



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

This standard is issued under the fixed designation D7206; 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. 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.

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

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

2. Terminology

2.1 Definitions:

2.1.1 *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.

2.2 Acronyms:

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

2.2.2 *FCC*—fluid catalytic cracking.

2.2.3 *FCCU*—fluid catalytic cracking unit.

2.2.4 *LGO*—light gas oil, fluid at 40°C, initial boiling point < 200°C, sulfur content < 1 mass percent.

2.2.5 *VGO*—vacuum gas oil, fluid at 70°C, initial boiling point > 250°C, sulfur content of 2-3 mass percent.

3. Significance and Use

3.1 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.

4. Reagents

4.1 *Feed, VGO.*

4.2 *Feed, LGO.*

4.3 *Hydrogen (H₂)*, 42.8 % in nitrogen balance.

4.4 *Nickel naphthenate* or nickel octoate solution.

4.5 *Nitrogen (N₂)*.

4.6 *Oxygen (O₂)*, 40 % in nitrogen balance.

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 April 1, 2006. Published April 2006. DOI: 10.1520/D7206-06.

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

- 4.7 *Vanadium naphthenate solution.*
- 4.8 *Cyclo-hexane.*
- 4.9 *N-pentane.*
- 4.10 *N-hexane.*
- 4.11 *Water, demineralized.*

5. Hazards

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

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

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

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

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

5.6 Evaporating dishes should be checked for cracks before use.

5.7 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.

5.8 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.

5.9 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.

6. CPS Method

6.1 *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, 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.

6.2 Procedure:

6.2.1 *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), then 3 h at 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.

6.2.2 *Steam Deactivation Pre-treatment*—Typical conditions included hydrothermal treatment for 2 h at 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 period into a 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.

6.2.3 *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.

6.2.4 Impregnation:

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

6.2.4.2 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.

6.2.4.3 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.

6.2.4.4 *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.

6.2.4.5 *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.

6.2.5 *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) and held at temperature for 1 h. The sample is then calcined at 593°C (1100°F) for 3 h before being removed and allowed to cool to room temperature.

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

TABLE 1 Standard CPS Procedure

NOTE—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)

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

7.1 Summary of Practice:

7.1.1 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.

7.1.2 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.

7.1.3 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.

7.2 Procedure:

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

7.2.2 Prepare the Feed:

7.2.2.1 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.

7.2.2.2 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 25-50 % of the actual E-cat metal content in order to simulate the deactivation effects discussed in the scope.

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

7.2.3 Set up the Reactor System:

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

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

7.2.3.3 Fill the water reservoir to the appropriate starting point.

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

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

7.2.4 Metallation and Regeneration:

7.2.4.1 Set the reactor temperature (500-530°C).

7.2.4.2 Inject xx grams of the LGO prepared in 7.2.2 (xx = total mass LGO / number of cycles). A good rule of thumb might be to set LGO per cycle equivalent to 20-50 % of the catalyst mass.

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

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

7.2.5 Deactivation:

7.2.5.1 Deactivation time and temperature are specific to the objectives of the catalyst simulation (732-815°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 30-60 min.

7.2.5.2 Ramp the temperature up to deactivation conditions.

7.2.5.3 Terminate the air gas flow through the feed tube and the sieve plate.

7.2.5.4 Activate the water pump and adjust the water flow rate to achieve the desired partial pressure of steam. 100 % steam is achievable, but 45-90 % is more typical for laboratory simulations.

7.2.5.5 Repeat steps 7.2.3.4 through 7.2.5.4 for the number of desired cycles.

7.2.6 At the conclusion of the final deactivation step, cool the furnace using the forced air circulation system.

7.2.7 Remove the catalyst.

7.2.8 Analyze the deactivated catalyst.

7.3 Variations:

7.3.1 The temperature of cracking and deactivation, as well as the partial pressure of steam, are variables that can be customized as needed.

7.3.2 Heavier feeds can be used in Approach 1 than the LGO cited here. Heavier, resid-containing oils would require heating of the pump and delivery lines.

7.3.3 When applying a high metal content in Approach 1, it is advisable to add catalyst in stages. In this variation, a portion of the catalyst charge will have a relatively low metal content, compared to the metal content of the bulk.

NOTE 1—During the deactivation cycles, a variety of special gasses that might be found within an FCCU regenerator (for example, SO_x) can be added with the steam-air mixture.

8. Crack-on Approach 2: Two-Step Cyclic Deactivation (TSCD)

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.

8.1.2 Crack-on Approach 2 (TSCD) is separated into two basic programs or steps:

8.1.2.1 *Metallation Step*—Only a very mild regeneration step occurs between each cracking cycle, sufficient to remove the coke, but with no steam, under conditions where little surface area loss occurs. A prescribed number of these cycles are performed to reach the desired metals loadings.

8.1.2.2 *Deactivation Step*—A second program of alternating reduction and oxidation cycles is initiated in the presence of steam to achieve the required level of hydrothermal deactivation. The intent of this approach is to control the vanadium oxidation state in a manner more consistent with actual FCCU operation, which has important implications for dehydrogenation activity and zeolite destruction.

8.2 Procedure:

8.2.1 Preparation of the Catalyst Sample:

8.2.1.1 Sieve several portions of the catalyst. First remove any coarse contaminants using a No. XXX (425 μm) ASTM sieve. Then sieve remaining sample on a No. 325 (45 μm) ASTM sieve to obtain approximately 200 g of +45 μm material.

8.2.1.2 Place the +45 μm material in a shallow ceramic dish sized so that the bed depth is less than $\frac{1}{2}$ inch.

8.2.1.3 Calcine the +45 μm material by placing it in a cool muffle furnace, ramping the temperature to 600°C in 1 h, and holding at 600°C for 2 h.

8.2.1.4 Transfer material to a desiccator for cooling and storage to prevent moisture uptake by the catalyst. (**Warning**—The catalyst is more absorptive than some drying agents. The use of drying agents can sometimes put moisture back onto the catalyst.)

8.2.2 Preparation of the Oil Feed:

8.2.2.1 Into 100 mL beakers, weigh out the appropriate amount of organic metal compounds for addition to the feed. The compounds should be weighed out according to the total mass of each metal to be added to the total quantity of catalyst.

8.2.2.2 Dilute each compound with hexane (2:1 ratio of hexane to organic-metal compound.)

8.2.2.3 Mix the solutions together.

8.2.2.4 Add VGO until the total mass of the solution is 650 g.

8.2.3 Load the Reactor:

8.2.3.1 Start the flow of 100 % nitrogen gas at 595 mL/min through the feed nozzle to prevent catalyst from entering the feed nozzle.

8.2.3.2 Load 150 g of calcined, +45 μm material to the reactor through the top with a funnel.

8.2.3.3 Fill the feed vessel with the entire quantity of the spiked VGO feed prepared in 8.2.2.

8.2.3.4 Stir the VGO with a mechanical stirrer to insure homogeneity of the mixture throughout the procedure.

8.2.3.5 Fill the water reservoir with XX mL of water.

8.2.3.6 Start the flow of 100 % nitrogen gas at 425 mL/min through the sieve plate.

8.2.3.7 Set temperatures on feed vessel, feed tube, preheat oil, and steam generator according to the following table:

Constant Temperature Settings	
Feed vessel	75°C
Feed line	75°C
Preheater oil	120°C
Steam generator	200°C

8.2.4 *Metallation Step (for cycle sequence and run parameters, see Table 2):*

8.2.4.1 Set furnace temperature to 500°C.

8.2.4.2 Inject feed prepared in 8.2.2 into reactor for 5 min at a rate of 6 g/min.

8.2.4.3 After feed injection is completed, run stripping cycle with pure nitrogen with no feed for 7 min. During this stripping step, ramp the furnace temperature from 500 to 650°C at a rate of 50°C/min and stabilize at 650°C.

8.2.4.4 After stripping step is completed, change the gas compositions through both the feed nozzle and the sieve plate to the 60 % N₂, 40 % O₂ mixture. Adjust the gas flow through the sieve plate to 1105 mL/min. Run this regeneration step for 30 min.

8.2.4.5 After the regeneration is completed, change the gas composition through both the feed nozzle and the sieve plate to 100 % N₂. Adjust the gas flow through the sieve plate to 425 mL/min. Cool the furnace to 500°C and stabilize. Run at least 2 min with the 100 % N₂ flow before proceeding to the next step.

8.2.4.6 Repeat steps 8.2.4.2 through 8.2.4.5 nineteen (19) more times.

8.2.5 *Deactivation Step (for cycle sequence and run parameters, see Table 3):*

8.2.5.1 Raise the furnace temperature to 770°C.

8.2.5.2 Change the gas composition through the nozzle to the 28 % N₂, 19 % O₂, 53 % H₂O mixture and adjust the gas flow through the nozzle to 1275 mL/min. Simultaneously change the gas composition through the sieve plate to 60 % N₂,

TABLE 2 Two-Step Cyclic Deactivation: Cycle Sequence and Run Parameters for the Metallation Step

20 four-part cycles of cracking, stripping, regeneration, and furnace cooling	
Cracking:	
Feed injection time	5 min
Feed injection rate	6 g/min
Furnace temperature	500°C
Gas flow through feed nozzle	595 mL/min, 100% N ₂
Gas flow through sieve plate	425 mL/min, 100% N ₂
Stripping:	
Stripping time	7 min
Furnace temperature	ramped to 650°C and stabilized over 7 min interval
Gas flow through feed nozzle	595 mL/min, 100% N ₂
Gas flow through sieve plate	425 mL/min, 100% N ₂
Regeneration:	
Regeneration time	30 min
Furnace temperature	650°C
Gas flow through feed nozzle	595 mL/min, 60% N ₂ , 40% O ₂
Gas flow through sieve plate	1105 mL/min, 60% N ₂ , 40% O ₂
Furnace Cooling:	
Cool down time	2 min
Furnace temperature	cooled to 500°C and stabilized over 2 min interval

TABLE 3 Two-Step Cyclic Deactivation: Cycle Sequence and Run Parameters for the Deactivation Step

120 four-part cycles of oxidation, stripping, reduction, and stripping	
Oxidation:	
Oxidation time	2 min
Furnace temperature	770°C
Gas flow through feed nozzle	1275 mL/min, 28% N ₂ , 19% O ₂ , 53% water
Gas flow through sieve plate	425 mL/min 60% N ₂ , 40% O ₂
Stripping after Oxidation:	
Stripping time	1.5 min
Furnace temperature	770°C
Gas flow through feed nozzle	1275 mL/min, 47% N ₂ , 53% water
Gas flow through sieve plate	425 mL/min 100% N ₂
Reduction:	
Reduction time	7 min
Furnace temperature	770°C
Gas flow through feed nozzle	1275 mL/min, 28% N ₂ , 19% H ₂ , 53% water
Gas flow through sieve plate	425 mL/min 60% N ₂ , 40% H ₂
Stripping after Reduction:	
Stripping time	1.5 min
Furnace temperature	770°C
Gas flow through feed nozzle	1275 mL/min, 47% N ₂ , 53% water
Gas flow through sieve plate	425 mL/min 100% N ₂

40 % O₂ and adjust the gas flow through the sieve plate to 425 mL/min. Run 2 min under these conditions (this is the oxidation step).

8.2.5.3 Change the gas composition through the feed nozzle to 47 % N₂, 53 % H₂O, maintaining the same flow. Simultaneously change the gas composition through the sieve plate to 100 % N₂, maintaining the same flow. Run 1.5 min under these conditions (this is the stripping step.)

8.2.5.4 Change the gas composition through the nozzle to the 28 % N₂, 19 % H₂, 53 % H₂O mixture and adjust the gas flow through the nozzle to 1275 mL/min. Simultaneously change the gas composition through the sieve plate to 60 % N₂, 40 % H₂ and adjust the gas flow through the sieve plate to 425 mL/min. Run 7 min under these conditions (this is the reduction step.)

8.2.5.5 Repeat the stripping step in 8.2.5.3.

8.2.5.6 Repeat steps 8.2.5.2 through 8.2.5.5 one hundred and nineteen (119) more times.

8.2.6 At conclusion of the metallation step, open furnace and allow apparatus and catalyst to cool.

8.2.7 Remove reactor from furnace.

8.2.8 Remove catalyst from reactor.

8.2.9 Analyze deactivated catalyst.

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