Designation: ~~D4481 – 10 (Reapproved 2015)~~ D4481 – 21

Standard Test Method for Total Nickel in Fresh Alumina-Base Catalysts[1]

This standard is issued under the fixed designation D4481; 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.

1. Scope

1.1 This test method covers the determination of nickel in fresh alumina-base catalysts and has been tested at nickel concentrations from 2.5 to 60 weight %, expressed as nickel oxide (NiO).

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to ~~its~~ use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D7442 Practice for Sample Preparation of Fluid Catalytic Cracking Catalysts and Zeolites for Elemental Analysis by Inductively Coupled Plasma Optical Emission Spectroscopy
E105 Guide for Probability Sampling of Materials
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 The test specimen (as received) is treated with concentrated hydrochloric acid to solubilize the nickel. If necessary, nickel is recovered from any insoluble residue by potassium pyrosulfate fusion, after hydrofluoric-sulfuric acid treatment to remove silica. Ammonium citrate is added to complex the aluminum and buffer the solution. Nickel is precipitated as nickel dimethylglyoxime, Ni $(C_4H_7O_2N_2)_2$, at a weakly alkaline pH. The precipitate is washed and weighed as Ni $(C_4H_7O_2N_2)_2$ after drying at ~~120°C.~~120 °C.

3.2 A separate test specimen is taken to determine loss on ignition (LOI) at ~~550°C.~~550 °C. The value is used to calculate the nickel as percent nickel oxide (NiO) on a ~~550°C~~550 °C dry basis.

[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.03 on Chemical Composition.
Current edition approved ~~Dec. 1, 2015~~June 1, 2021. Published ~~December 2015~~June 2021. Originally approved in 1985. Last previous edition approved in ~~2010~~2015 as ~~D4481~~D4481 – 10~~–10.~~(2015). DOI: ~~10.1520/D4481-10R15.~~10.1520/D4481-21.

[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.

4. Significance and Use

4.1 This test method sets forth a procedure by which catalyst samples can be compared either on an interlaboratory or intralaboratory basis. It is anticipated that catalyst producers and users will find this method of value.

5. Interferences

5.1 Cobalt, molybdenum, and aluminum do not interfere. Interferences by elements that precipitate as hydroxides, such as iron, chromium, aluminum, lead, tin, manganese, titanium, and zirconium, are avoided by the addition of ammonium citrate before making the solutions ammoniacal. Copper, present in the 2 to 10 % range, tends to be co-precipitated with the nickel dimethylglyoxime. The only other metal ions precipitated by dimethylglyoxime are palladium, gold, and bismuth.

6. Apparatus

6.1 *Beakers,* 600-mL, 150-mL.

6.2 *Hotplate.*

6.3 *Furnace,* electric muffle. Calibrated and capable of maintaining temperatures of 550 ± ~~25°C,~~25 °C, and 950 ± ~~25°C.~~25 °C.

6.4 *Platinum Dishes,* 100-mL[3] capacity.

6.5 *Mortar and Pestle,* agate, or equivalent mechanical grinder.

6.6 *Crucibles,* sintered-glass, 30-mL, medium porosity frit.

6.7 *Fiberglass Filter,* 3.2 cm.

6.8 *Drying Oven* capable of maintaining a temperature of ~~120°C.~~120 °C.

6.9 *Vacuum Filtering Flask,* 500-mL.

6.10 *Filter Holder* and *Filter Disk*, Millipore 0.65 µm-47-mm diameter.

6.11 *pH Paper* to detect a value of 9.

6.12 *Screen,* 250-µm openings, 60-mesh.

6.13 *Analytical Balance,* capable of weighing to nearest 0.1 mg.

6.14 *Ashless Filter Pulp.*

6.15 *Desiccator.*

6.16 *Laboratory Fume Hood,* suitable for use with Hydrofluoric acid.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean type IV reagent water as defined in Specification D1193.

7.3 *Ammonium Citrate,* dibasic crystal, $(NH_4)_2HC_6H_5O_7$.

7.4 *Ammonium Hydroxide,* 10 and 25 % solutions.

NOTE 1—Refer to Section 8 on Hazards in Practice D7442 for hazards associated with handling of acids.

7.5 *Hydrochloric Acid,* concentrated 38 %.

7.6 *Hydrofluoric Acid,* concentrated 48 %.

7.7 *Methyl Red Indicator (o-carboxy benzene azodimethylaniline)*—Dissolve 0.02 g in 60-mL reagent grade ethanol. Add 40.0 mL of distilled water.

7.8 *4A Molecular Sieve,* activated for 2 h at ~~275°C.~~275 °C.

7.9 *Potassium Hydrogen Sulfate,* fused power-acid-flux grade.

7.10 *Sodium Dimethylglyoxime,* 8-Hydrate, crystal, $CH_3C{:}NONaC{:}NONaCH_3{\cdot}8H_2O$. Prepare a 1 weight % per volume solution in water.

7.11 *Sulfuric Acid,* 10 and 50 % solutions.

NOTE 2—The sodium salt of dimethylglyoxime is recommended, rather than the organic reagent, dimethylglyoxime because the salt is water soluble. Large excesses added to precipitate the nickel do no harm as the excess dimethylglyoxime is eliminated during the filtration and washing part of the procedure. The organic reagent, dimethylglyoxime, is not very soluble in water and is often added as a 1 % solution in ethanol. When added in this way, some of the excess reagent may contaminate the precipitated nickel complex. For this reason, an aqueous solution of the sodium salt is preferred. If the alcohol solution of dimethylglyoxime is to be used, add an amount so that the alcohol content of the sample solution does not exceed 50 % or some of the precipitated nickel dimethylglyoxymate may dissolve.

8. Sampling

8.1 The selection of a representative analytical sample from the bulk material is outside the scope of the present test method. It is presumed that parties using this test method for comparison purposes will have agreed on the selection of an analytical sample. If a sampling procedure is desired, Practice E105 is recommended.

8.2 Grind the sample to pass through a 60-mesh screen. Grind and screen the sample inside of a suitable laboratory fume hood. Avoid inhaling dust from the grinding and screening step. Nickel and its compounds are regulated by the EPA as possible carcinogens. For more information, go to EPA.gov for a list of extremely hazardous substances. Consult a material safety data sheet for additional information.

9. Procedure

9.1 **Warning—**This test method requires the use of an Extremely Hazardous substance, Hydrofluoric acid (HF). Additional information for the safe handling of this chemical, HF, is included as Appendix X1. Read Appendix X1 and assemble the necessary

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

safety equipment before proceeding with this test method. **Warning—**All heating of acid solutions on a hot plate or with a gas burner should be conducted in a fume hood. Fusions on a gas burner should be conducted in a fume hood.

9.2 Weigh three test specimens sufficient to yield 50 to 75 mg of NiO into 150-mL beakers. Record mass to the nearest 0.1 mg as *G*.

9.3 Weigh three 1-g test specimens into platinum dishes or porcelain crucibles. Record mass to the nearest 0.1 mg as G_1. Calcine for 2 h in a ~~550°C~~550 °C muffle furnace. Transfer to a desiccator containing freshly activated 4A molecular sieve. Cool, weigh, record mass as G_2, and calculate percent solids.

9.4 To test specimens from ~~9.1~~9.2, add 20-mL of concentrated hydrochloric acid and heat gently on a hotplate until only a paste of solids is left. Do not boil the solution. Do not bake solids or subsequent re-solution will be difficult.

9.5 Add 20 mL of concentrated hydrochloric acid and warm on a hotplate 15 to 30 min to dissolve salts. Cool and dilute to about 100 mL with deionized water.

9.6 Filter solids on 0.45-µm filter, using a 500-mL filter flask as a receiver. Wash the beaker with four approximately 20-mL portions of deionized water, transferring the washes to the filter. Wash the solids on the filter with three more 20-mL portions of deionized water. Quantitatively transfer the filtrate plus washes to a 600-mL beaker. Keep the beaker covered until ready to precipitate nickel.

9.7 Put a filter disk into a platinum dish and cover with ashless filter pulp. Carefully char over a gas burner, then ignite at red heat until the carbon is essentially burned off. Put the dish in a muffle furnace at ~~960°C~~960 °C for 50 min.

9.8 To solids in the platinum dish, add 10 mL of 48 % hydrofluoric acid and 5 mL of 10 % sulfuric acid and evaporate carefully to dryness on a hotplate. Then, carefully bring to a red heat over a gas burner until the sulfur trioxide fumes cease. Cool and add 5 g of reagent potassium pyrosulfate and fuse over a gas burner until a clear melt is obtained. Cool, add 10 mL of 10 % sulfuric acid, 20 mL of deionized water, and heat gently on a hot plate until the melt dissolves.

9.9 Filter the solution (~~9.7~~9.8) through a 0.45-µm filter, using a 500-mL filter flask as a receiver. Wash crucibles with four approximately 20-mL portions of deionized water. Combine filtrate with solution in beaker (see ~~9.5~~9.6). Wash the filter flask with three approximately 20-mL portions of deionized water, adding washings to beaker.

9.10 Add 20 mL of ammonium citrate to solution. Heat to 70 to ~~80°C~~80 °C on a steam bath. Add 10 drops of methyl red indicator solution and adjust pH to the yellow color by careful addition of 25 % of ammonium hydroxide or 10 % of sulfuric acid.

9.11 Add 60 mL of 1 % dimethylglyoxime solution. Immediately add concentrated ammonium hydroxide dropwise until the precipitation takes place. Continue dropwise addition until the solution reads pH 9 with pH paper. Cover the beaker. Place the beaker on a steam bath and heat for 30 min to coagulate the precipitate. Remove from the steam bath, allow to cool to room temperature, and check the pH. If pH is not 9 by pH paper, adjust to that pH.

9.12 Allow the precipitate to settle at least 10 h. Test for complete precipitation by adjusting pH to 9 if necessary and adding an additional 3 mL of 1 % dimethylglyoxime solution. If precipitation is incomplete, add an additional 5 mL of 1 % dimethylglyoxime solution and return to steam bath for 30 min. Allow to cool and check again for completion. If precipitation is still incomplete, discard sample. Recheck calculation of the test specimen size.

9.13 Dry and weigh a sintered glass crucible containing a 3.2-cm fiberglass filter. Record the weight at G_0.

NOTE 3—The use of a 3.2-cm fiber glass filter facilitates filtering and minimized clogging of the pores of the sintered glass frit of the crucible. This makes it easier to clean crucibles for re-use. Weigh the dry crucible plus the fiber glass filter prior to the filtration of nickel dimethylglyoxymate.

9.14 Filter the mixture from ~~9.11~~9.12, using a gentle suction, through the crucible and filter as prepared in ~~9.12~~9.13. Wash the precipitate in the crucible five times with water. Dry the crucible for 2 h at 120°C, allow to cool in a desiccator containing activated