JOURNAL OF CATALYSIS 17, 272–275 (1970)

NOTES

The Rapid Measurement of Small Surface Area by Xenon Adsorption

In the studies of catalysis by solid surfaces, the solids are often used in the form of evaporated films or foils, and thus surface areas are usually small, 10–100 cm^2. In these cases, the precise measurement of such small surface areas is required. Many approaches to small surface area determination have been attempted by means of volumetric (*1–6*) and gravimetric (*7*) methods. For a volumetric method, it is suitable to apply krypton (*1–3*) or xenon (*4–6*) as the adsorbate, since their saturation vapor pressures are rather small at the temperature of boiling nitrogen (78°K). With most of the suggested methods, however, it usually takes several hours to obtain a BET plot, because of the difficulty of controlling the gas introduction and of requiring the fairly long time for cooling specimens to liquid nitrogen temperature. The present authors have developed an apparatus by which the BET plots can be obtained in only half an hour or less, by using ordinary xenon adsorption.

A block diagram of the apparatus used for area determination is shown in Fig. 1. The apparatus includes a vacuum system capable of obtaining a pressure of 10^{-9} Torr by means of a sputter ion pump and two pressure measuring portions separated by a variable leak valve, these portions being denominated as "adsorption cell" and "reference cell," respectively. The volume of each cell was determined to be 250 and 160 cc by means of the gas expansion method. The amount of the adsorbent gas introduced into the adsorption cell can be measured by the pressure change in the reference cell only by handling the variable leak valve without any other performance. High-purity xenon (>99.9%) contained in a glass cylinder was used after distillation at liquid nitrogen temperature. Helium in a commercial container, passed through silica gel and active carbon traps in liquid nitrogen, was stored in a reservoir. The detailed procedure is given as follows. After the specimen was outgassed until the residual pressure was below 1×10^{-7} Torr at 350°C, helium (about 10 Torr) was introduced to accelerate cooling of the specimen and then,

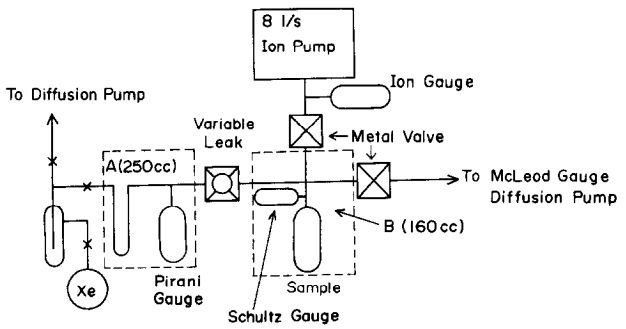

FIG. 1. Block diagram of the apparatus.

TABLE 1
RESULTS ON GLASS SURFACES

Source of results	C	V_m ($\times 10^4$ cc STP)	Surface area (cm^2)	Geometric surface area (cm^2)	Roughness factor
This work	54	6.95	46.7	40	1.17
	39	4.24	28.6	23	1.24
	49	3.73	25.2	22	1.14
P. Chénebault *et al.* (*4*)	24	0.595	4	4.1	1
T. J. Adams *et al.* (*5*)			3.4	3.5	1
T. Kabe *et al.* (*6*)	41	4.88	32.6	30.1	1.08

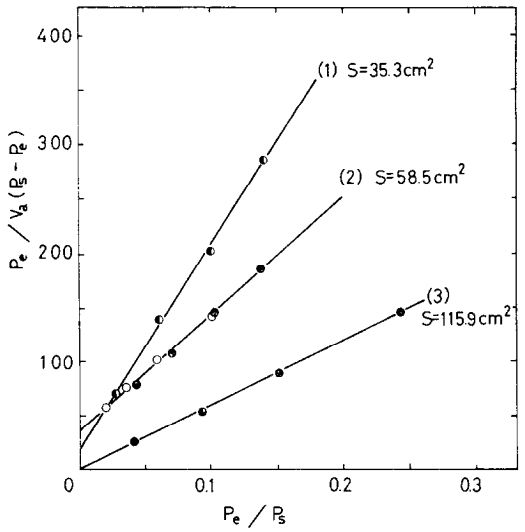

FIG. 2. BET plots for several specimens: (1) quartz, (2) glass, (3) copper-nickel alloy (80% Cu). The alloy was treated at 300°C, 2 hr in hydrogen (16 Torr) after oxidation at 500°C, 1 min in oxygen (2.3 Torr).

after pumping of the helium, xenon gas was admitted carefully into the adsorption cell from the reference cell in which it had been stored in a pressure range of $1–3 \times 10^{-2}$ Torr; i.e., $2–5 \times 10^{-3}$ cc STP. Changes in the pressure of each cell with adsorption were detected by two gauges with a recorder. After a constant pressure in the adsorption cell had been achieved in one adsorption experiment, xenon under higher pressure was added repeatedly. Thus, it only takes half an hour to obtain a BET plot with four or five points, because an adsorption equilibrium can be achieved in a few minutes.

Several examples of BET plots thus obtained are shown in Fig. 2. By replicate measurements, reproducibility in the determination of the surface area was found to be better than 10%. Some of these results, together with those of others working with glass surfaces, are summarized in Table 1. The roughness factor of the glass surfaces obtained by the author's method shows a fairly good agreement with those obtained by other workers.

It is emphasized that the size of the surface area can be determined precisely in only half an hour by this method, which is extremely more rapid than by those reported previously.

REFERENCES

1. ROSENBERG, A. J., *J. Amer. Chem. Soc.* **78**, 2929 (1956).
2. ALYMORE, D. W., AND JEPSON, W. B., *J. Sci. Instrum.* **38**, 156 (1966).
3. MEYER, D. E., AND WELLS, J. M., *J. Colloid Interface Sci.* **22**, 503 (1966).
4. CHÉNEBAULT, P., AND SCHÜRENKÄMPER, A., *J. Phys. Chem.* **69**, 2300 (1965).
5. ADAMS, T. J., SHERWOOD, T. N., AND SWINTON, F. L., *J. Chem. Soc.* (A) 1195 (1966).
6. KABE, T., MIZUNO, T., AND YASUMORI, I., *Bull. Chem. Soc. Jap.* **40**, 2047 (1967).
7. RHODIN, T. N., JR., *J. Amer. Chem. Soc.* **72**, 4343 (1950).

KUNIAKI WATANABE
TOSHIRO YAMASHINA

Department of Nuclear Engineering
Faculty of Engineering
Hokkaido University
Sapporo, Japan
Received September 19, 1969