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Standard Guide for Cyclic Deactivation of Fluid Catalytic Cracking (FCC) Catalysts with Metals¹

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^{e1} NOTE—Editorially changed 8.2.1.1 in March 2013.

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. ~~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). Deactivation for purposes of 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 ~~may are~~ not necessarily exact equivalents; therefore, to ensure conformance with the standard, each system shall be used independently of the other. Combining other, and values from the two systems may result in non-conformance with the standard; 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 ~~health~~ 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.*

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. Current edition approved March 1, 2013 April 1, 2019. Published March 2013 April 2019. Originally approved in 2006. Last previous edition approved in 2012 2013 as D7206/D7206M-06(2012) D7206/D7206M-06(2013)^{e1}. DOI: 10.1520/D7206_D7206M-06R13E01-10.1520/D7206_D7206M-19.

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

2. Referenced Documents

2.1 ASTM Standards:³

[D3907 Test Method for Testing Fluid Catalytic Cracking \(FCC\) Catalysts by Microactivity Test](#)

[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](#)

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 ; 40°C , initial boiling point $<200^{\circ}\text{C}$; $<200^{\circ}\text{C}$, sulfur content <1 mass percent.

3.2.5 *VGO*—vacuum gas oil, fluid at 70°C ; 70°C , initial boiling point $>250^{\circ}\text{C}$; $>250^{\circ}\text{C}$, sulfur content of 2 to 3 mass percent.

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 (H₂), 42.8 % in nitrogen balance.*

5.4 *Nickel naphthenate* or nickel octoate solution.

5.5 *Nitrogen (N₂).*

5.6 *Oxygen (O₂), 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.

³ 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.

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. CPS Method

7.1 *Summary of Practice*—A fresh FCC catalyst is impregnated with nickel, or vanadium, or both. Nickel and vanadium levels are controlled by a predetermined concentration for the sample. The catalyst is wetted with a mixture of pentane and ~~nickel~~, nickel naphthenate, or vanadium naphthenate, or solutions of both and then mixed to dryness. After drying, the sample is thermally treated to remove residual naphthenates. The sample is then ready for hydrothermal treatment ~~of analysis~~ as desired.

7.2 Procedure:

7.2.1 *Catalyst Pre-treatment Before Impregnation*—For a muffle furnace pre-treatment (standard), place the sample in a dish using a shallow bed (½ in. maximum). Calcine the sample for 1 h at ~~204°C [400°F]~~, 204 °C [400 °F], then 3 h at ~~593°C [1100°F]~~, 593 °C [1100 °F]. The sample is then removed and allowed to cool to room temperature. Catalyst should be returned to a sealed container as soon as it is cool.

7.2.2 *Steam Deactivation Pre-treatment*—Typical conditions included hydrothermal treatment for 2 h at ~~816°C [1500°F]~~, 816 °C [1500 °F], 100 % steam, and 0 psi. The catalyst is charged to a pipe reactor, fluidized in air, and then lowered over a ~~3-h~~ 3 h period into a ~~816°C [1500°F]~~ 816 °C [1500 °F] sand bath furnace. Air flow is switched off and steam introduced for 2 h. The reactor is then removed from the furnace and allowed to cool to room temperature under a nitrogen purge.

7.2.3 *Preparation of Nickel and Vanadium Mixture*—The desired nickel/vanadium levels are calculated for the quantity of sample to be impregnated. The mass of nickel or vanadium naphthenate used to obtain the desired levels on the catalyst sample are determined as follows:

$$N = T/S \times W \quad (1)$$

where:

N = naphthenate (nickel or vanadium mass used to obtain the desired metal level on the catalyst),
 T = target level (the desired mass percent of nickel or vanadium, or both, to be loaded on the catalyst),
 S = metal solution (the known mass percent of nickel or vanadium in the naphthenate solution), and
 W = mass of catalyst sample to be impregnated.

7.2.4 Impregnation:

7.2.4.1 Catalyst is poured into an evaporating dish. The dish shall be large enough to allow for a catalyst bed height of ½ in.

7.2.4.2 Slowly pour the dissolved metals solution into the dish with catalyst while mixing at the same time. Wash the residual naphthenate from the glass beaker with pentane and add the wash to the catalyst.

7.2.4.3 Stir the sample with a spoonula until it is completely dry. The appearance of very small lumps in the catalyst after drying is normal. Large lumps indicate improper drying and shall be avoided. This can be done by adding enough pentane to moisten the catalyst then repeating the stirring process. High levels of vanadium naphthenate will cause the sample to appear gummy and is normal.

7.2.4.4 *High Levels of Vanadium Naphthenate*—When an impregnation calls for more than 5000 ppm vanadium, the impregnation should be done in two steps. Otherwise, the volume of naphthenate will overwhelm the volume of catalyst used, affecting the accuracy in reaching the target level. If over 5000 ppm vanadium is required, divide the required volume of vanadium naphthenate in half, impregnate, post-treat, and impregnate again by adding the second half followed by a second post-treat. If nickel is also requested, this should be divided and added to the catalyst along with the vanadium.

7.2.4.5 *Antimony Addition*—If antimony is requested, triphenylantimony is added to the catalyst after the nickel and vanadium have been added and the post treatment has been completed. The impregnation procedure is the same as the nickel and vanadium impregnation except that cyclohexane is used instead of pentane. Antimony will not dissolve in pentane.

7.2.5 *Catalyst Post-treatment After Impregnation*—After the impregnated sample has dried, it is placed in a vented muffle furnace and heat treated to remove the naphthenates and coke formed. The dishes are placed in the furnace at room temperature and the temperature is raised to ~~204°C [400°F]~~, 204 °C [400 °F] and held at temperature for 1 h. The sample is then calcined at ~~593°C [1100°F]~~, 593 °C [1100 °F] for 3 h before being removed and allowed to cool to room temperature.

7.2.6 *Steam Deactivation*—Several methods exist, each requiring specific conditions. An example of such a method is shown in [Table 1](#).

8. Crack-on Approach 1: Alternating Cracking and Deactivation Cycles

8.1 Summary of Practice:

8.1.1 The crack-on units consist of a fluid bed reactor with a fritted gas distributor on the bottom. Nitrogen, air, steam, and other specialty gasses can be fed through the bottom. Oil can be delivered either from the top or bottom of the reactor depending on the method. Temperature is controlled by a three zone electric furnace. A disengaging section on the top of the reactor prevents catalyst loss during operation.

TABLE 1 Standard CPS Procedure

NOTE 1—This scheme is considered standard and represents the case in which the treatment ends in a state of reduction. A similar scheme in which the cycles end in oxidation can also be configured.

Catalyst pre-treatment	1 h at 204°C [400°F] followed by 3 h at 593°C [1100°F]
Impregnation	2000 ppm nickel and 3000 ppm vanadium
Post-treatment	1 h at 204°C [400°F] followed by 3 h at 593°C [1100°F]
Steam deactivation	788°C [1450°F], 50% steam, 0 psig, 20 h (30 cycles)
Cycles consist of:	10 min, 50% mass percent N ₂ 10 min, 50% mass percent 4000 ppm SO ₂ in air 10 min, 50 mass percent N ₂ 10 min, 50 mass percent propylene-N ₂ mixture —(5% propylene in N ₂)

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Cycles consist of:	10 min, 50 % mass percent N ₂ 10 min, 50 % mass percent 4000 ppm SO ₂ in air 10 min, 50 mass percent N ₂ 10 min, 50 mass percent propylene-N ₂ mixture (5 % propylene in N ₂)

8.1.2 The crack-on method involves depositing metals on the catalyst at cracking temperature using a feed with enhanced metals content. The catalyst is regenerated after each cracking cycle.

8.1.3 In Crack-on Approach 1, the catalyst is subjected to severe hydrothermal deactivation after each cracking and regeneration cycle. By this method, significant deactivation has taken place by the time the metals addition is complete.

8.2 Procedure:

8.2.1 *Preparation of the Catalyst*—Optionally screen the catalyst to remove coarse contaminants and fine particles that would be lost during fluidization.

8.2.2 Prepare the Feed:

8.2.2.1 Weigh out and transfer the appropriate amount of LGO into the feed vessel. The minimum amount of LGO will equal the number of cracking cycles times the amount fed per cycle.

8.2.2.2 Individually add the organic metal compounds. The mass of each metal added shall be calculated to give the desired metal loading on the catalyst. If using this technique to perform an E-cat simulation, the metal target may have to be substantially reduced by 25 to 50 % of the actual E-cat metal content in order to simulate the deactivation effects discussed in the scope.

8.2.2.3 Stir the LGO with a mechanical stirrer, and optionally heat, to ~~insure~~ensure homogeneity of the mixture throughout the procedure.

8.2.3 Set up the Reactor System:

8.2.3.1 Load the catalyst into the fluidized bed reactor. The amount of catalyst charged depends on the geometry of the reactor vessel.

8.2.3.2 Attach all external control, input, exhaust, and safety devices.

8.2.3.3 Fill the water reservoir to the appropriate starting point.

8.2.3.4 Start the flow of 100 % nitrogen gas through the LGO feed tube.

8.2.3.5 Start the flow of 100 % nitrogen through the sieve plate.

8.2.4 Metallation and Regeneration:

8.2.4.1 Set the reactor temperature (500 to 530°C):530 °C).

8.2.4.2 Inject xx grams of the LGO prepared in ~~7.2.28.2.2~~ (xx = total mass LGO / number of cycles). A good rule of thumb might be to set LGO per cycle equivalent to 20 to 50 % of the catalyst mass.

8.2.4.3 Run a stripping cycle with pure nitrogen (no feed) for 7 to 10 min, while ramping temperature to regeneration conditions (600 to 700°C):700 °C).

8.2.4.4 After the stripping step is complete, change the gas composition through both the feed tube and sieve plate to 100 % air for regeneration.

8.2.5 Deactivation:

8.2.5.1 Deactivation time and temperature are specific to the objectives of the catalyst simulation (732 to 815°C):815 °C). The total deactivation time from start to finish is established to achieve a certain degree of surface area reduction. Therefore, the steaming time per cycle is variable, but typically 30 to 60 min.