



# Standard Guide for Cyclic Deactivation of Fluid Catalytic Cracking (FCC) Catalysts with Metals<sup>1</sup>

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## 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)<sup>2</sup> 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 not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

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 to 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

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

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 (H<sub>2</sub>), 42.8 % in nitrogen balance.*
- 4.4 *Nickel naphthenate or nickel octoate solution.*
- 4.5 *Nitrogen (N<sub>2</sub>).*
- 4.6 *Oxygen (O<sub>2</sub>), 40 % in nitrogen balance.*
- 4.7 *Vanadium naphthenate solution.*
- 4.8 *Cyclohexane.*
- 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.