Designation: D4824 – 13

Standard Test Method for Determination of Catalyst Acidity by Ammonia Chemisorption[1]

This standard is issued under the fixed designation D4824; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

This test method involves the measurement of total catalyst acidity by chemisorption of ammonia in a static volumetric system. Acidity is a very important property in determining catalyst activity and selectivity in many commercial reactions. Zeolite based catalysts used in the petroleum industry for catalytic cracking are a prime example. This test method describes a simple procedure employing inexpensive equipment that could readily be assembled in most laboratories.

1. Scope

1.1 This test method covers the determination of acidity of catalysts and catalyst carriers by ammonia chemisorption. A volumetric measuring system is used to obtain the amount of chemisorbed ammonia.

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:*[2]

D3766 Terminology Relating to Catalysts and Catalysis

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—See Terminology D3766.

3.2 *Symbols:*

V_k = calibrated expansion volume, cm^3.
T_1 = temperature of V_k at initial ammonia pressure, K.
T_2 = temperature of V_k at final ammonia pressure, K.
P_1 = initial ammonia pressure, torr.
P_2 = final ammonia pressure, torr.
W_s = mass of sample, g.
W_1 = tare of sample tube, g.
W_2 = sample mass plus tare of tube, g.
P_{1T} = initial ammonia pressure corrected to standard temperature, torr.
P_{2T} = final ammonia pressure corrected to standard temperature, torr.

4. Summary of Test Method

4.1 A sample is degassed by heating in a vacuum to remove adsorbed vapors from the surface. The sample is then exposed to an excess of gaseous ammonia and the excess ammonia is removed by freezing it into a trap cooled with liquid nitrogen. The chemisorbed ammonia is calculated as the difference between the volume of ammonia before exposure and the volume recovered in the liquid nitrogen trap.

5. Significance and Use

5.1 This test method can be used to determine the acidity of catalysts and catalyst carriers by ammonia chemisorption for materials specifications, manufacturing control, and research and development in the evaluation of catalysts.

6. Apparatus

6.1 A schematic diagram of one type of apparatus is shown in Fig. 1. It may be constructed of glass or metal and may operate manually or automatically. It has the following features:

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[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.01 on Physical-Chemical Properties.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

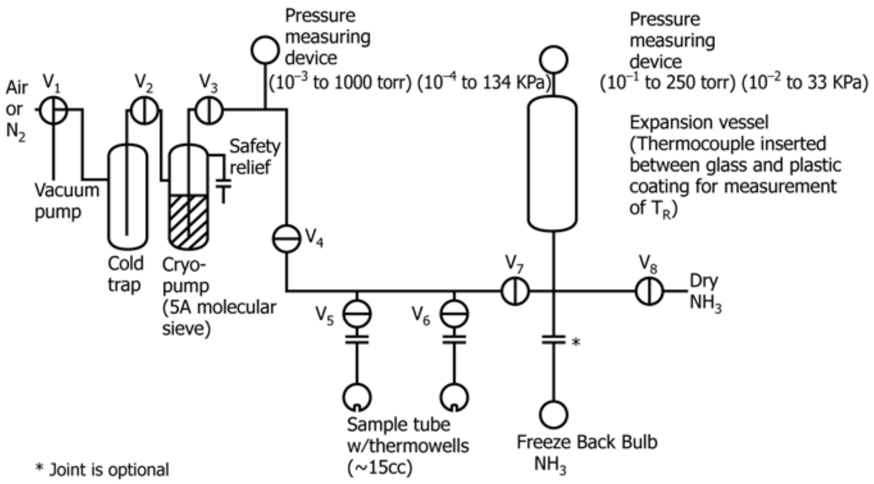

FIG. 1 Apparatus

6.1.1 *Vacuum System,* capable of attaining and maintaining pressures below 10^{-4} torr (0.01 Pa) in the absence of catalyst.

6.1.2 *Expansion Vessel,* having a volume between 300 to 500 cm^3 (V_k) known to the nearest 0.01 cm^3 (Note 1). This volume is defined as the volume between stopcocks V_7 and V_8 and includes the pressure gage and ammonia bulb.

Note 1—An expansion vessel of smaller volume is recommended for materials of low surface area or smaller sample size.

6.1.3 *Pressure Sensing Device or Pressure Transducer,* capable of measuring 0 to 250 torr to the nearest 10^{-1} torr (10 Pa).

6.1.4 *Pressure Sensing Device or Pressure Transducer,* capable of measuring 0 to 1000 torr to the nearest 10^{-3} torr (0.1 Pa).

6.1.5 *Valve,* (V_8) from ammonia supply to the expansion volume.

6.1.6 *Sample Tubes,* with volume between 5 and 25 cm^3. The sample tube(s) may be connected to the apparatus with standard taper joints, glass-to-glass seals, or compression fittings.

6.1.7 *Dewar Flask(s),* for immersion of ammonia (freeze-back bulb) in liquid nitrogen.

6.1.8 *Thermometer or Thermocouple,* for measuring the temperature of the expansion volume, V_k. Alternatively, the expansion volume may be thermostatted a few degrees above ambient to obviate the necessity of recording this temperature.

6.1.9 *Heating Mantle or Small Furnace,* for each sample tube.

6.1.10 *Balance,* with 0.1-mg sensitivity.

6.1.11 *Thermometer or Thermocouple,* for measuring the temperature of the sample tube.

6.1.12 *Liquid Nitrogen Cold Trap,* for vacuum system.

6.1.13 *Drying Tube,* for drying ammonia gas (for example, a 3A molecular sieve or BaO).

7. Reagents

7.1 *Ammonia Gas,* at least 99.9 % pure.

7.2 *Liquid Nitrogen.*

7.3 *Nitrogen Gas,* at least 99.9 % pure, passed through drying tube.

8. Procedure

8.1 Weigh sample tubes to 0.1 mg and record as W_1. Place approximately 2 g of sample into the sample tube.

8.2 Attach the sample tube to the apparatus.

8.3 Open the sample valves (V_5 or V_6, or both).

8.4 Slowly open the valve to the vacuum system (V_4), monitoring the rate of pressure decrease to avoid too high a rate, which might lead to excessive fluidization of powdered samples.

8.5 Place a heating mantle or furnace around each sample and raise the temperature to 673 K.

Note 2—Take special precautions if the moisture content exceeds approximately 5 % to avoid "bumping" of powdered sample. It is recommended that the heating rate not exceed 100 K/h under these circumstances.

8.6 Continue degassing at 673 K for a minimum of 3 h, at a pressure not to exceed 10^{-3} torr (0.1 Pa) Pa. Overnight degassing is permissible.

Note 3—Certain materials will decompose at 673 K or will sinter. Lower degassing temperatures are permissible for such materials; however, the degassing temperature should be specified when reporting the results.

8.7 After outgassing, lower the sample temperature to 448 K.

8.8 Close stopcock V_7 to isolate the samples from the expansion volume, V_k, and admit ammonia to V_k through valve V_8. Assume a chemisorption of approximately 5 cm^3/g and admit sufficient ammonia to give an excess pressure of 100 to 150 torr (13 to 20 KPa) during exposure.

8.9 Close the ammonia valve, V_8, and freeze the ammonia into the ammonia bulb by immersing the bulb in liquid nitrogen.

8.10 After the ammonia is frozen, close the sample valves V_5 and V_6, open valve V_7, and pump out noncondensible impurities. (Two minutes is normally sufficient pump time.)

8.11 After pumping out noncondensible impurities, close valve V_7 to the vacuum source and remove the liquid nitrogen from the ammonia bulb so the ammonia may expand into V_k. Measure the pressure, P_1 and temperature T_1.

8.12 Close valve V_4 to the vacuum source and open sample valves V_7 , then V_5 or V_6, exposing the sample(s) to excess ammonia for 30 min. Sample temperature should be 448 K.

8.13 After 30-min exposure, freeze ammonia back into the ammonia bulb for a period of 2 h by immersion in liquid nitrogen.

8.14 After freeze-back period, close valve V_7 to separate sample tube(s) from expansion volume, V_k. If the pressure is not less than 0.1 torr (10 Pa) at the end of the freeze-back period, then the system leaks and the test should be repeated. Remove liquid nitrogen and allow ammonia to expand into V_k. If system does not leak there should be no condensibles. Measure pressure, P_2, and temperature, T_2.

8.15 Remove the mantle or furnace from around the sample tube(s) and cool to ambient temperature. Backfill the sample tube(s) with nitrogen to atmospheric pressure or slightly above. Close the sample valve.

8.16 Detach the sample tube(s) from the apparatus and weigh. Record as W_2 to 0.1 mg. (If standard tapered joints are used, take care to remove grease prior to weighing.)

9. Calculation

9.1 Calculate the mass of sample, W_s, as follows:

$$W_s = W_2 - W_1 \tag{1}$$

9.2 Calculate the pressures at standard temperature, P_{1T} and P_{2T}, as follows:

$$P_{1T} = P_1 \times \frac{273}{T_1} \tag{2}$$

$$P_{2T} = P_2 \times \frac{273}{T_2} \tag{3}$$

9.3 Calculate the volume adsorbed, V_{ads} as follows:

$$V_{ads} = \left(\frac{P_{1T} - P_{2T}}{760} \right) V_k \tag{4}$$

9.4 Calculate the acidity, *A*, in cubic centimetres per gram as follows:

$$A = V_{ads}/W_s \tag{5}$$

10. Report

10.1 The report shall include pretreatment, outgassing temperatures, and the temperature of the samples during exposure.

10.2 Report the result as cubic centimetres per gram to three significant figures or the nearest 0.01 cm^3/g, whichever is greater.

11. Precision and Bias[3]

11.1 *Test Program*—An interlaboratory study was conducted in which the named property was measured in four separate test materials in nine separate laboratories. Practice E691, modified for nonuniform data sets, was followed for the data reduction. Analysis details are in the research report. The 95 % repeatability interval is about 10 % and the 95 % reproducibility interval is about 30 %.

11.2 *Bias*—The procedure described is without known bias.

12. Keywords

12.1 catalysts; nitrogen adsorption; pore size distribution

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1023.