JOURNAL OF CATALYSIS 155, 163–165 (1995)

NOTE

Direct Determination of Effective BET-Area of Xe, Kr, and CH_4

The surface area by adsorption is obtained by multiplying the product of the number of adsorbed molecules and the effective area per molecule. The absolute value of the effective area of Xe or Kr is important because the surface area estimated from the gas uptake of Xe or Kr can be compared with the geometrical surface area to give the roughness factor (1).

The effective area of the adsorbed molecules could be estimated from the density of the adsorbate in the bulk liquid or solid state (2). However, there is no certainty that the monolayer packing will be the same as in the bulk. The effective area can be larger than the value expected from the van der Waals size of the adsorbed molecule, if the interaction energy between the adsorbed molecule and the surface is periodic across the surface and is larger than RT (3).

For example, the one-dimensional expansion coefficient of Xe adsorbed on NaCl was found to be strongly increasing above 55 K and exceeded by far the value for bulk Xe at these temperatures using LEED and AES techniques (4). The purpose of the present paper is to determine the effective area σ of adsorbates such as Xe, Kr, and CH_4 by using the known area S of steel balls in the equation,

$$\sigma = (22414/V_m)\,(S/N_0), \qquad [1]$$

where V_m and N_0 are the BET monolayer volume in STP cm^3 and Avogadro's constant, respectively.

Ten thousand steel ball bearings obtained from AKS Inc., Japan were used as a substrate. The diameter and roughness of the balls were reported to be 0.9988 mm and 0.005 μm, respectively. The total surface area S of the balls amounted to 314 cm^2, assuming that the balls were spherical with diameters of 0.9988 mm.

The adsorption isotherms of Xe, Kr, and CH_4 were measured volumetrically. The Xe adsorption experiments were carried out with a metal apparatus equipped with a glass adsorption cell and a micromanometer (5, 6). The Kr adsorption experiments were carried out with a conventional glass apparatus equipped with another micromanometer (7).

The CH_4 adsorption experiments were carried out with a temperature-compensated, differential tensimeter (7). This apparatus reduces measurement uncertainties due to fluctuations in temperature. It consists of a differential micromanometer whose two arms are connected to a pair of sample and reference cells for dosing gas into sample and reference cells nearly equal in volume. Surface areas as small as 1000 cm^2 can be measured through volumetric measurements of nitrogen uptake at liquid nitrogen temperature.

The nonlinear response of each micromanometer was numerically determined from the data gathered by expanding helium into another vessel at a constant temperature (6).

The amount adsorbed is given by the difference between the amount of adsorbate gases admitted and the amount remaining in the gas phase. The amount adsorbed, V', in the single dose is given by the equation

$$V' = (22414/RT_1)\,(p_1^{(1)}V_A + p_1V_{B1} + p_2V_{B2} - p_1^{(2)}(V_A + V_{B1}) - p_2^{(2)}V_{B2}), \qquad [2]$$

where V_A, V_{B1}, and V_{B2} are the (apparent) dead-space volume of the buret kept at room temperature T_1, of the upper part of the adsorption cell kept at T_1, and of the lower part of the adsorption cell kept at liquid nitrogen temperature T_2, respectively (5). The pressures $p_1^{(1)}$, $p_1^{(2)}$ and $p_2^{(2)}$ represent the pressure in the buret at T_1 before the Xe expansion, the pressure in the adsorption cell at T_1, and the pressure at T_2 after the expansion, respectively. The pressures p_1 and p_2 are the pressure in the adsorption cell at T_1 and in the adsorption cell at T_2 remaining in the previous dose.

The accumulated adsorption amount V is given by the summation of the single doses, V' in Eq. [2].

The vapor pressure of Xe in the adsorption cell at liquid nitrogen temperature is around 0.3 Pa. The BET adsorption experiments are carried out at the equilibrium pressures ranging from 0.01 to 0.1 Pa. At these low pressures, the pressure $p_1^{(2)}$ at T_1 and the pressure $p_2^{(2)}$ at T_2 are not equal to each other even in equilibrium because of the

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TABLE 1

Xe Adsorption Run with Steel Balls at Liquid Nitrogen Temperature

Dose	p_1 (Pa)	p_2 (Pa)	$p_1^{(1)}$ (Pa)	$p_1^{(2)}$ (Pa)	$p_2^{(2)}$ (Pa)	V' (10^{-3} cm^3)	V (10^{-3} cm^3)
1	0	0	4.9583	0.0147	0.0079	1.97	1.97
2	0.0147	0.0079	1.7314	0.0277	0.0152	0.67	2.64
3	0.0277	0.0152	1.7209	0.0440	0.0247	0.66	3.30
4	0.0440	0.0247	1.6007	0.0613	0.0352	0.60	3.91
5	0.0613	0.0352	1.7382	0.0986	0.0589	0.63	4.54
6	0.0986	0.0589	2.1448	0.1394	0.0862	0.78	5.31
7	0.1394	0.0862	1.4806	0.1758	0.1118	0.50	5.81

Note. p_0 = 0.3808 Pa, T_1 = 295.35 K, T_2 = 79.83 K, V_A = 43.80 cm^3, V_{B1} = 51.35 cm^3, V_{B2} = 28.48 cm^3.

thermal transpiration effect (8). Therefore the dead-space volume, V_{B1}, of the adsorption cell kept at T_1 and the volume, V_{B2}, kept at T_2 must be determined separately in the Xe adsorption experiments.

The dead-space volumes, V_{B1} and V_{B2}, with two different temperatures were determined by the He expansion method in the low pressure range (5). The pressures $p_2^{(2)}$ could not be determined directly with the micromanometer kept at room temperature T_1 and were calculated by an empirical equation (8) with $p_1^{(2)}$.

The vapor pressure of Xe was determined by the micromanometer in consideration of the thermal transpiration effect. The temperature T_2 of the liquid nitrogen was calculated from the vapor pressure of Xe with the Clapeyron–Clasius values in the literature (9).

Table 1 summarizes the experimental data, from a single run, on the adsorption of Xe over the steel balls at liquid nitrogen temperature. The ratios, $p_2^{(2)}/p_1^{(2)}$, in the Xe adsorption experiments were around 0.6. Therefore consideration of the thermal transpiration effect was definitely necessary in the Xe adsorption experiments at liquid nitrogen temperature. According to our knowledge, the Xe adsorption experiments have never been carried out with separate dead-space volumes of adsorption cells.

The calculated adsorbed amounts obtained without consideration of the thermal transpiration effect were equal to those obtained with consideration of the thermal transpiration effect, within experimental errors, while the former equilibrium pressures were 1.7 times those of the latter equilibrium pressures. The monolayer volume obtained without consideration of the thermal transpiration effect was 0.8 times that obtained with consideration of the thermal transpiration effect.

The BET plots for Xe at liquid nitrogen temperature for the empty adsorption cell and for the adsorption cell with the balls are shown in Fig. 1. The effective area of Xe obtained from the difference between the monolayer volumes of the adsorption cell with the balls and of the empty cell was 0.28 nm^2.

There were some differences between the Kr adsorption isotherms obtained with and without consideration of the thermal transpiration effect at pressures lower than 1 Pa (relative pressure 0.005). However, there were no differences between the monolayer volumes obtained from the BET plots. Therefore, it is not necessary to consider the thermal transpiration effect for the BET adsorption experiments for Kr at liquid nitrogen temperature.

The BET plot for Kr at liquid nitrogne temperature for the adsorption cell with the balls is shown in Fig. 2. The effective area obtained for Kr was 0.23 nm^2.

The isotherms for CH_4 obtained through the conventional adsorption apparatus had large experimental errors. Therefore, the adsorption measurements were car-

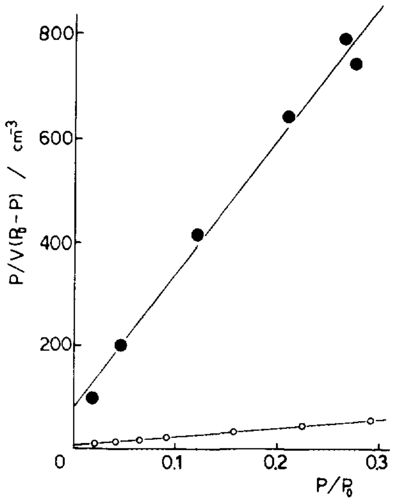

FIG. 1. BET plots of Xe adsorption for empty adsorption cell (●) and adsorption cell with steel balls (○) at liquid nitrogen temperature.

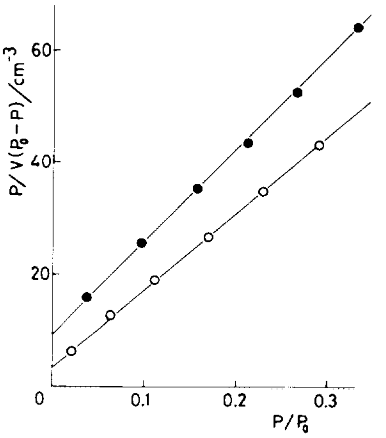

FIG. 2. BET plots of Kr (●) and CH_4 (○) adsorptions for adsorption cells with steel balls at liquid nitrogen temperature.

ried out with the temperature-compensated, differential tensimeter for measuring gas adsorption (7).

The monolayer volumes obtained with the temperature-compensated, differential tensimeter for measuring gas adsorption agreed with those obtained with the conventional apparatus within experimental errors. The BET plot for CH_4 at liquid nitrogen temperature for the adsorption cell with the balls is shown in Fig. 2. The effective area of CH_4 obtained here was 0.19 nm^2.

The effective areas obtained for Xe (0.28 nm^2), Kr (0.23 nm^2), and CH_4 (0.19 nm^2) were a little larger than the values (Xe, 0.17–0.27 nm^2; Kr, 0.17–0.22 nm^2; CH_4, 0.15–0.17 nm^2) in the literature (10). The experimental errors for effective areas estimated from their standard deviations were 0.01 nm^2 and the effective areas obtained with the another lot of balls agreed with the values obtained here, within experimental errors.

It should be noted that larger values for the effective area might be obtained if the total surface area of the balls, S in Eq. [1], is larger than 314 cm^2 because of their roughness.

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Received September 30, 1994