Designation: D 4222 – 03 (Reapproved 2008)

Standard Test Method for
Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts and Catalyst Carriers by Static Volumetric Measurements[1]

1. Scope

1.1 This test method covers the determination of nitrogen adsorption and desorption isotherms of catalysts and catalyst carriers at the boiling point of liquid nitrogen.[2] A static volumetric measuring system is used to obtain sufficient equilibrium adsorption points on each branch of the isotherm to adequately define the adsorption and desorption branches of the isotherm. Thirty points evenly spread over the isotherm is considered to be the minimum number of points that will adequately define the isotherm.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [3]
D 3663 Test Method for Surface Area of Catalysts and Catalyst Carriers
D 3766 Terminology Relating to Catalysts and Catalysis
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E 456 Terminology Relating to Quality and Statistics
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—See Terminology D 3766.

3.2 *Symbols*:

PH_1 = initial helium pressure, torr.
PH_2 = helium pressure after equilibration, torr.
TH_1 = temperature of manifold at initial helium pressure, °C.
TH_2 = temperature of manifold after equilibration, °C.
P_1 = initial N_2 pressure, torr.
T_1 = manifold temperature at initial N_2 pressure, K.
T'_1 = manifold temperature at initial N_2 pressure, °C.
P_2 = pressure after equilibration, torr.
T_2 = manifold temperature after equilibrrium, K.
T'_2 = manifold temperature after equilibrium, °C.
P_3 = initial N_2 pressure during desorption, torr.
T_3 = manifold temperature at initial N_2 pressure, K.
T'_3 = manifold temperature at initial N_2 pressure, °C.
P_4 = pressure after equilibration during desorption, torr.
T_4 = manifold temperature after equilibration, K.
T'_4 = manifold temperature after equilibration, °C.
P_0 = liquid nitrogen vapor pressure, torr.
T_s = liquid nitrogen temperature, K.
X = relative pressure, $P_{2(4)}/P_0$.
V_d = volume of manifold, cm^3.
V_s = the dead-space volume factor, cm^3 (STP)/torr.
W_s = mass of sample, g.
W_1 = tare of sample tube, g.
W'_2 = sample mass + tare of tube after degassing, g.
W_2 = sample mass + tare of tube after adsorption, g.
V_{ds} = volume of nitrogen in the dead-space, cm^3 (STP).
V_1 = see 12.4.3.
V_2 = see 12.4.4.
V_t = see 12.4.5.
V_{ad} = see 12.4.7.
V_{de} = see 12.5.

4. Summary of Test Method

4.1 The sample is heated and evacuated to remove adsorbed vapors from the surface. The nitrogen adsorption branch of the isotherm is determined by evacuating the sample, cooling the
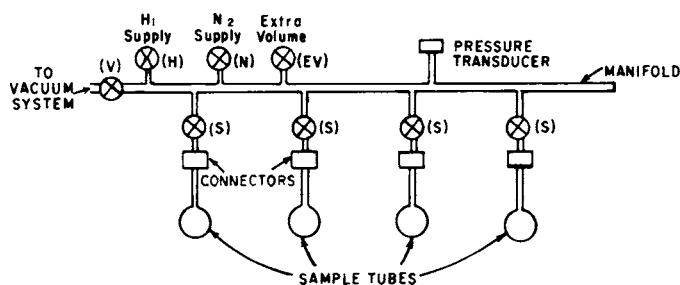

FIG. 1 Schematic Diagram of Adsorption Apparatus

sample to the boiling point of liquid nitrogen (~77.3 K), and subsequently adding stepwise, known amounts of nitrogen gas to the sample in such amounts that the form of the adsorption isotherm is adequately defined and the saturation pressure of nitrogen is reached. Each additional dose of nitrogen is introduced to the sample only after the foregoing dose of nitrogen has reached adsorption equilibrium with the sample. By definition, equilibrium is reached if the change in gas pressure is no greater than 0.1 torr/5 min interval. The desorption isotherm is determined by desorbing nitrogen from the saturated sample in a stepwise mode with the same precautions taken to ensure desorption equilibration as applied under adsorption conditions. It is essential that the experimental points be distributed over the isotherm in such a manner as to correctly identify and define the isotherm. If the additions or withdrawals of nitrogen are too large, the temporarily too-high nitrogen gas pressure during adsorption or too-low gas pressure during desorption, may result in so-called scanning effects within the hysteresis loop of the adsorption-desorption branches of the isotherm. The occurrence of scanning may result in too-high equilibrium values for the adsorption isotherm and too-low values for the desorption isotherm.

5. Significance and Use

5.1 The test method has two main functions: first, it provides data useful for establishing the pore size distribution of catalyst materials, which in turn may influence their performance; and second, it serves as a laboratory test which may be used to study porosity changes that may occur during the manufacture and evaluation of catalysts.

6. Apparatus

6.1 A generic schematic diagram of the minimum apparatus requirement is shown in Fig. 1. A commercial instrument may be used and may be constructed of glass or of metal. The specific commercial apparatus chosen may have a different configuration than that shown in Fig. 1 and may require modification of the sequence of valve operation and of the calculations and equations used. It should have the following features as a minimum:

6.1.1 *Distribution Manifold*, having a (V_d), known to the nearest 0.05 cm^3. This volume is defined as the volume between the stopcocks or valves and includes the pressure gage.

6.1.2 *Vacuum System*, capable of attaining pressures below 10^{-4} torr (1 torr = 133.3 Pa). This will include a vacuum gage (not shown in Fig. 1). Access to the distribution manifold is through the valve *V*.

6.1.3 *Pressure Sensing Devices or Pressure Transducers*, capable of measurements with a sensitivity of at least 0.1 torr, in the range from 0 to 1000 torr (1 torr = 133.3 Pa).

6.1.4 *Value (H)*, from the helium supply to the distribution manifold.

6.1.5 *Valve (N)*, from the nitrogen supply to the distribution manifold.

6.1.6 The connection between the sample tube and the *S* valve can be a standard-taper glass joint, a glass-to-glass seal, or a compression fitting.

6.2 *Sample Tubes*, with volumes from 5 cm^3 to 100 cm^3 depending on the application.

6.3 *Heating Mantles or Small Furnaces*.

6.4 *Dewar Flasks*.

6.5 *Laboratory Balance*, with 0.1-mg (10^{-7}kg) sensitivity.

6.6 *Thermometer or Thermocouple*, for measuring the temperature of the distribution manifold [$T'_1(i)$ or $T'_2(i)$] in °C.

6.6.1 The manifold may be thermostated at a particular temperature, a few degrees above ambient, to obviate the necessity of recording this temperature at each reading.

6.7 *Thermometer*, for measuring the temperature of the liquid nitrogen bath ($T_s (i)$) in Kelvin. Preferably, this thermometer will be a nitrogen vapor-pressure-thermometer, often referred to in a commercial instrument as a pressure saturation tube, that gives P_0 directly and has greater precision, or a resistance thermometer from which P_0 values may be derived.

NOTE 1—A pressure transducer may be placed between the sample tube and the manifold to monitor equilibrium pressure, but this is not a requirement of the system.

7. Reagents

7.1 *Helium Gas*—A cylinder of helium gas at least 99 % pure.

7.2 *Liquid Nitrogen* , of such purity that P_0 is not more than 20 torr above barometric pressure. A fresh daily supply is recommended.

7.3 *Nitrogen Gas*—A cylinder of nitrogen gas at least 99.999 % pure.

8. Procedure-Sample Preparation and Degassing

8.1 Select a sample tube of the desired size. To minimize the dead-space, a 5-cm^3 sample tube is preferred for samples not exceeding about 1 g. However, to avoid boiling when degassing is started, a 25-cm^3 sample tube may be preferred for finely powdered catalysts. A small glass-wool plug or fritted disk placed in the neck of the sample tube above the liquid nitrogen level, will eliminate the possibility of any small catalyst particles entering the vacuum system.

8.2 Fill the sample tube with nitrogen or helium at atmospheric pressure, after removing air by evacuation. This may be done on the adsorption unit or on a separate piece of equipment.

8.3 Remove the sample tube from the system, cap, and weigh. Record the mass as W_1.

8.4 Place the catalyst sample, whose approximate mass is known, into the sample tube. Choose the sample size to provide an estimated total sample surface area of approximately 20 m^2 or greater.