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Nanotechnologies - Measurement of the hydrogen storage capacity of nanoporous materials - Gas adsorption method

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3 Terms and definitions

The terms defined in GB/T 19587, GB/T 21650.3, GB/T 24499 and GB/T 30544.4 apply together with five terms given here. A nanoporous material (3.1) is a solid material in which nanopores are present, taken from GB/T 30544.4-2019, 3.4. A micropore (3.2) is a pore whose size is smaller than or about equal to 2 nm, taken from GB/T 19587-2017, 3.15.

Physisorption (3.3) is the weak bonding of an adsorbate, reversible through a small change of pressure or of temperature; the definition is taken with modification from GB/T 21650.3-2011, 3.12. Hydrogen storage by physisorption (3.4) is the storage mode in which hydrogen is adsorbed in a porous material of high specific surface area on the physical adsorption principle, taken from GB/T 24499-2009, 4.4.

Hydrogen storage capacity (3.5) is the amount of hydrogen adsorbed by unit mass or unit volume of the material at a given temperature and pressure. A first note says that it is commonly expressed as a mass fraction in percent, as shown in 8.1.5; a second note lists the other units in common use, kilogram per kilogram, mole per kilogram, kilogram per cubic metre and mole per cubic metre.

4 Principle

4.1 The amount of hydrogen adsorbed is generally obtained by measuring an adsorption isotherm, from which the storage capacity is then calculated. The isotherm is measured by

holding the nanoporous material at constant temperature in an atmosphere of high purity hydrogen, waiting for adsorption equilibrium, measuring the equilibrium pressure of the hydrogen and deriving from it the amount of hydrogen adsorbed at that pressure.

4.2 In the static volumetric method a known quantity of adsorbate gas is admitted to the sample tube, which holds the adsorbent at the adsorption temperature, as shown in Figure 1. In the fixed finite volume the pressure falls as the sample begins to adsorb, until adsorption reaches equilibrium; the quantity adsorbed at the equilibrium pressure is the difference between the gas admitted to the tube and the gas that remains in the gas phase. Volume and temperature are measured along with the system pressure, the volume being determined by expansion of an inert gas such as helium. The legend of Figure 1 names the specific adsorbed volume at standard conditions in cubic metres per gram and the equilibrium adsorption pressure in pascals, and numbers the sample, the thermostatic device, the vacuum system, the pressure gauge, the gas burette, an optional saturation pressure tube, the adsorbate gas (hydrogen) and the gas used to measure the free space, such as helium.

5 Reagents or materials

Three gases are listed: helium, nitrogen and hydrogen, each of a purity of at least 99.999 % by volume.

6 Apparatus

6.1.1 Any physical adsorption analyser whose temperature and pressure measuring ranges and whose measuring principle meet this document is suitable; the usual adsorption test temperature range is -196 °C to 50 °C and the usual measuring pressure range 0 kPa to 20 000 kPa. 6.1.2 The vacuum reached shall be no worse than 1 Pa, the accuracy of the pressure transducer +/-0.15 %, that of the gas burette temperature sensor +/-0.1 °C and that of the thermostatic device +/-0.1 °C.

6.1.3 The heating mantle and the other sample pretreatment devices control temperature from room temperature to 400 °C with an accuracy of +/-5 °C. 6.2 The analytical balance used to weigh the sample has a scale division of 0.1 mg.

7 Measurement procedure

7.1 The amount of sample taken should take account of the ratio between the sample and the system volume and of the accuracy of the pressure transducer, so that the storage capacity can be determined precisely. Where the sample comes from a large batch it is taken according to GB/T 5314 or ISO 8213, and the portion taken is to be uniform and representative.

7.2.1 Degassing removes the physically adsorbed substances from the sample surface

while avoiding damage to its structure and properties. The highest degassing temperature, that is the highest temperature at which the properties of the sample stay stable, may be found by thermogravimetric analysis, by spectroscopy, or by trying different degassing temperatures and times; where vacuum treatment is used, a vacuum of about 1 Pa or lower is enough. After the degassing heating the sample tube is left to cool naturally to room temperature, and the sample temperature needs some time to reach equilibrium because the thermal conductivity inside the tube falls at low pressure. For sensitive samples the degassing rate and the heating rate are controlled so that the pore structure does not change and the sample is not elutriated.

7.2.2 The empty tube is weighed accurately before the measurement; after degassing a protective gas is backfilled and the tube and sample are weighed together, the mass of the degassed sample being the total less the mass of the empty tube, to 0.1 mg. The empty sample tube is degassed for at least 0.5 h under the same conditions and backfilled with protective gas afterwards; with in situ degassing the backfill follows the completion of the measurement and the evacuation for desorption.

7.3.1 Before the measurement the instrument shall be shown to be leak free at the measuring pressure. In a pressure hold test the system at its maximum working pressure shall not lose more than 0.1 % of that pressure in 30 min; an alternative check is that after evacuation the system pressure shall not rise by more than 20 Pa in 10 min.

7.3.2 For the hydrogen isotherm, absolute pressure sampling points are set in a number sufficient to resolve the shape of the isotherm; the relative equilibration interval is at least 10 s; the free space is measured after the isotherm has been completed, so as to avoid contamination by helium, and during sample analysis and free space measurement the volume of the sample tube is kept as stable as possible at the measuring temperature. Once the measuring conditions have been set the measurement starts, and it ends when all the sampling points have been measured.

8 Calculation of the hydrogen storage capacity

8.1.1 and 8.1.2 give the equations for the hydrogen adsorbed in the first step and for the cumulative amount after m adsorption steps. Their legends name the amount of hydrogen adsorbed in moles, the starting pressure and the equilibrium pressure of a single adsorption step in pascals, the volume of the gas burette of Figure 1 and the free space of the sample tube in cubic metres, the compressibility factors of hydrogen at those pressures and at the system and the sample temperatures, the ideal gas constant taken as 8.314 joules per mole kelvin, and the temperature of the measuring system in which the gas burette sits and the temperature of the sample tube, both in kelvin.

8.1.3 The hydrogen compressibility factor should be taken from the NIST standard database or calculated from the virial equation. 8.1.4 In practice not every part of the sample tube free space is at the sample temperature, so the cold zone volume and the hot

zone volume are measured separately and the two equations are modified accordingly; the detailed calculation is given in GB/T 21650.2-2008, 9.4.

8.1.5 The storage capacity by the static volumetric method is obtained as a mass fraction from the specific adsorbed volume at standard conditions in cubic metres per gram, the molar mass of hydrogen in grams per mole and the molar volume of an ideal gas at standard conditions in cubic metres per mole. A first note states that the ratio of the specific adsorbed volume to that molar volume is the cumulative hydrogen adsorption; a second note states that the equation has several variant forms with correspondingly different units, the other units in common use being those listed in the second note to 3.5. 8.2 Worked examples of the determination are given in Annex A.

9 Factors influencing the uncertainty

The main sources of uncertainty in the hydrogen storage capacity are the accuracy of the balance, the accuracy of the pressure transducer, the accuracy of the temperature sensor, and the repeatability and the accuracy of the measurement of the amount adsorbed.

10 Test report

The test report shall include at least the number of this document; the laboratory, the equipment model, the operator and the test date; the sample identification and its characteristics, for example the origin of the sample, its chemical composition, its purity, the sampling method and the subdivision of the sample; the sample pretreatment and degassing conditions, such as vacuum degassing with its temperature and time; the mass of the sample after degassing; the adsorbate gas; the adsorption isotherm and the measuring temperature; the storage capacity at a stated pressure and temperature; and the certified reference material or laboratory reference sample used to measure the performance of the instrument and to verify the results.

A Annex A (informative) Examples of the determination of the hydrogen storage capacity of nanoporous materials

A.1 The low pressure example is run on a 5A molecular sieve material with a low pressure physical adsorption analyser at the Micromeritics Asia-Pacific demonstration laboratory, by the low pressure static volumetric method, over an absolute pressure range of 0 kPa to 120 kPa at a measuring temperature of -196 °C, with a sample mass of 1.2542 g. Figure A.1 gives the capacity against pressure isotherm. The sentence that reports the result reads, at an absolute pressure of 100 kPa and a measuring temperature of -196 °C, that the hydrogen storage capacity of a graphene-heteropolyacid composite is a mass fraction of 1.25 %; the material named in that sentence is not the 5A molecular sieve announced at the head of the example, and the text is translated here as printed.