Chinese Journal of Catalysis 34 (2013) 1797–1810

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Review

Theoretical and practical discussion of measurement accuracy for physisorption with micro- and mesoporous materials

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ARTICLE INFO

Article history:
Received 21 December 2012
Accepted 17 April 2013
Published 20 October 2013

Keywords:
Physisorption
Specific surface area
Pore size distribution
Measurement accuracy
Microporous material
Mesoporous material

ABSTRACT

The surface area and pore size distribution are two very basic properties of a solid catalyst powder. Physisorption is still the only macroscopic method for measuring these two properties. To better understand the pore structure and surface properties of materials, it is very important to make accurate physisorption measurements. Unfortunately there are still many misunderstandings about physisorption. In fact, hardware design, operation of the instrument and data reduction can all contribute to the accuracy of a measurement. In this paper, the measurement accuracy of physisorption was discussed from these three aspects.

The surface area and pore size distribution are two very basic properties of a solid catalyst or material powder. As a result, physisorption is one of the most basic characterization method for catalyst study and material research. As the only macroscopic method that can give both surface area and pore size information, the static volumetrictric method is widely used in the characterization of catalysts, advanced materials and carbon materials. Nowadays these parameters are also important for quality control in many industries. Therefore, it is more important than ever to know more details about the method used in physisorption measurement and its accuracy.

Traditionally, physisorption was considered a measurement but not an analysis. In practice, there are many misunderstandings of the physisorption process and its data reduction. Today, more new and complex materials need to be characterized. Automated instruments can collect isotherm data automatically based on previous settings, but no instrument can automatically choose the correct analysis settings and data reduction models for a particular material and its properties. In this case, if one simply relies on getting data automatically from the instrument, there can be erroneous conclusions [1].

A difference from other regularly used analysis methods, e.g. spectroscopy, chromatography, and electronic spectroscopy, is that the static volumetric method collects pressure-volume data at a specific temperature from a physical process to give the isotherm. After data collection, the isotherm can be analyzed by different physical models and algorithms to get the surface area and pore size information. So the question of whether the hardware and firmware is designed scientifically, accurately, and reasonably and whether the experimental operation is precise will all influence data accuracy. Also, the data reduction process must be based on the properties of the sample. The researcher needs to be very flexible and scientific during the whole process.

Here, we discuss the influence of instrument hardware design, operation, and data reduction on measurement accuracy.

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DOI: 10.1016/S1872-2067(12)60601-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal.,Vol. 34, No. 10, October 2013

1. Accuracy concerns due to instrument hardware design

The gas sorption amount is a function of pressure. It can be measured by either the volumetric or gravimetric method. The gravimetric method instrument is composed of a very sensitive microbalance and pressure gauge. It measures the adsorption amount directly with buoyance calibration, but this method can only be used when the measurement temperature is close to room temperature.

The static volumetric method is based on the gas law. When the system volume and temperature are exactly known, the adsorbed gas amount can be calculated by the volume difference before and after the gas sorption process. In practice, this method is easier, and so most commercial instruments nowadays are based on this method (Fig. 1). During the analysis, the manifold is dosed with a specific amount of gas, which is measured by the pressure difference from before and after the dosing, which are recorded by the manifold pressure transducer. After the sample valve is opened, gas will flow into the sample cell. The pressure there is recorded by the sample cell pressure transducers. After the pressure reaches equilibrium after sorption, the system will go on to the next pressure (dose). By repeating this process, the isotherm is obtained and drawn.

Clearly, the system volume, temperature, pressure measurement accuracy, and saturation pressure (p_0) accuracy will all influence measurement accuracy.

1.1. System volume

There are two components of the system volume, the volume above the sample valve, and the volume below the sample valve. The volume above the sample valve is called the manifold volume, and the volume below the sample valve is called the void volume or free space.

The manifold volume is the basis used to calculate the initial gas input amount. It is part of the instrument design. The manifold volume can be very accurate by manufacturer calibration [2]. It is easy to understand that a larger pressure difference during the gas dosing process gives a more accurate gas amount calculation. So a smaller manifold gives a more sensitive instrument.

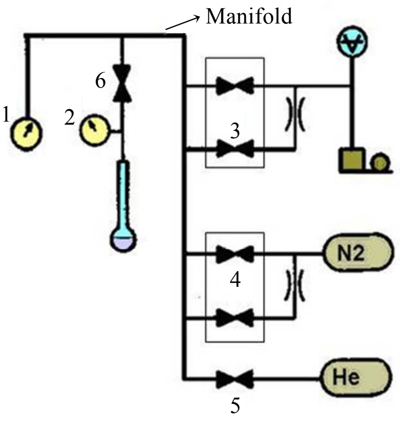

Fig. 1. Basic hardware components of the static volumetric method. 1 is manifold pressure transducer; 2 is sample cell pressure transducer; 3 is vacuum valve with different evacuation limits; 4 is gas input valves with different input pressure; 5 is inert gas (helium) input valve; 6 is sample valve.

The void volume (free space) is the space that the dosed gas occupies during every dose of the analysis. An accurate void volume is the basis to calculate the exact adsorbed gas amount. Because the molecular volume at liquid nitrogen (LN_2) temperature (77.35 K) is about four times the molecular volume at room temperature (e.g. 300 K), it is necessary to know both the physical void volume and the exact volume for the cold zone and warm zone, which depends on the LN_2 level.

There are different methods to get the void volume, including measurement, reference method, and density calculation. The advantage of the reference method is that it is both fast and does not need to use helium. In detail, the system gets the volume of the blank sample cell volume with the adsorbate at room temperature and then does a blank run with the same analysis settings (ISO 15901, Material pore size distribution and porosity by mercury intrusion method and gas sorption method). The system saves these information and uses this reference for each analysis.

In order to measure the void volume (free space) it is necessary to introduce a non-adsorbing gas such as helium before or after analysis both at room temperature and at the analysis temperature. The helium void volume measurement is based on the assumptions that helium is not adsorbed and that helium does not penetrate into regions which are inaccessible to the analysis adsorbate. If the assumptions do not hold true for a given sample, it will be required that special settings for removing helium from the sample surface and pores before the analysis in case of isotherm error below $p/p_0 < 10^{-6}$.

1.2. Manifold temperature

An accurate system temperature is the basis of an accurate measurement. Almost all instruments now have a thermal transducer attached to the manifold to record the real-time temperature for calculation. Currently, most commercial instruments use thermal transducer with ±0.1 K sensitivity. This is precise enough for physisorption measurements.

The newest research level instruments all have “high resolution” transducers. This means that the instrument uses a 0.1 mmHg transducer instead of the traditional 1 mmHg transducer for more stable and higher resolution data in the low pressure range (relative pressure less than 10^{-6}). Researchers need to know that besides high resolution, a more stable system temperature is also required, which needs a special system heating design to avoid system temperature change during analysis.

1.3. Bath temperature

It has been described that the system volume can be influenced by the bath temperature and bath level. We call the difference the cold zone volume and warm zone volume. Practically, there are two methods to accurately measure the void volume: using a resistant temperature detector (RTD) feedback