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Precision Evaluation in Kr Adsorption for Small BET Surface Area Measurements of Less Than 1 m^2

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Abstract. A volumetric Kr-adsorption apparatus using a precise capacitance manometer has been developed. A specially designed adsorption cell (CVC: constant volume adsorption cell) utilizing a vacuum jacket (Joyner et al., 1949) is adopted to keep the adsorption cell volume constant regardless of the variation in liquid nitrogen level throughout the experiment. Using the CVC, the pressure change in accordance with liquid N_2 supply cycle has been minimized to less than 0.01 Pa compare to about 1 Pa for conventional cell. Time dependent change of the adsorption cell volume and repeatability in its measurements have been demonstrated in detail using helium gas. Good linearity of the BET plot of the Kr adsorption isotherm on several hundred cm^2 samples are demonstrated in the relative pressure range from 0.05 to 0.35.

Keywords: Kr adsorption, BET surface area, vacuum jacket, constant volume adsorption cell

1. Introduction

The BET theory (Brunauer et al., 1938) has been used in the field of powder industry as a means for routine measurements of solid surface area. Nitrogen is commonly used as an adsorbate for surface area measurements of several tens of m^2. In the electronics industry, for example, for process technology development and reliability improvement, gas adsorption measurement is an effective tool for characterizing the fine structure of thin film materials which compose the electronic devices. However, in this case, surface area of several hundred cm^2, (that is, two orders of magnitude smaller than that of powder materials) should be investigated. Therefore, for measuring electronic devices, a highly sensitive gas adsorption method must be developed, and its precision evaluation is important issue. Using gasses with lower saturated vapor pressure has found to be effective method to measure small surface area by BET method. According to this strategy, we can find several reports using Kr (Beebe et al., 1945, ASTM D32-4708, Takei and Chikazawa, 1998) and Xe (Suzuki and Oosawa, 1997) in literature. We feel that discussion on measurement precision is rather difficult even though it becomes more important in small surface area measurements. So, in this report, we will show crude adsorption data in detail aiming to contribute further discussion. In this study, Kr is adopted for volumetric apparatus with constant volume adsorption cell (CVC).

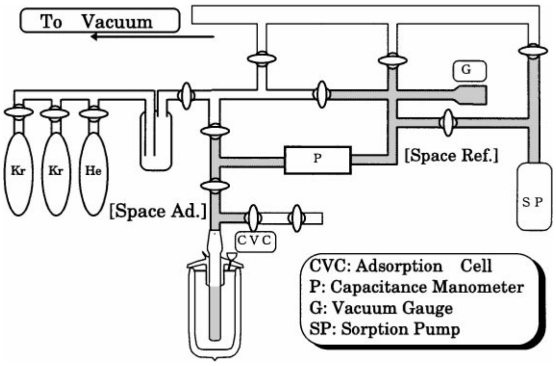

Figure 1. Diagram of home-made Kr adsorption apparatus.

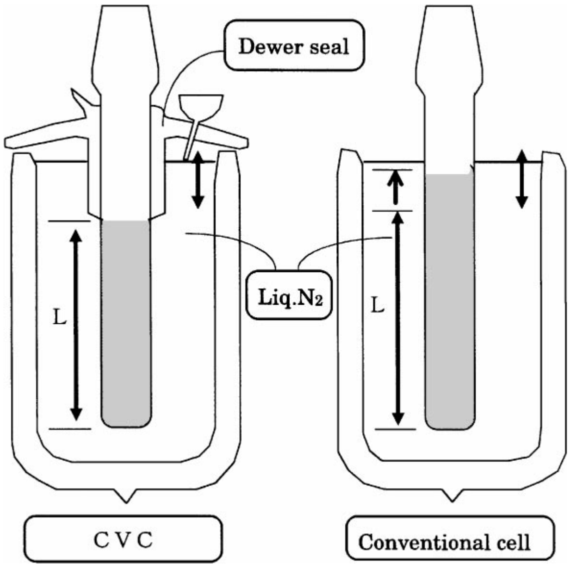

Figure 2. Detailed cross section of home-made adsorption cell. (CVC: constant volume adsorption cell)

2. Experimental

Adsorption Apparatus

Figure 1 shows a diagram of our home-made adsorption apparatus. It is made of all glass and is equipped with differential-type capacitance manometer, P (Datametrics, electronic manometer). Glass stop cocks were used with Apiezon grease. The apparatus was evacuated using an oil diffusion pump and built-in sorption pump, SP, to the highest vacuum of 4×10^{-5} Pa. Background pressure was monitored by a conventional emission vacuum gauge G, and during the adsorption measurements, the reference pressure at Space Ref. in the diagram was kept below 1.3×10^{-4} Pa by using the sorption pump. Kr and He were supplied through a liquid N_2 trap for purification in each adsorption run. The adsorption cell is connected to the manometer through the Space Ad.

The adsorption cell is specially designed one named CVC, which is shown in Fig. 2 in comparison with conventional one. In this report we refer to this cell as CVC, standing for a constant volume adsorption cell. It features a vacuum jacket mounted at the neck which keeps the adsorption cell volume (shaded part, 1.7 cm in diameter and 10 cm long which was kept at liquid N_2 temperature for adsorption measurements) constant regardless of the difference in liquid N_2 level. As shown by both direction arrows in Fig. 2, the liquid N_2 level varies according to an evaporation/supply cycle. This variation directly affects the adsorption cell volume of the conventional cell. Contrary to this, in case of CVC, because the vacuum jacket thermally isolates the adsorption cell from the liquid N_2, only the shaded part is cooled. When we control the liquid N_2 level within the vacuum jacket part as illustrated in Fig. 2, its level variation does not affect the adsorption cell volume. In addition to this, to suppress the evaporation of liquid N_2, the top part of the vacuum jacket was designed as an umbrella, providing a cap for the liquid N_2 vessel (see Fig. 2). The effectiveness of this method is demonstrated in the Results and Discussion section below. The CVC is made of quartz to allow the sample to be heat treated at above 500°C if needed.

Dead Space Volume Calibration

As is well known, in volumetric adsorption measurement, the dead space volume of the adsorption cell should be precisely calibrated. It is known that the variation in liquid N_2 level strongly affects the dead space volume. Two series of experiments using He gas were carried out as follows. The first series investigated the pressure change, which reflects the change in adsorption cell volume caused by the variation in liquid N_2 level. A defined amount of He gas was introduced into the adsorption cell, and then the cell was cooled with liquid N_2 supplied every 6 minutes into the outer vessel (see Fig. 2). And the pressure of He was measured every 30 seconds and plotted against time. The adsorption cells tested were two kinds of CVC and a conventional cell for comparison. The second series of experiments was repeated measurements of dead space volume of CVC in order to demonstrate repeatability. The dead space is shown in Fig. 1 as Space Ad. (shaded) +

connection (shaded) + CVC with liquid N_2 cooling. The room temperature of the laboratory was controlled to 18 ±2°C throughout the adsorption experiments.

Kr Adsorption Isotherm and BET Analysis

Silicon powder was used as a standard sample for Kr adsorption. Various amount of Si powder, ranging from 1.5 to 6 g, were tested using CVC. In the BET analysis, the saturated vapor pressure of Kr at 77 K and the adsorption cross section of Kr were cited from literature (Gregg, 1967) as 1.767 Torr (235.6 Pa) and 19.5 Å^2 (1.95×10^{-15} cm^2), respectively. In one adsorption experiment, aiming to confirm the applicability of BET theory, 15 data points were measured in the range of equilibrium pressure of from 0.0036 to 0.52 in relative pressure.

In order to evaluate our method, the detection limit, and its repeatability, we carried out several Kr adsorption isotherm measurements on the CVC itself with no samples. To change the surface area to be measured, four CVCs with different adsorption cell lengths of 5, 10, 15, and 20 cm (shaded part in Fig. 2), were tested. The inner diameter of the CVC is 1.7 cm. The adsorption procedure was a conventional one and was performed in the equilibrium pressure range from 12 to 80 Pa measuring at least 6 points. Before the Kr adsorption, the dead space volume was measured using He after thermal equilibrium was reached in 20 minutes. Then He was evacuated keeping the adsorption cell at liquid N_2 temperature. In each Kr adsorption, the pressure reading became constant within 3 minutes after introduction of Kr to the adsorption cell, so Kr pressure was measured 5 minutes after its introduction.

3. Results and Discussion

Dead Space Volume Calibration

Figure 3 demonstrates the effectiveness of CVC. A defined amount of He gas was introduced into the Space Ad + CVC (Fig. 1). Then the cell was cooled with liquid N_2, and the He pressure was measured every 30 seconds. The first pressure was measured at 98.60 Pa by the manometer P, and followed pressures were plotted against time as denoted as curve a in Fig. 3. For comparison, a similar result using a conventional cell, without vacuum jacket, is shown in the same figure as curve c. The pressure readings in the conventional cell, curve c, are varied with liquid N_2 supply interval (every 6 minutes) with about 1 Pa variation. This result shows that the conventional adsorption cell volume was varied with liquid N_2 level variation. Contrary to this, for the CVC, as shown by curve a, in the first 18 min. the pressure readings gradually decreased to a value of 95.03 Pa then remained constant, any variation in pressure reading was detected in the manometer P, regardless of the liquid N_2 supply interval. This means that in the first 18 min. the adsorption cell was cooled down to the temperature of 77 K then reached an equilibrium. Curve b in the same figure shows an identical result for another CVC. The difference in the two CVCs is the length of the vacuum jacket, 6 and 3 cm for a and b, respectively. Curve b shows an intermediate behavior between a and c, which means the vacuum jacket length of 3 cm is not sufficient to avoid the effect of varying liquid N_2 level. From these experiments, we adopted the CVC with a 6-cm vacuum jacket shown in Fig. 2 throughout this work. And measurements of dead space volume were conducted 20 min. after the first introduction of He. Then after the second introduction of He, 5 min. was sufficient to reach equilibrium.

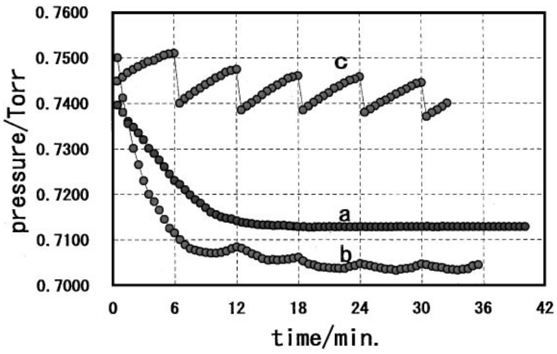

Figure 3. Adsorption cell volume change versus time. Effect of the liquid nitrogen level variation.

Repeatability in Dead Space Volume Measurements

Dead space volume measurements were carried out for 28 runs. The CVC used has an adsorption cell 1.7 cm in diameter and 10 cm in length with an umbrella shaped vacuum jacket of 6 cm long. The average dead space volume is 149.5 cm^3, with the standard deviation $\sigma = 0.32$ cm^3. For comparison, identical experiments were performed, with a conventional adsorption cell for 19 runs, and gave an average of 130.1 cm^3 with $\sigma = 0.78$ cm^3.

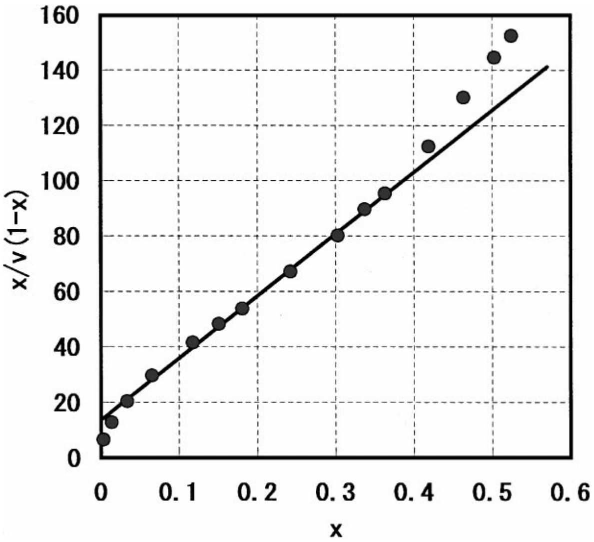

Figure 4. A typical example of a BET plot.

Kr Adsorption Isotherm and BET Analysis

A typical BET plot which was obtained from a Si powder sample, is shown in Fig. 4. The data in the relative pressure range from 0.05 to 0.35 lie on a straight line. This result is consistent with the applicability of the BET theory (Kantro et al., 1964). The surface area obtained is 1,309 cm^2 and the specific surface area is 222.4 cm^2/g. The BET constant C is calculated as 16.

The measured BET surface areas from other experiments are plotted against the sample weight in Fig. 5. Here, three data on the ordinate show the maximum, the average and the minimum value of the inner surface area of the CVC. The straight line shows

$$S_{\text{BET}} = 222.4 \times \text{Sample Weight} + 65.8, \quad (1)$$

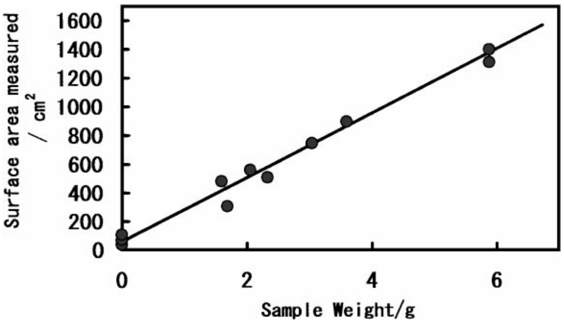

Figure 5. BET surface area of Si powders.

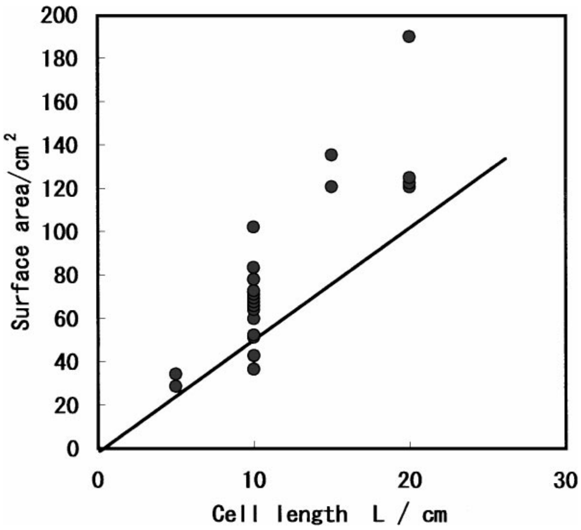

Figure 6. BET surface area of inner surface of CVC with different cell lengths.

where 222.4 is the specific surface area in cm^2 obtained from the experiment shown in Fig. 4, and 65.8 cm^2 is the average inner surface area of the CVC obtained from the 16 adsorption runs. The maximum deviation of 140 cm^2 from the straight line is observed for the data at a sample weight of 1.7 g and a surface area of about 400 cm^2. From this result, we estimated the detection limit of our method as 400 cm^2.

The inner surface area measurements of the CVC are summarized in Fig. 6, which plots surface area versus length of the adsorption cell L (see Fig. 2). The fact that the measured surface areas range from 25 to 200 cm^2 is unreasonable because we had just mentioned that the detection limit is 400 cm^2. However, we dare to show the crude data. The surprising thing is that all BET plots have very good linearity as shown by the two representative examples in Fig. 7. However, the scatter of the surface areas is fairly large; for example, the surface areas of the CVC with a 10-cm long adsorption cell is varied from 36.5 to 102 cm^2 (with the average value of 65.8 cm^2) in the 16 adsorption experiments. The C values are distributed from 9 to 27 and show no correlation with the surface area. Good linearity of the BET plot is not sufficient to show the reliability of surface area measurements in the range smaller than 400 cm^2. Further analysis should therefore be done to explain this deviation.

At present, the data reported here show that we can measure the BET surface area of several hundred cm^2,

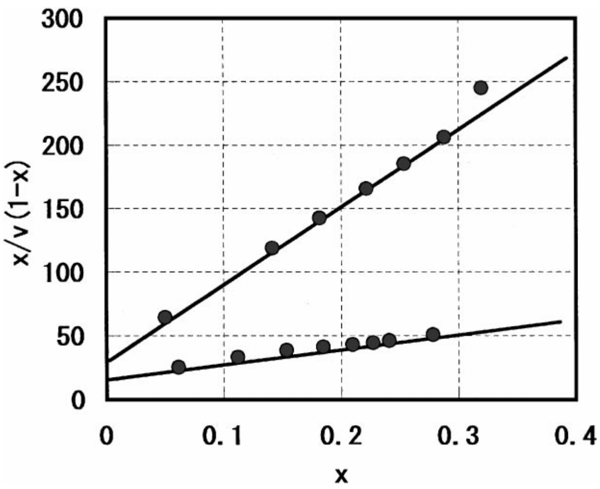

Figure 7. Examples of BET plots for CVC inner surface area measurements.

larger than 400 cm^2, by Kr adsorption with an accuracy of about ±10%.

4. Conclusion

Usefulness of the constant volume adsorption cell in pressure measurement was experimentally demonstrated. The pressure change in accordance with liquid N_2 supply cycle has been minimized to less than 0.01 Pa, which is two orders of magnitude smaller than that of conventional adsorption cell. The combination of this adsorption cell and a capacitance manometer enables precise measurement in the pressure range required for the BET analysis of Kr adsorption isotherm. As a result, the BET plot of Kr adsorption isotherm showed good linearity. This work showed the possibility to measure the BET surface area as small as 400 cm^2 with an accuracy of about ±10%.

Acknowledgments

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