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A Method for Measuring Surface Area of Carbon of Carbon-Coated Silica Gel

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Synopsis. An adsorption method for determining the surface area of only the carbon of carbon-coated silica gel has been developed. In this method *p*-nitrophenol (PNP) was used as an adsorbate owing to its selective adsorbability on a carbon surface. This method was applied to carbon-coated silica gel prepared by a CVD method to determine the surface area of the carbon.

Colin et al. studied the coating of silica gel with pyrolytic carbon for modificating the chromatographic characters of silica gel.[1] Bebris et al.[2] and Leboda et al.[3,4] also studied similar composites. Youtsey et al.[5] fabricated electically conductive materials by coating an alumina surface with pyrolytic carbon. Visser et al.[6] prepared a similar composite for use as a catalyst support in coal liquefaction. In studies of these composites, the extent of the coating with carbon is quite important. However, no measurement of the extent of the coating was carried out in those studies, since there is no established method to measure only the surface area of the carbon of carbon-coated oxides. We are also studying carbon-coated silica gel in order to make a new-type adsorbent. We have therefore developed a method to measure only the surface area of carbon on the basis of the following idea.

If a adsorbate satisfies the following prerequisites, an adsorption method can be used for the measurement of the surface area of only a particular component in a porous composite:

1) The adsorbate is selectively adsorbed on the surface of only a particular component to be measured.

2) The amount of monomolecular layer adsorption can be calculated from the adsorption data.

3) The molecular diameter of the adsorbate is sufficiently small to enter narrow pores of the composite.

In the present paper the authors show a new method using *p*-nitrophenol (PNP) as adsorbate and an application of this method to a carbon-coated silica gel.

Experimental

Reagents. Hydrochloric acid and PNP of special grade were used. A standard PNP aqueous solution was prepared by dissolving 3.673 g of PNP in 0.5 dm^3 of 0.01 mol dm^{-3} hydrochloric acid solution. The hydrochloric acid solution was employed to minimize changes in pH during adsorption. The concentration of the standard PNP solution relative to the corresponding saturated concentration of PNP at 30 °C was 0.4; the saturated concentration of PNP in the hydrochloric acid solution was 0.132 mol dm^{-3}.

Materials. Graphitized Carbon Black: Commercial carbon black, Seast-300 (Tokai Carbon), was graphitized at 2600 °C. The graphitized carbon black was sieved to a particle size range of 100—200 mesh and then dried at 60 °C under vacuum.

Silica Gel: Microbead silica gel-4B (Fuji-Davison Chemical) was sieved to a particle size range of 100—200 mesh and then air-dried at 120 °C for 1 h. Carbon-coated silica gel was prepared as follows: three grams of the original silica gel-4B was placed in a quartz tubular reactor and then heated to 800 °C under nitrogen gas stream. Benzene was pumped to the reactor at the rate of 5 $cm^3 h^{-1}$ for periods of 1,2, and 3 h while rotating the reactor; carbon was deposited on the silica gel. These products are represented as carbon-coated silica gel-1H,-2H, and -3H, respectively. Silica gel heated at 800 °C in nitrogen was also prepared for a comparison with carbon-coated silica gel.

The surface areas of the graphitized carbon black, original silica gel, and heat-treated silica gel were 62, 407, and 326 $m^2 g^{-1}$, respectively. These surface areas were calculated from adsorption data of argon at 77 K by the BET equation.

Adsorption Procedure. One cm^3 of the standard or a diluted PNP solution and a prescribed amount of a powdered sample were mixed in a glass vessel with a polyethylene cap. The vessel was shaken at 30 °C for 20 h. The powdered sample was allowed to sediment, and 25 mm^3 of the supernatant was diluted into 50 cm^3 with 1 mmol dm^{-3} sodium hydroxide solution. The absorbance of both the diluted solution and the reference solution prepared from the standard solution was measured at 400 nm. The adsorption amount of PNP on the powdered sample was calculated from the difference of the absorbances.

Results and Discussion

We tested phenols such as phenol, 2-naphthol, and

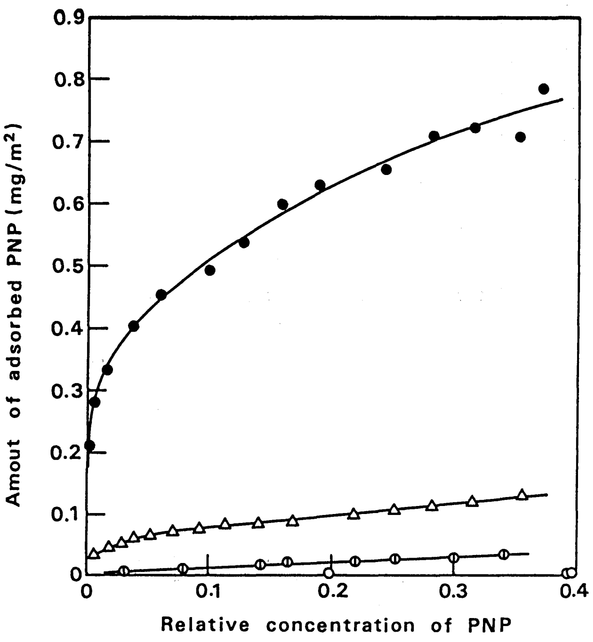

Fig. 1. Adsorption isotherms of PNP for several materials.
○: Original silica gel, ⦶: Heat-treated silica gel, △: Carbon-coated silica gel-2H, ●: Graphitized carbon black.

PNP as the adsorbates for the measurement of surface area of carbon on silica gel. PNP was found to be most suitable as an adsorbate owing to its appropriate solubility in water and its facility in quantitative analysis. The adsorption selectivity of PNP on carbon was studied using silica gel and graphitized carbon black as an adsorbent.

Figure 1 shows the adsorption isotherms of PNP for the original and heat-treated silica gel, graphitized carbon black, and carbon-coated silica gel-2H. The original silica gel did not adsorb PNP at all, and heat treated silica gel adsorbed only a very small amount of PNP. The effect of the heat treatment on the amount of adsorption would be ascribed to a change of hydroxyl groups on the surface of silica gel to siloxane bridge bondings having a more hydrophobic property. The graphitized carbon black adsorbed about 30 times as much PNP as heat-treated silica gel did at a relative concentration of 0.3. From these results it is evident that PNP molecules are selectively adsorbed on the surface of carbon with a highly hydrophobic property.

The adsorption isotherm of PNP for carbon-coated silica gel-2H lies between those for the silica gel and graphitized carbon black.

The BET equation was adopted in order to calculate the amount of monomolecular layer adsorption from those adsorption data, since it is known that the data concerning adsorption of PNP do not conform to the Langmuir adsorption equation,7) but fit a modified BET equation.8) The BET plots are shown in Fig. 2. The adsorption data could be described by straight lines over a wide concentration range from 0.02 to 0.4. From the data of graphitized carbon black in Fig. 2, the amount of monolayer adsorption of PNP was calculated to be 5.28×10^{-8} g cm^{-2}. Puri studied the adsorption of PNP on various kinds of carbons such as activated carbon, carbon black, and graphitized carbon black from aqueous solution and showed that the amounts of adsorbed PNP per a unit surface of these carbons were almost same.8) Therefore, the amount of monolayer adsorption calculated by the BET equation can be adopted to determine the surface area of carbon prepared at various temperatures.

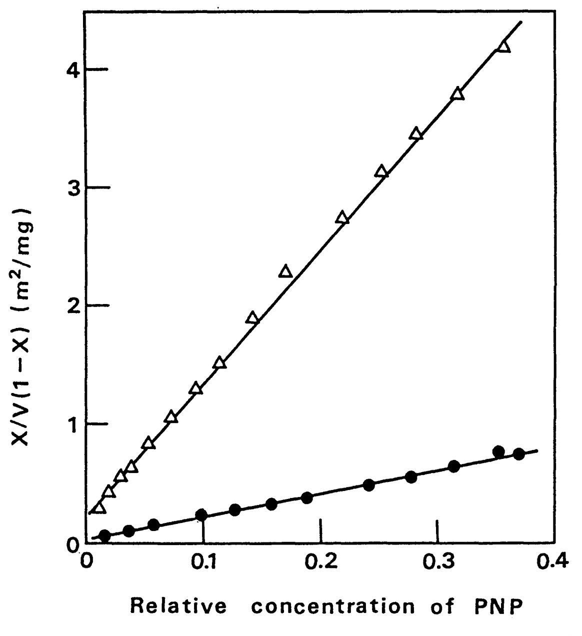

Fig. 2. BET plots for adsorption of PNP on several materials.
△: Carbon-coated silica gel-2H, ●: Graphitized carbon black.

The amount of PNP adsorbed on carbon-coated silica gel is the sum of those on the surface of the carbon and silica gel. Accordingly, the amount of monolayer adsorption of PNP on carbon-coated silica gel, PC (g g^{-1}), is represented by the equation: $PC=5.28\times10^{-8}\cdot SC+(TS-SC\cdot PS/SG)$, where SC (cm^2 g^{-1}) is the surface area of carbon of the carbon-coated silica gel, TS is the total surface area of the carbon-coated silica gel measured by the adsorption of argon at 77 K, PS is the amount of PNP adsorbed on heat-treated silica gel at a concentration at which the monolayer adsorption of PNP on the carbon-coated silica gel is completed, and SG is the total surface area of the heat-treated silica gel measured by the adsorption of argon at 77 K. By a transformation of the above equation, SC was calculated using $SC=(PC-TS\cdot PS/SG)/(5.28\times10^{-8}-PS/SG)$. The surface area of the carbon of a carbon-coated silica gel and the percentage of carbon coating are listed in Table 1.

Though the percentage of carbon coating increased with the coating time, the values did not exceed 20%, even after 3 h. It had been reported from chromatographic and adsorptive properties that carbon-coated silica gel prepared by heat CVD methods was partly covered by carbon.1,2) The values given in Table 1 quantitatively show the state of the surface covered partly by carbon. As described in this paper, a method using PNP as adsorbate has been found to be very useful for determining the surface area of carbon on an oxide, such as silica gel.

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Table 1. Surface Area of Carbon of Carbon-Coated Silica Gel

Coating time	Carbon content	Total surface area, *A*	Surface area of carbon, *B*	Percentage of coating, 100*B*/*A*
h	%	m^2 g^{-1}	m^2 g^{-1}	%
1	8.2	267	20	7.5
2	17.4	254	35	13.8
3	30.6	169	33	19.5

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