Designation: D7206/D7206M – 25

Standard Guide for Cyclic Deactivation of Fluid Catalytic Cracking (FCC) Catalysts with Metals[1]

This standard is issued under the fixed designation D7206/D7206M; 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 guide covers the deactivation of fluid catalytic cracking (FCC) catalyst in the laboratory as a precursor to small scale performance testing such as catalyst activities (Test Method D3907) or activities plus selectivities (Test Methods D5154 and D7964). FCC catalysts are deactivated in the laboratory in order to simulate the aging that occurs during continuous use in a commercial fluid catalytic cracking unit (FCCU). This guide constitutes hydrothermal deactivation of the catalyst and metal poisoning by nickel and vanadium. Hydrothermal treatment is used to simulate the physical changes that occur in the FCC catalyst through repeated regeneration cycles. Hydrothermal treatment (steaming) destabilizes the faujasite (zeolite Y), resulting in reduced crystallinity and surface area. Further decomposition of the crystalline structure occurs in the presence of vanadium, and to a lesser extent in the presence of nickel. Vanadium is believed to form vanadic acid in a hydrothermal environment resulting in destruction of the zeolitic portion of the catalyst. Nickel's principle effect is to poison the selectivity of the FCC catalyst. Hydrogen and coke production is increased in the presence of nickel, due to the dehydrogenation activity of the metal. Vanadium also exhibits significant dehydrogenation activity, the degree of which can be influenced by the oxidation and reduction conditions prevailing throughout the deactivation process. The simulation of the metal effects that one would see commercially is part of the objective of deactivating catalysts in the laboratory. Catalyst deactivation by hydrothermal treatment only is addressed in Guide D4463/D4463M.

1.2 The two basic approaches to laboratory-scale simulation of commercial equilibrium catalysts described in this guide are as follows:

1.2.1 *Cyclic Propylene Steaming (CPS) Method,* in which the catalyst is impregnated with the desired metals via an incipient wetness procedure (Mitchell method)[2] followed by a prescribed steam deactivation.

1.2.2 *Crack-on Methods,* in which fresh catalyst is subjected to a repetitive sequence of cracking (using a feed with enhanced metals concentrations), stripping, and regeneration in the presence of steam. Two specific procedures are presented here, a procedure with alternating metal deposition and deactivation steps and a modified Two-Step procedure, which includes a cyclic deactivation process to target lower vanadium dehydrogenation activity.

1.3 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are not necessarily exact equivalents; therefore, to ensure conformance with the standard, each system shall be used independently of the other, and values from the two systems shall not be combined.

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

1.5 *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:*[3]

B215 Practices for Sampling Metal Powders

D3663 Test Method for Surface Area of Catalysts and Catalyst Carriers

[1] This guide is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.04 on Catalytic Properties.

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[2] Mitchell, B. R., *Industrial and Engineering Chemistry Product Research and Development*, 19, 1980, p. 209.

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

D3766 Terminology Relating to Catalysts and Catalysis
D3907 Test Method for Testing Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test
D3942 Test Method for Determination of the Unit Cell Dimension of a Faujasite-Type Zeolite
D4365 Test Method for Determining Micropore Volume and Zeolite Area of a Catalyst
D4463/D4463M Guide for Metals Free Steam Deactivation of Fresh Fluid Cracking Catalysts
D5154 Test Method for Determining Activity and Selectivity of Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test
D7964 Test Method for Determining Activity of Fluid Catalytic Cracking (FCC) Catalysts in a Fluidized Bed
E105 Guide for Probability Sampling of Materials
E122 Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process
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. Terminology

3.1 *Definitions:*

3.1.1 *crack-on*—technique of depositing metals onto a catalyst through cracking of an FCC feed with enhanced metal content in a fluidized catalyst bed that is at cracking temperature.

3.2 *Acronyms:*

3.2.1 *E-cat*—equilibrium catalyst from commercial FCCU.

3.2.2 *FCC*—fluid catalytic cracking.

3.2.3 *FCCU*—fluid catalytic cracking unit.

3.2.4 *LGO*—light gas oil, fluid at 40 °C, initial boiling point <200 °C.

3.2.5 *VGO*—vacuum gas oil, fluid at 70 °C, initial boiling point >250 °C.

4. Significance and Use

4.1 This guide describes techniques of deactivation that can be used to compare a series of cracking catalysts at equilibrium conditions or to simulate the equilibrium conditions of a specific commercial unit and a specific catalyst.

5. Reagents

5.1 *Feed, VGO.*

5.2 *Feed, LGO.*

5.3 *Hydrogen* (H_2), 42.8 % in nitrogen balance.

5.4 *Nickel naphthenate* or nickel octoate solution.

5.5 *Nitrogen* (N_2).

5.6 *Oxygen* (O_2), 40 % in nitrogen balance.

5.7 *Vanadium naphthenate solution.*

5.8 *Cyclohexane.*

5.9 *n-pentane.*

5.10 *n-hexane.*

5.11 *Water,* demineralized.

6. Hazards

6.1 The operations described in this guide involve handling heated objects, fragile glassware, and toxic organic nickel and vanadium compounds.

6.2 All work with organic metals precursor solutions and other organic solvents should be completed in suitable vented fume hood.

6.3 Appropriate personal protection equipment, including chemical goggles, laboratory smock, and disposable gloves should be worn.

6.4 Waste organic metal solutions and organic solvents shall be disposed of properly in suitable waste containers and according to regulations.

6.5 Vented furnaces and hoods should be regularly monitored for proper ventilation before using.

6.6 Evaporating dishes should be checked for cracks before use.

6.7 The muffle furnace used for the post-impregnation thermal treatment of the sample shall be appropriately and adequately ventilated. Catalyst load sizes should be selected to avoid overwhelming the ventilation capacity of the furnace and allowing fumes to escape into the laboratory.

6.8 To avoid the potential hazard of explosion in the muffle furnace, impregnated samples shall be completely dry of pentane prior to beginning the thermal post-treatment.

6.9 Material safety data sheets (MSDS) for all materials used in the deactivation should be read and understood by operators and should be kept continually available in the laboratory for review.

7. Sampling

7.1 Catalytic materials are, by nature, non-homogeneous. The chemical composition as well as the physical properties of the catalytic material such as size and shape can vary from particle to particle. Sampling a non-homogeneous material to obtain representative specimens for analysis can be difficult but it is extremely important. It is recommended that the analyst develop a sampling plan suitable for the method, practice or guide and the material(s) being tested. For example, the test samples shall be obtained from larger composites by riffling or splitting in accordance with subsection 5.12 of STP 447A[4] with the aim of obtaining representative samples that mirror the method relevant properties such as chemistry, shape and size distribution of the larger composite. Guide E105 provides guidance on constructing a sampling plan and Practice E122 assists the analyst with determining the representative sample size. The analyst is also urged to consult Practice B215 – 20 which contains excellent sampling.

[4] STP 447A – Manual on Test Sieving Methods.