Measurement of surface area of molecular sieves using BET theory

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The surface area of different models of molecular sieves are measured using BET theory adopting nitrogen as the adsorbates.
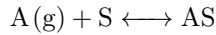
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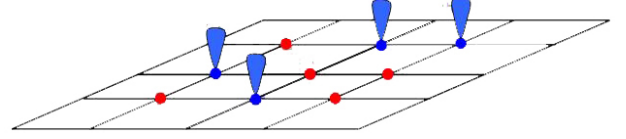
CONTENTS

FIG. 1. A simple graphic representation of the Langmuir adsorption model, where the red dots signify the unoccupied area, the blue points the occupied area.
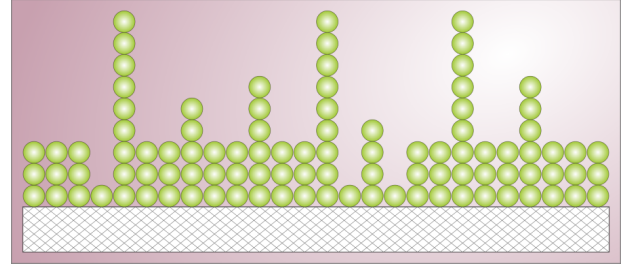

FIG. 2. Sketch of the multilayered adsorption

I. INTRODUCTION

In 1916, Irving Langmuir first presented his model describing the absorption of species on a simple surface[1]. In 1938, Stephen Brunauer, P. H. Emmett and Edward Teller proposed the first theory of gases adsorption in multi-molecular layers, the BET theory, which has become a standard method to measure the surface area of the solid[2]. Its application includes analysis towards the physical structure of hardened cement paste, approximation of the surface area of activated carbon, and evaluation of catalysts.

A. Langmuir: unimolecular equilibrium

The surface adsorption can be regarded as a equilibrium

$$A(g) + S \longleftrightarrow AS$$

which represents the process of adduction between the two substances, $A(g)$ being the gas molecule in the gas phase, while AS is the adduction product of the gas molecule and the molecule on the surface of the condensed substance.

Langmuir supposed that the adsorption rate is proportionl to the pressure of gas A and the area on the surface which haven't been occupied, while the desorption rate is proportional to the area occupied, which is shown by

$$k_{ad}pS_0 = k_{de}S_1 \qquad (1)$$

where k_{ad}, k_{de} represent the reaction rate constant of the adsorption and the desorption respectively, S_0, S_1 the unoccupied and the occupied area, and p the pressure of gas A in bulk phase.

Define the occupied percentage θ

$$\theta = \frac{S_1}{[S]} = \frac{S_1}{S_0 + S_1} = \frac{k_{ad}p}{k_{ad}p + k_{de}} \qquad (2)$$

and the adsorption equilibrium constant $K = \frac{k_{ad}}{k_{de}}$, then

$$\theta = \frac{Kp}{1 + Kp} \qquad (3)$$

B. BET: multi-molecular equilibrium

It is supposed that many layers of adsorbed molecules can be formed on the surface of condensed substance, and s_i is defined as the surface area that covered by i layers of adsorbed molecules. When considering monolayer system, it is derived from the Langmuir's equation

that

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \tag{4}$$

where the term $e^{-E_1/RT}$ is separated from K in the Langmuir's equation w.r.t. the Boltzmann distribution achieved between the adsorbed molecules and those in the bulk phase. For another system including only two layers of adsorbed molecules, the equilibrium is given by

$$a_2 p s_1 + b_1 s_1 e^{-E_1/RT} = b_2 s_2 e^{-E_2/RT} + a_1 p s_0 \tag{5}$$

with each term representing condensation on the first layer, evaporation from the first layer, evaporation from the second layer and condensation on the first layer, with a_2, b_2, E_2 similarly defined to a_1, b_1 and E_1. Considering that (4) still holds in this system for the first layer, it is easily derived that

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \tag{6}$$

Similar mechanism can be applied for an arbitrary index i, namely

$$a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \tag{7}$$

or

$$p s_{i-1} = g_i s_i e^{-E_i/RT} \tag{8}$$

The total surface area is given by

$$A = \sum_{i=0}^{\infty} s_i \tag{9}$$

and the total volume adsorbed is

$$v = v_0 \sum_{i=0}^{\infty} i \cdot s_i \tag{10}$$

where v_0 is the volume of gas adsorbed on unit area of the adsorbent surface when it is covered with a complete unimolecular layer of adsorbed gas. Then

$$\frac{v}{Av_0} = \frac{v}{v_0} = \frac{\sum_{i=0}^{\infty} i \cdot s_i}{\sum s_i} \tag{11}$$

It is assumed that $E_i = E_j = E_L, g_i = g_j = g$ for $i, j \geq 2$, in the consideration of the similarity among these layers, and s_i is given by

$$s_0 = cx^i s_0 \tag{12}$$

where $x = (p/g)e^{E/RT}, c = gg_1 e^{(E_1-E_L)/RT}$. Thus

$$\frac{v}{v_m} = \frac{c \sum_{i=1}^{\infty} i x^i}{1 + c \sum_{i=1}^{\infty} x^i} \tag{13}$$

Then

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \tag{14}$$

w.r.t. the fact that

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \tag{15}$$

(14) indicates that endless adsorption will occur if $x \to 1$, which is evidently the result of $p \geqslant p_0$, p_0 representing the saturated vapor pressure of the adsorbed substance. Considering that $x \propto p$, it is assumed that

$$x = \frac{p}{p_0} \tag{16}$$

Then (14) is reduced to

$$\frac{v}{v_m} = \frac{cp}{(p_0 - p)\left[1 + (c-1)\frac{p}{p_0}\right]} \tag{17}$$

or its linear form

$$\frac{cp}{V(p_0 - p)} = \frac{1}{V_m}\left[1 + (c-1)\frac{p}{p_0}\right] \tag{18}$$

C. Methodology

The use of nitrogen adsorption becomes one of the most widely-used method for the characterization of porous materials. The earliest reported studies of the adsorption nitrogen and other gases at liquid air temperature ($\sim$88 K) appear to have been made by Dewar and Ramsay in the course of their investigations of the composition of the atmosphere and the separation of the noble gases.[3]

Gas adsorption manometry is the method generally used for the determination of adsorption isotherms of nitrogen at the temperature of liquid nitrogen ($\sim$77 K). This type of approach was known as a 'volumetric determination' (or alternatively as the 'BET volumetric method') since it originally involved the measurement of gas volumes, before and after adsorption. However, it has been pointed out that it is no longer appropriate to use the term 'volumetric' since the amount adsorbed is now generally evaluated by measuring the change of gas pressure, rather than a change in gas volume.

Two different operational procedures can be used for the determination of the adsorption isotherm. The conventional technique makes use of a discontinuous, point-by-point procedure. Successive amounts of the adsorptive are introduced and at each stage the system is allowed sufficient time to attain equilibrium, which of course corresponds to a series of single points on the adsorption isotherm. The continuous approach is more recent and is dependent on the principle of 'quasi-equilibrium'. In this case, the introduction of the adsorptive must be slow enough to provide a continuous 'equilibrium' isotherm (i.e. with an infinite number of points). If properly used, the continuous manometric procedure

TABLE I. $\frac{p/p_0}{V(1-p/p_0)} - p/p_0$ data of the four models of molecular sieves

Model	$10^2 p/p_0$	$\frac{10^3 p/p_0}{V(1-p/p_0)/(\text{g/cm}^3)}$
5A	5.12330	0.399627
	9.83880	0.785563
	14.6168	1.21400
	19.5029	1.69589
	25.0192	2.30527
	29.8112	2.90425
TDX	10.0683	0.397445
	12.8209	0.519410
	16.5952	0.699721
	20.8693	0.924308
	25.5477	1.19937
	30.1600	1.50676
13X	5.08190	0.325157
	10.0178	0.657681
	14.9074	1.02933
	19.9015	1.45437
	25.0599	1.95200
	30.0583	2.50321
3A	6.13740	4.21262
	10.1525	6.75755
	14.5214	9.56977
	20.0749	13.2330
	24.6837	16.3957
	29.8449	20.1105

FIG. 3. $\frac{p/p_0}{V(1-p/p_0)} - p/p_0$ plot of the four models of molecular sieves

has the great advantage that it is possible to reveal inconspicuous features (e.g. sub-steps), which may not be detectable by the discontinuous method.

The aims of outgassing are two-fold —(a) to reach a well-defined intermediate state by the removal of physisorbed molecules; (b) to avoid any drastic change as a result of ageing or surface modification. Conventional vacuum outgassing is the generally preferred technique, but with fine powders, there is always a risk of spurting. Spurting can be avoided and changes in the adsorbent minimised by controlling the rate of outgassing by the application of a form of controlled rate thermal analysis, CRTA, which is also termed 'sample controlled thermal analysis'.

II. RESULTS AND ANALYSIS

degassed samples of 0.1215 g, 0.0910 g, 0.0814 g, 0.2577 g of 5A, TBX, 12X, 3A models of molecular sieves are weighed respectively and was subjected to adsorption analysis using Nova 4000e surface area analyzer, using nitrogen as the adsorbed substance and liquid nitrogen as the cooler.

The data obtained is shown in Table.I, with its graphic representation and analysis shown in Fig.3. The lines
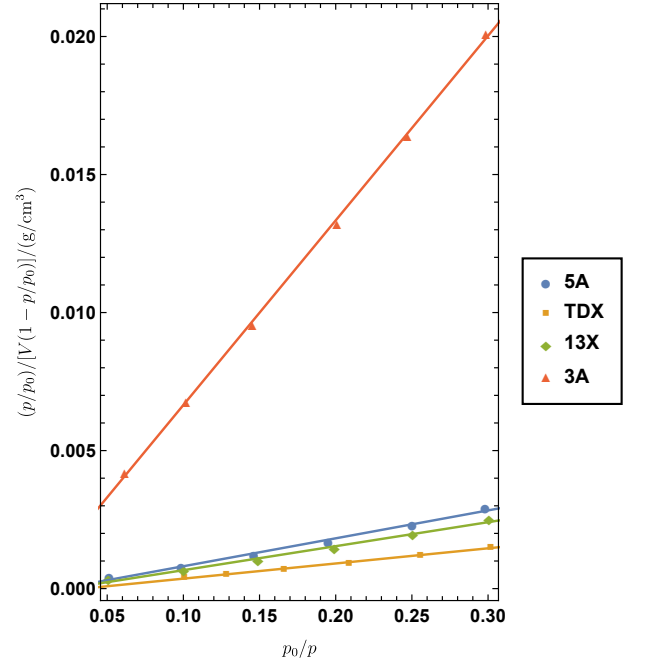
fitted are

$$\left.\frac{p/p_0}{V(1-p/p_0)}\right|_{\text{5A}} = 0.0101150\frac{p}{p_0} - 0.000201015$$

$$\left.\frac{p/p_0}{V(1-p/p_0)}\right|_{\text{TDX}} = 0.00549478\frac{p}{p_0} - 0.000188385$$

$$\left.\frac{p/p_0}{V(1-p/p_0)}\right|_{\text{13X}} = 0.00869008\frac{p}{p_0} - 0.000200860$$

$$\left.\frac{p/p_0}{V(1-p/p_0)}\right|_{\text{3A}} = 0.0668795\frac{p}{p_0} - 0.0000369612$$

with

$$\left.R^2\right|_{\text{5A}} = 0.994307$$

$$\left.R^2\right|_{\text{TDX}} = 0.994965$$

$$\left.R^2\right|_{\text{13X}} = 0.992158$$

$$\left.R^2\right|_{\text{3A}} = 0.999460$$

Thus

$$V_m\bigg|_{5A} = 100.868\,\mathrm{cm^3/g}$$

$$V_m\bigg|_{TDX} = 188.452\,\mathrm{cm^3/g}$$

$$V_m\bigg|_{13X} = 117.796\,\mathrm{cm^3/g}$$

$$V_m\bigg|_{3A} = 14.9605\,\mathrm{cm^3/g}$$

and

$$A\bigg|_{5A} = 439.\,\mathrm{m^2/g}$$

$$A\bigg|_{TDX} = 821.\,\mathrm{m^2/g}$$

$$A\bigg|_{13X} = 513.\,\mathrm{m^2/g}$$

$$A\bigg|_{3A} = 65.2\,\mathrm{m^2/g}$$

w.r.t. the equation 18 and the fact that

$$A = V_m N_A \sigma_{\mathrm{N_2}}, \quad \sigma_{\mathrm{N_2}} = 16.2 \times 10^{-20}\,\mathrm{m^2} \qquad (19)$$

Deviation arises from the approximation of the BET theory, namely that the constant g_i as well as E_i is regarded the same among layers, which might lead to faulty description of the system, considering that a high pressure can be obtained on the adsorption surface due to the Lennard-Jone interactions among layers and between layers and the adsorbent surface[4]. Deviation from adsorption equilibrium might also contribute to the error, whose clues can be found in the R^2 of the four samples, among which only 3A model cannot adsorb nitrogen into its pores, thus having least surface area measured, and the best linearity obtained.

A closer look at the distribution of data points reveals a tendency of a positive second derivative of $\frac{p/p_0}{V(1-p/p_0)}$ towards p/p_0, which should be attributed to deviation from theoretical adsorption equilibrium, also indicating the problem of non-equal interaction among layers. Non-positive intercepts of the lines may also derive from these factors, which results in fluctuations of the linear fitting results.

III. CONCLUSION

The surface area of different models of molecular sieves are measured using BET theory adopting nitrogen as the adsorbates. The falty assumption of BET theory as well as deviation from adsorption equilibrium are considered to be the main error-contributing factors.

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