

Research on influence factors on determination of specific surface area of carbon material by N₂ adsorption method

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Abstract. Activated carbon can be widely used as adsorbent, catalyst and catalyst support for many chemical reactions. The specific surface area of activated carbon is one of the important physical structure parameters, the accuracy of its measured value is essential for realistic reference significance. In this paper, the N₂ adsorption method was adopted to measure the specific surface area of activated carbon by NOVA2000e surface area & pore size analyzer, the factors affecting on the measured value of specific surface area of activated carbon, such as the conditions of sample pretreatment and adsorption point numbers, was discussed. The results show that the optimum conditions of sample pretreatment is to desorb for more than 5 h under 300 °C. The measured value of specific surface area of sample treated under such conditions is closer to the actual value. The measured value of specific surface area of sample by multipoint BET method got better accuracy with the increase in adsorption points. When the adsorption points is 5, the relative error of the measured value is only 1.15%. Single point BET method can be used as an approximate method, the relative error of the single point BET value measured by this analyzer is about 5%. In the allowable experimental accuracy range, The advantages the measurement of materials surface area by the single point BET method is quite simple and effective.

Introduction

Specific surface area of the material is the amount of the surface area per unit volume or unit mass. Interface is the boundary between solid and its surrounding environment: liquid, gas, or another solid [1]. It is one of the important parameters used in evaluating many capabilities of powders and porous materials, such as activity, adsorptive performance, catalytic performance and so on [2]. As important adsorbent and catalyst support, activated carbon has been widely used [3-5], and specific surface area is one of the important parameters characterized its physical properties. It has very important significance to measure specific surface area of material accurately.

Many method can be used to measure specific surface area of material including chromatography method, N₂ adsorption method and gravimetric method [6]. As a kind of classic method to measure specific surface area of solid materials, N₂ adsorption method has the advantage that the measurement results are accurate, so the method has been widely used in laboratories and factories. In this review, the N₂ adsorption method was adopted to measure the specific surface area of activated carbon which would be used as catalyst support. The factors affecting on the measured value of specific surface area of activated carbon, such as degassing temperature, degassing time and

adsorption point numbers were experimentally investigated. Thus, a general consideration of all the factors should be taken in measurement, which will be useful for improving testing accuracy and providing meaningful reference.

Experimental

Laboratory instruments and reagents. Surface area & pore size analyzer, Quantachrome company in the United States, NOVA2000e type; activated carbon sample, specific surface area $S_g = 690 \text{ m}^2/\text{g}$.

The experiment principle and steps. Testing instrument used by this paper is high-speed automatic surface area and pore size analyzer produced by Quantachrome Corporation in the United States, it is also known as multiple point adsorption instrument. It is a kind of intelligent instrument that widely used for determination specific surface area and micropore volume of powder and porous material. This instrument is mainly consisted with vacuum pump, vacuum pipelines, nitrogen and helium cylinder, solenoid valve, pressure sensor, sample tube etc. Before measurement, samples are degassed under high vacuum at appropriate temperature until gases and impurities on the surface of the samples have been desorbed, and then samples adsorbed N_2 step by step under liquid nitrogen temperature nitrogen. So we can obtain many relative pressure (P/P_0) and the corresponding value of the adsorption amount, and then make the adsorption isotherms according to the above experimental data. Adsorption pressure can be measured by pressure sensor, and adsorption amount can be yielded by adsorption pressure from the gas equation of state.

Experimental data are used into the BET equation (1) [7]. V of equation (1) is the adsorption amount corresponding with relative pressure (P/P_0); C is adsorption constant associated with the adsorption strength between adsorbent and sorbent. According to expression (1), when $P^{1/[V(P_0 - P)]}$ is plotted against P/P_0 , we can get a straight line with slope $(C-1)/[V_m C]$ and intercept on the vertical axis $1/[V_m C]$. Then the monolayer saturated adsorption amount can be calculated according to expression (2).

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

$$V = 1/(\text{slope} + \text{intercept}) \quad (2)$$

Give A_m (nm^2) as cross-sectional area of each nitrogen molecule adsorbed, and use ml/g as unit for V_m , then the specific surface area of the tested sample S_g is given by expression (3):

$$S_g = \frac{A_m \times N_a \times V_m \times 10^{-12}}{22414} \text{ m}^2 / \text{g} \quad (3)$$

N_0 is Avogadro constant.

Flow chart of NOVA2000e surface area & pore size analyzer is showed in figure 1. The sample tubes on the left are degas station, the other two sample tubes on the right are detecting station. In experiment, firstly samples are degassed in degas station, and then transferred to detecting station.

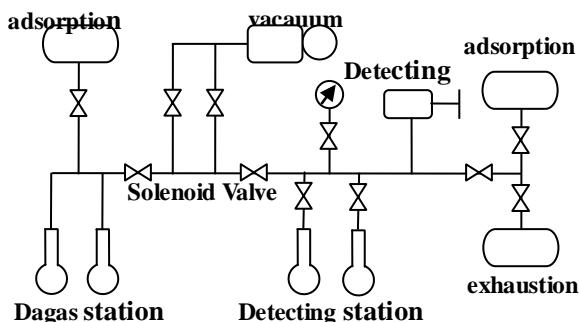


Fig.1 Flow chart of NOVA2000e surface area & pore size analyzer

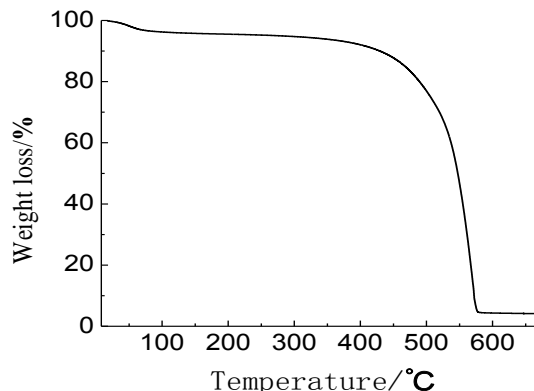


Fig.2 Thermal analysis curve of activated carbon

Results and discussion

Thermogravimetric analysis of activated carbon. The degas temperature chosen should be lower than the thermal decomposition reaction temperature of material, so thermogravimetric analysis was carried out on the activated carbon, Thermal analysis curve of activated carbon was shown in figure 2. It can be seen from the curve, within room temperature to 70 °C temperature range, the weight loss of activated carbon was about 4%, it caused by weight loss of surface water. No thermogravimetric reaction occurs within the temperature range from 70 °C to 390 °C, TG curve was smooth. When temperature was higher than 390 °C, weight loss reaction can be observed apparently. Taking the weight loss of activated carbon caused by the loss of surface water into account, the optimal degas temperature range determined was from 70 °C to 390 °C .

Influence of degas temperature on measurement of specific surface area of activated carbon. In order to study the influence of degas temperature on measurement of specific surface area of activated carbon, samples were measured under different degas temperature respectively, all the measurement were carried out after samples have been degased for 3 hours. Experiment condition, experimental data and relative errors of measured value compared with actual value are all shown in Tab.1.

Tab.1 Specific surface areas of the samples under different degas temperature

Degassing time /°C	100	200	300	400
Specific surface area /m ² /g	671.73	678.17	685.72	671.87
The relative error /%	2.65	1.71	0.62	2.63

It can be seen from table 1, when degas temperature was lower than 300 °C, with the increase of temperature, the measured value of specific surface area of sample were more closer to the actual value. And when degas temperature was higher than 400 °C, the measured value decreased slightly.

In degassing process, water and other impurities desorbed from the samples surface continuously. When degas temperature was lower than temperature range within which activated carbon can decompose, the higher the temperature was, the better the desorption effect was. Thus, the measured value of specific surface area of sample were more closer to the actual value. When sample degassed at 300 °C, relative error of measured value compared with actual value are is only 0.62%. while when sample degassed at lower temperature, samples surface can't be exposed completely, the measured value of specific surface area of sample were is lower than the actual value. When degas temperature was higher than 400 °C, activated carbon samples decomposed, grain surface of

samples were destroyed partly, or particles sintered partly, that all can cause the measured value of specific surface area of sample lower than the actual value.

Influence of degassing time on measurement of specific surface area of activated carbon.

Activated carbon samples were degassed under 300 °C for different time, and then their specific surface area were measured respectively, the results are showed in table 2.

Tab.2 specific surface areas of the samples under different degassing time

Degassing time /°C	1	3	5	7
Specific surface area /m ² /g	679.47	685.72	688.01	679.87
The relative error /%	1.53	0.62	0.29	1.47

It can be seen from table 2, when the degassing time was less than 5 hours, with the increase of degassing time, value of specific surface area of sample increased, but when the degassing time was more than 7 hours, with the increase of degassing time, value of specific surface area of sample was slightly down.

When Samples were degassed for 5 hours at optimum degassing temperature, water and other impurities on the surface of samples have been basically desorbed, clean samples surface of samples can be exposed completely, so the measured value of specific surface area of sample were more closer to the actual value, and relative errors of measured value compared with actual value was only 0.29%. While when degassing time was too short, water and impurities on the surface of samples can't be desorbed completely, inner surface of samples can be exposed completely, the measured value of specific surface area of sample were smaller than the actual value. But when degassing time was too long, the experiment efficiency declined, and part crystal surface of samples were destroyed by degassing at higher temperature for a long time.

Influence of adsorption point numbers on measurement of specific surface area of activated carbon. The measurement results of specific surface area of activated carbon were influenced by choosing adsorption points number during the process of adsorption isotherms test^[8]. According to the application of the BET equation, several adsorption point numbers were chosen to adsorb N₂ at the condition of relative pressure less than 0.3^[9], the results and relative errors of measured value compared with actual value are shown in table 3.

Tab.3 Effect of adsorption point numbers on measurement of specific surface area of activated carbon

Adsorption points	1	2	3	4	5
Specific surface area/m ² /g	728.23	652.47	706.58	703.71	700.44
The relative error /%	5.54	5.43	2.40	1.98	1.51

It can be seen from table 3, with the increase of numbers of adsorption points selected, the measured value of specific surface area of sample were more closer to the actual value, the relative error decreased. When single point BET method was adopted to measure the specific surface area of carbon samples, relative error of measured value compared with actual value was 5.54%; while when the number of adsorption points selected was 5, relative error had been decreased to 1.51%. We can predicate that the more adsorption points be selected, more closer the measured value of specific surface area of sample to the actual value be, but it may increase the working load greatly.

We should specify that, in actual measurement operation, single point BET method often be adopted in order to decrease the working load, reduce the measurement cost, or obtain the experiment result rapidly and accurately^[10]. Comparing with multiple point BET method, the relative error of the single point BET value measured was not only decided by the characteristics of

materials (C value) but also related with relative pressure chosen in single point method. According to the BET equation, it is not difficult to derive relative errors d . Compared the single point BET method and multipoint BET method, as is showed in expression (4).

$$d = \frac{(V_m)_B - (V_m)_s}{(V_m)_s} = \frac{1 - \frac{P}{P_0}}{1 + (C-1)\frac{P}{P_0}} \quad (4)$$

$(V_m)_B$ —The monolayer saturated adsorption amount derived by multipoint BET method;

$(V_m)_s$ —The monolayer saturated adsorption amount derived by single point BET method.

For certain adsorption system, C keeps no change. According to expression (4), we can find out that with the increase of relative pressure value chosen in single point method, the relative error decreased. When the relative pressure was chosen around 0.3, the relation curve based on the expression (1) had better linear relations. Thus the relative pressure chosen in single point BET method in this experiment was 0.3. The experimental results showed that relative error of the single point BET value measured was around 5%. In the allowable experimental accuracy range, the advantages of the measurement of materials surface area by the single point BET method is quite simple and effective.

Conclusion

(1) The optimal degas temperature range for activated carbon samples determined by thermogravimetric analysis was from 70 °C to 390 °C. Within this temperature range, when sample degassed at 300 °C, its measurement value was closer to the true value.

(2) The basis for determining the degassing time was whether impurities adsorbed by the samples surface can desorb from the surface completely. At the optimum temperature, when samples degassed for 5 hours, true surface of samples can be exposed completely, and the measured value of specific surface area of sample were more closer to the actual value.

(3) With the increase of numbers of adsorption points selected, the measured value of specific surface area of sample were more closer to the actual value, the relative error decreased, when the number of adsorption point is 5, the relative error is only 1.15%.

(4) Within the allowable experimental accuracy range, as one of the approximate methods, surface area measurement by single point BET method is quite simple and effective.

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