treated at 300°C. Figure 5 shows the change in the roughness factor, the ratio of the real surface area to the geometrical area, of the palladium foil catalyst due to annealing. The surface area of the foil catalyst increased with annealing at 400°C, and then decreased with annealing above 600°C. The decrease in the surface area with the progress of annealing between 150—300°C was attributed to the sintering of the surface, while the increase in the area with annealing at 400°C may occur because of a structural change in the palladium foil, such as those due to thermal etching of the surface. However, there is another possibility, that the hydrocarbon which remained on the surface after reduction is carbonized by the annealing at 400°C, so that the surface roughness seems to be increased. In order to distinguish these effects, it is necessary to carry out an experiment without any contamination by hydrocarbon; the specimens have to be treated in a clean vacuum at a high temperature and then cold-worked under similar conditions. Therefore, final decision must be reserved until these advanced experiments can be performed.

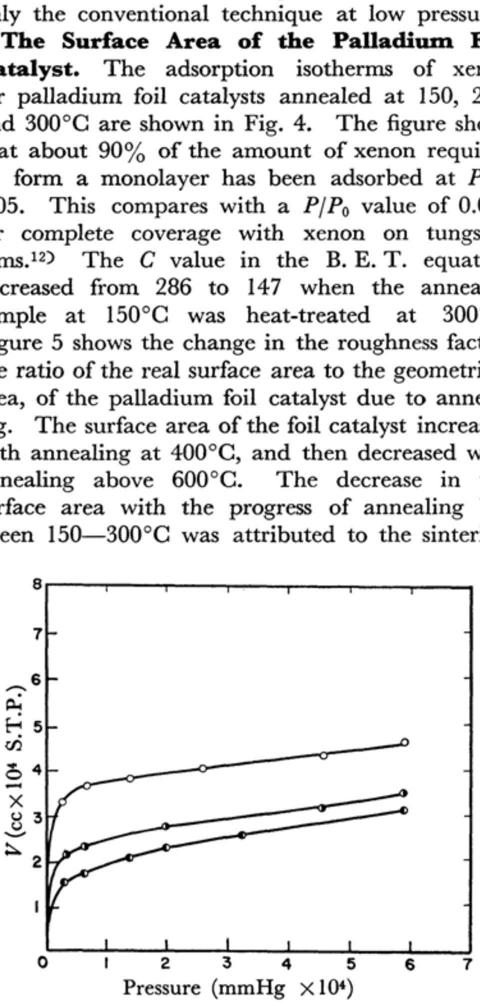

Fig. 4. Adsorption isotherms of xenon on annealed palladium foil.
Annealing temperature:
150°C (○), 200°C (◑), 300°C (◐)

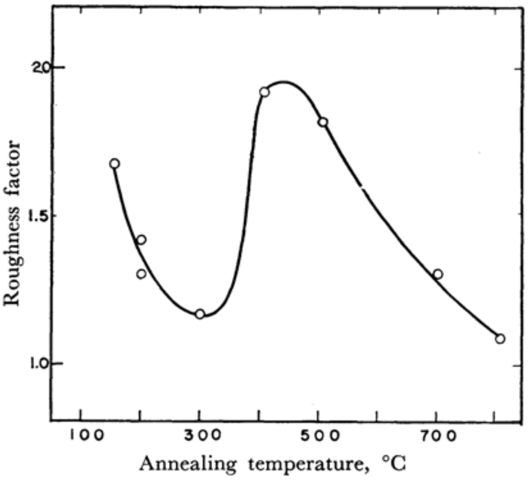

Fig. 5. Roughness factor of palladium foil annealed at various temperatures.

**Chemisorption of Carbon Monoxide.** As an alternative method of estimating the surface area of metals, the chemisorption of carbon monoxide has been used because of its high adsorbability on palladium. Taylor and McKinney have noted that the heat of chemisorption at full coverage on palladium black is 15 kcal/mol.[13] Stephens has found that a rapid chemisorption of carbon monoxide occurs on palladium film up to a coverage of $\theta=0.95$ at room temperature and a pressure of $10^{-2}$ mmHg.[14] Hence, the equilibrium of chemisorption leans heavily toward the side of the adsorbed phase at room temperature.

Figure 6 shows the adsorption isotherms of carbon monoxide at 20, 70, and 100°C obtained on the palladium foil annealed at 800°C. The adsorption volumes obtained by the extrapolation were 5.3, 4.6, and $4.4\times10^{-4}$ cc (S. T. P.) at 20, 70, and 100°C respectively. According to Scholten and Montfoort,[15] the surface area of the foil

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[12] J. R. Anderson and B. G. Baker, *J. Phys. Chem.*, **66**, 482 (1962).

[13] H. S. Taylor and P. V. McKinney, *J. Am. Chem. Soc.*, **53**, 3610 (1931).

[14] S. J. Stephens, *J. Phys. Chem.*, **63**, 188 (1959).

[15] J. J. F. Scholten and A. Van Montfoort, *J. Catalysis*, **1**, 85 (1962).

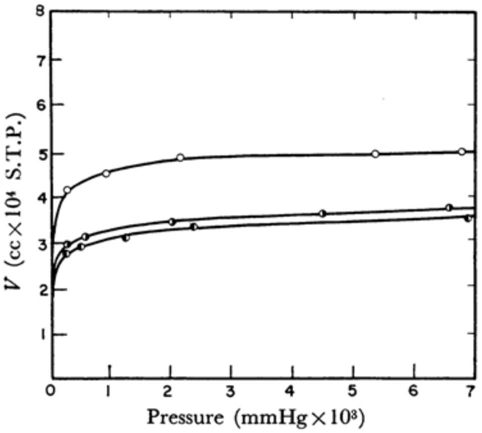

Fig. 6. Adsorption isotherms of carbon monoxide on annealed palladium foil; annealing temperature: 800°C.
○ 20°C, ◑ 70°C, ◐ 100°C

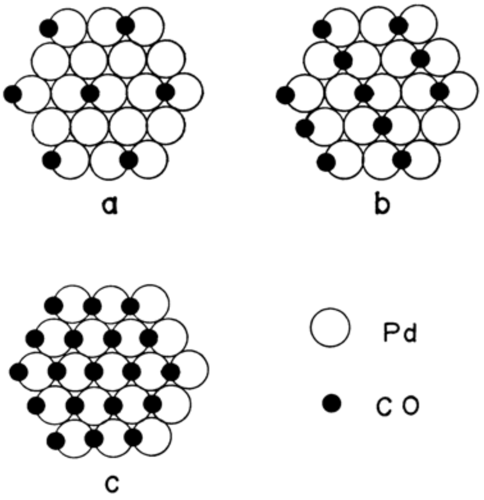

Fig. 7. Regular patterns of adsorbed carbon monoxide on (111) plane of palladium.

catalyst was, therefore, calculated to be 17.0 cm$^2$ from the value at 20°C, provided that $8.6\times10^{14}$ molecules of carbon monoxide form a monolayer per 1 cm$^2$ of palladium. The value will increase to 29.4 cm$^2$ if it is assumed that the (111) plane was only exposed on the surface and that each CO molecule was chemisorbed on two adjacent palladium atoms in the bridged form, as was proposed by Eischens *et al.*[16]

However, those values are still small compared with that obtained from the B. E. T. analysis of xenon adsorption, 48 cm$^2$. A similar difference was also found in the case of the supported palladium catalyst; this fact was explained as the retardation of carbon monoxide adsorption by the presence of preadsorbed hydrogen.[15,17] However, there is no appreciable amount of hydrogen on the surface in the present case, because of the evacuation at 800°C. It may, then, be suggested that CO adsorption did not form a complete monolayer under the present pressures, but reached only a certain limited saturation. Although the surface structure of the palladium foil has not yet been precisely established, if the exposed surface of an annealed foil is supposed to be a (111) plane, as is suggested by the preliminary study of electron diffraction, there are several regular patterns of adsorbed carbon monoxide on the plane which incorporate the above consideration; some of them are shown in Fig. 7. If carbon monoxide was adsorbed in the form shown in Fig. 7(a), where four palladium atoms are required to hold each molecule, the surface area of the palladium foil catalyst may be estimated to be 37 cm$^2$, which approaches the value obtained by the xenon adsorption. Under the pressure of $10^{-3}$ mmHg, the chemisorption of carbon monoxide in the form of Fig. 7(a) will come to saturation, but at higher pressures other adsorbed state, such as those shown in (b) or (c), may occur to increase the total amount of adsorption. This consideration suggests that the application of chemisorption to surface-area determination has an essential limitation in its nature and that special attention must be paid to the ratio of the so-called "active" surface to the total surface.

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[16] R. P. Eischens, S. A. Francis and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956).

[17] T. Kabe and I. Yasumori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 410 (1964).