

Chapter 17

Gas Adsorption on Surface of Solid Materials



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Abstract Gas adsorption measurement provides essential information on surface properties of powder. In this chapter, theoretical background, process of measurement, and reading of obtained data are briefly introduced.

The adsorbate gas molecules are attracted by van der Waals force in physisorption. The relationship between adsorbed amount and activity (pressure), so-called adsorption isotherm, had been developed in early studies. Various isotherms have been proposed based on Langmuir monolayer adsorption theory, and the most important one is BET theory. Analysis of isotherm gives some important characteristics on solid surface, such as specific surface area, pore volume, pore size distribution, etc. The type of adsorption isotherm is classified into six types according to IUPAC criteria.

In actual measurement process, dry process in preparation of sample is very important to obtain accurate data. And measurement parameters should be set carefully taking various characteristics of samples into account. The obtained isotherm is analyzed by various analysis methods by computational calculations.

Keywords Gas adsorption and desorption · Adsorption isotherm · Pore size distribution · BET-specific surface area

17.1 Introduction

Interfaces between solid and gaseous phase are sometimes referred simply as “surface” and are very important to understand the behavior of liquid-solid interface. Basic characteristics of solid surfaces are usually characterized by interaction of gas molecules and solid surface. The specific surface area, one of the most important properties of solid surface, is estimated by measurement of adsorbed amount of gas molecules onto solid surface. In this chapter, outline of measurement technique of gas adsorption will be introduced.

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Atoms or functional groups on the most outer surface of solids show different behavior compared to inner part of the solids and attract surrounding molecules because of the asymmetric arrangement of surrounding atoms or groups. The phenomenon that molecules are attracted to the surface is called “adsorption.” Attracted molecules are referred as “adsorbent,” and the substance that attracts the surrounding molecules is referred to as “adsorbate.”

When molecules adsorb onto the surface of solid materials, the potential energy decreases. And the system releases heat according to the decreased potential energy and stabilizes. This heat is referred as heat of adsorption and is always positive (exothermic).

Two attractive interactions are taken into account when the gaseous molecules adsorb onto solid surfaces. One is intermolecular-induced dipole-dipole interaction, so-called van der Waals force. Another is exchange of electrons between gaseous molecules and surface. The latter type of adsorption is chemisorption, and chemisorption always results in monolayer of adsorbed molecules. Chemisorption occurs in relatively high temperature and shows large amount of heat of adsorption, and the rate of adsorption is small due to its large activation energy. In contrary, adsorption induced by intermolecular attraction (van der Waals forces) is referred as physisorption and observed in relatively low temperature. The heat of adsorption is very low compared to chemisorption, and the rate of physisorption is a large and reversible process. One example of physisorption is nitrogen molecules onto carbon; on the other hand, adsorption of oxygen molecules onto carbon surface is classified as chemisorption.

Many equations have been proposed to quantitative analysis of gas adsorption amount. The most simple one is Henry’s adsorption isotherm, assuming that the adsorption amount simply be in proportional to the pressure of gas. The actual surface of solids is not a flat surface but complex geometry with unevenness and pores. An isotherm that is proposed by Langmuir can be applied to such complex surfaces. The isotherm was derived by consideration of monolayer adsorption dynamically.

At constant temperature T , the adsorbed volume of gas at standard condition V follows the equation shown below:

$$V = \frac{KpV_m}{1 + Kp} \quad (17.1)$$

Here, K is a constant, p is an equilibrium pressure, and V_m is saturated adsorption amount, respectively. And Eq. (17.1) is converted to the equation below:

$$\frac{1}{V} = \frac{1}{KpV_m} + \frac{1}{V_m} \quad (17.2)$$

For example, adsorption amount of oxygen or carbon dioxide molecules onto silica gels follows this isotherm well.

The sites that gaseous molecules adsorb onto the surface distribute uniformly on the solid surface. One molecule occupies just one site in adsorption process, and one adsorption site can accept just one molecule for Langmuir's adsorption model. So once all adsorption sites were occupied by adsorbent, no further adsorption occurs by applying higher pressure. Such type of adsorption is referred as monolayer adsorption. The adsorption of Ar, N₂, CO₂, CO, and O₂ onto the activated carbon is categorized to monolayer adsorption.

BET adsorption isotherm was derived by Brunauer, Emmett, and Teller, and expanded Langmuir monolayer adsorption model to multilayer adsorption. At first at very low pressure, adsorbed molecular layer formed on the surface; after the monolayer was formed on the surface, the adsorbent gas adsorbs on the adsorbed gas molecules in monolayer and finally forms multilayers of adsorbed gas molecules on the surface. Such type of adsorption is called BET adsorption.

BET isotherm is expressed as equation below:

$$V = - \frac{V_m K_p P}{(P - P_0) \left\{ \frac{(K_p - 1)P}{P_0} + 1 \right\}} \quad (17.3)$$

Here, P_0 is saturated vapor pressure of adsorbent, p is relative pressure, and K_p is a constant. When $P_0 \gg P$ (at low pressure), the term p/p_0 is negligible compared to 1, and then Eq. (17.3) is equal to Langmuir's isotherm.

BET adsorption model is based on the conditions below in addition to the assumptions of Langmuir monolayer adsorption.

- The heat of adsorption is equal to heat of condensation of adsorbent molecules after second layer adsorption.
- When the p approaches to p_0 , the adsorbed amount increases to infinity.
- No interactions between adsorbed molecules in each layer.

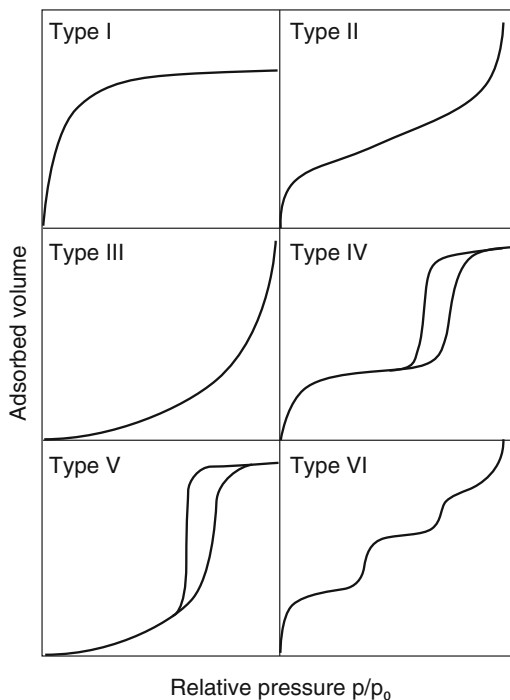
Adsorption on nonporous solid follows this type, and the main cause of attraction is van der Waals forces.

The adsorption process promoted by various interactions is described above. And adsorption isotherm was classified to some types, according to the properties of adsorbate such as pore size distribution, the morphology of pores, and chemical properties of the surface.

The classification of isotherms by IUPAC is shown in Fig. 17.1.

1. Type I: Monolayer Langmuir-type adsorption. Also applied to adsorbates with micropores (pores with diameter below 2 nm).
2. Type II: BET-type multilayer adsorption. Often seen in systems with strong interaction between surface and gas molecules.
3. Type III: Observed in systems with weak interaction between adsorbate and adsorbent and shows multilayer adsorption with inhomogeneous interactions.
4. Type IV: Observed with mesoporous surface with strong interaction between adsorbent and adsorbate. Often shows hysteresis loops with type H1–H4.

Fig. 17.1 The IUPAC classifications of adsorption isotherms



5. Type V: Observed with type III solid with mesopores. Also shows loops as type IV isotherm.
6. Type VI: Isotherm represents stepwise multilayer adsorption on a uniform homogeneous surface.

17.2 What You Get

The data directly obtained from measurement are the adsorbed amount in each relative pressure at a constant pressure. From an isotherm of nitrogen gas adsorption, we can obtain specific surface area (surface area per unit mass of adsorbent), pore size distribution, pore volumes, and so on. The morphology of pores can be estimated by comparison of hysteresis loop of the isotherm with IUPAC classification. For example, a solid with micropores shows steep rise at low p because of micropore condensation. The isotherm with hysteresis loop for H_2 in IUPAC classification is sometimes connected with ink-bottle-shaped mesopores.

Distribution of metals on the surface can be estimated by measuring adsorption volumes with various gases which differently interact with a certain metal. Molecular probe method utilizes molecules with different sizes comparable to the micropores. The difference of adsorbed amount of different molecular cross sections gives

information of smaller pores below limitation of normal pore size distribution calculation from nitrogen adsorption. Water vapor adsorption gives information about hydrophilicity of the surface. For nonporous spherical powders, the diameter of the particles can be obtained by BET.

17.3 Essentials and Tips

The measurement methods of adsorption volume of gas onto solid particles are classified as constant volume, constant flow, and weight measurement. The most popular one is the constant volume method. In constant volume method, the adsorbent gas is introduced to manifold with strictly defined volume at controlled temperature, and then the valve between the sample cell and manifold opened to introduce the gas into sample cell. The adsorption amount was calculated from the change of pressure using equation of the state of gas.

In actual measurement, ① the sample is set in the cell and weighed and thoroughly dried, ② cell is connected to the instrument and dried in vacuum if required, ③ input measurement conditions to PC of the instrument, ④ set liquid nitrogen to Dewar vessel, ⑤ start the measurement, and ⑥ analyze the isotherm.

17.4 Preparation of the Instrument

The measurement instrument (Fig. 17.2) is composed of a control panel (connected to PC), manifold, transducers (pressure meter), and vacuum pump for fine vacuum. Some connecting ports connect the instrument to adsorbent gases, roughing pump, and samples. Helium gas cylinder is connected to the instrument to flush the pipelines and measure the dead volume of sample cells. High purity of nitrogen gas is required to obtain high-quality data. Liquid nitrogen is used as coolant in nitrogen gas adsorption measurement. For the solids with very low specific surface area, krypton gas is often used.

17.5 Preparation of Sample

The typical diameter of sample cell is about 6–8 mm and 15–20 cm in length for powder samples. The cells are made of glass or quartz pipe with one end is closed. In typical instrument, the total surface area of introduced samples is recommended between 10 and 100 m². In case with too low surface area, it is hard to detect pressure change in adsorption, and with too large area, it takes very long time to reach equilibrium. When multiple samples were measured simultaneously, it is recommended that the pore volume or the total surface area is in close amount.

Fig. 17.2 An surface area and pore size analyzer
(Photo credit Quantachrome
a brand of Anton Paar)



The instrument measures only the pressure of gas. The weight of samples should be measured before or after the adsorption measurement with balance. Take care not to touch the sample cell with naked hand to avoid error in weighing.

Pretreatment of the sample (drying) should be done prior to the measurement. Residual moisture in the sample powder causes error in the pressure measurement because of the evaporation of moisture. The residual water also causes capping of pore. And evaporation of water sometimes causes the dispersion of powders resulting in the contamination of instrument or other samples. Samples are dried by heating in vacuum or gas flow. The operator should take care about the dispersion of powder during rapid decreasing of pressure and changes in crystalline and surface and morphological changes at high temperature. Dispersion of powder is caused by rapid expansion of water vapor, so slow pressure reduction or rough drying before introduction in vacuum is recommended. The amount of powder should not be excessive, and sample filter should be set in the open end of sample cell. For block samples, there is no need to care about dispersion, but these should be cut to introduce in the cell.

To avoid structural change by heating, the operator should set the pretreatment temperature below the phase transition temperature.

17.6 Setting of Parameter

Required properties are different for each instruments; the operator should input some parameters prior to the measurement. Select the adsorbate gas from the list in the PC, or if the gas is not in the list, input the values from literature. Set sample weight by the measured value by balance. Other detailed conditions, such as the duration of leak test, number of the point of measurement, criteria of judgment of equilibrium, and rate of gas introduction, should be set according to the instrument manual. In terms of the number of the point of measurement, 1 is enough for rough estimation of surface area, and for BET analysis, 7 points in 0.15–0.35 in p/p_0 are usually enough, and for pore size distribution analysis, some tens of measurement point are required in both adsorption and desorption process. For micropore analysis, many points in low p/p_0 should be measured. And sample drying and leak test should be conducted in strict condition.

It is recommended to determine these conditions after a rough measurement if possible.

17.7 What to Look Out for

Rough isotherm is obtained often when the total surface area is very low. In such case, one more measurement should be done with larger amount of sample, or use other adsorbate gas (e.g., Kr gas). Or each measurement does not reach equilibrium. In such cases, take longer duration to judge the equilibrium.

If the desorption branch of isotherm is below adsorption branch, leakage or evaporation of residual gas from powders may occur.

17.8 Understanding Your Data

A typical isotherm is shown in Fig. 17.3. The shape of the isotherm itself has meaning as described above; to obtain parameters such as specific surface area, etc., calculation with PC is required. For specific surface area, the BET method is most applied, and in labs, the adsorption instrument is merely called as “BET.” Five or seven sets of adsorbed volume between $p/p_0 = 0.15 - 0.35$ are input to BET equation. And monolayer adsorption amount is obtained by intercept and slope of BET plot. Then the cross section of molecules is multiplied with monolayer adsorption amount to give surface area. These calculation processes are done automatically by PC, but the fitting should be checked by the operator. The operator should select the line with highest correlation coefficient in $p/p_0 = 0.15 - 0.35$ or around $p/p_0 = 0$.

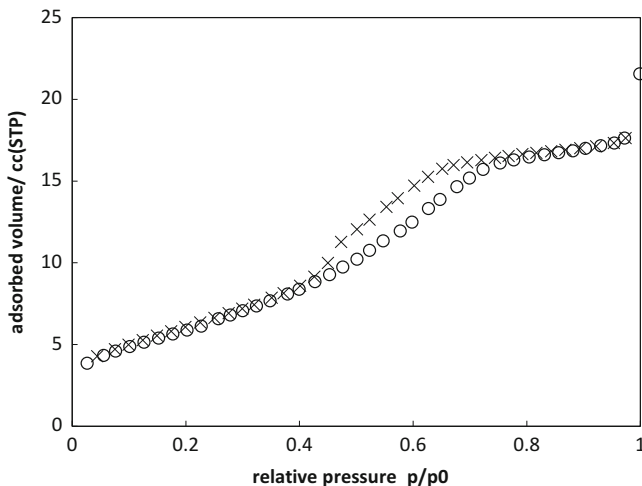


Fig. 17.3 Nitrogen gas adsorption-desorption isotherm of mesoporous titania

For pore size distribution, calculation method is different for mesopores (50–2 nm) and micropores (< 2 nm). Popular calculation methods are usually installed in PC, for example, BJH, DH, and CI method for mesopores and MP and t-plot method for micropores. In these days NLDFT (nonlocalized density function theory) calculation is installed in the analysis software, and this method is purely theoretical.

17.9 Useful Hints

Gas adsorption measurement is the most reliable method to obtain the value of specific surface area and most powerful method to investigate mesopores and micropores to which fluids other than gas cannot penetrate in because of the surface tension. TEM observation cannot be applied to evaluate inner pore of particles because of the incapable transmittance of electrons. For the analysis of pores, mercury or oil intrusion is suitable for larger sizes above 100 nm, absorption of positron beam is applied for smaller pores below 2 nm, and gas adsorption covers in between. By the combination of these analyses and electron microscopy, the researcher can obtain almost all morphological information of powders.

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