

## FCC Pretreatment Hydrotreating Catalysts

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### FCC pretreatment process (FCC-PT)

FCC-PT is a hydrotreating step used to treat a wide range of Vacuum Gas Oils (VGO) as well as cracked stocks such as Coker Gas Oil (CGO) before entering the FCC unit. Traditionally, FCC-PT has been practiced with different objectives: 1. Removal of S to meet FCC gasoline S specifications, 2. Hydrogen addition to increase conversion and reduce coke formation in the FCC, 3. Removal of N to improve conversion and selectivity in the FCC, 4. Reducing SO<sub>x</sub> and NO<sub>x</sub> emissions from the FCC flue gas and 5. Enable processing of heavier and more sour feedstocks. The result is a wide range of conditions being applied with the main variables being hydrogen pressure (60-130 bar), H<sub>2</sub> to oil ratio (250-500 NI/I) and temperature (350-400 °C). Catalyst performance in FCC-PT is limited by reaction conditions, the typical conversion levels being: HDS ≥ 80%, HDN ≥ 50% and hydrodearomatization (HDA) ≥ 20%. FCC-PT catalysts must provide not only high HDS, HDN and HDA activities but also sufficient stability against coke formation and metal deposition.

### VGO Feedstocks

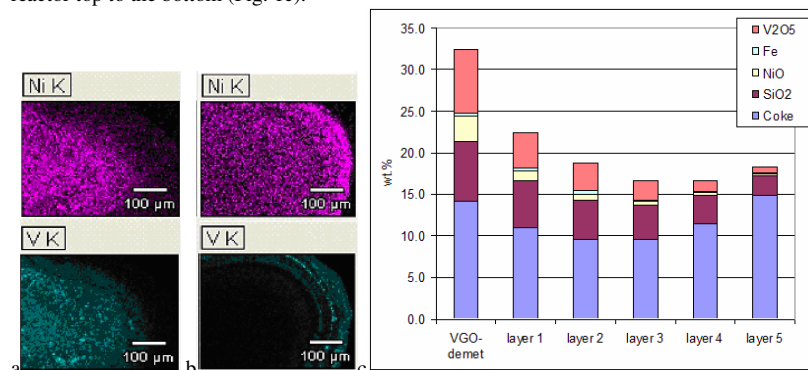
While all VGO feedstocks generally fall into the same distillation range (330-600 °C) they differ strongly with respect to S (1-3 wt.%), N (1000-5000 ppm), aromatics (40–60 wt.%) and metals contents, particularly Ni/V (1-10 ppm). In addition, other contaminants such as Si and As are becoming more prevalent as carbon rejection technology, i.e. coking, and more contaminated crude use is on the rise. Analysis of fractionated VGO's typically shows that while S, mono- and di-aromatic contents are more or less constant over the entire distillation range, N, tri-aromatic and metal concentrations increase with boiling temperature.

### Typical FCC-PT Catalysts

The consequence of the wide range of reaction conditions applied in FCC-PT is the large variety of catalysts used in the commercial units. A typical unit contains a stacked bed consisting of several layers. Except for the top layer, which will almost always contain a VGO demet catalyst, the loading scheme will depend on the specific operating strategy and conditions of the each unit. To ensure a good accessibility for the large VGO molecules (molecular diameter range between 0.9 and 1.7 nm), the “main bed” FCC-PT catalysts typically have an MPD of at least 10 nm. The catalysts contain Ni and/or Co (3-5 wt.% CoO/NiO) in combination with Mo (18-24 wt.% MoO<sub>3</sub>) and acidic components such as B, Si or P in variable amounts. The usual design rules apply, i.e. CoMo and NiMo are preferred for lower pressure-maximum HDS and higher pressure-maximum HDN, respectively. The optimum performance is achieved by combining several catalysts with functionality selected to match conditions and desired reactions in a particular part of the reactor.

### Catalyst Deactivation due to Metal Deposition and Coke Formation

VGO demet catalysts are designed as metal trap and are specific to the type of contaminant. For Si and As, the demet catalysts need high surface area and high metal content, respectively. For Ni/V, the catalysts have very high MPD and relatively low activity to prevent that Ni and V deposit mainly in the outer part of the extrudates. Because of its lower MPD and high activity, the “main bed” FCC-PT catalysts can typically tolerate only limited amount of metals. The difference can best be seen by comparing the Ni and V distributions over the catalyst particles (Fig. 1a). The concentration of metallic contaminants decreases from the reactor top to the bottom (Fig. 1c).



**Figure 1.** SEM-EDX maps of a. VGO demet catalyst with Ni and V deposited throughout the extrudate and b. main bed FCC-PT catalyst with deposits mainly in the outer part of the extrudate. c. Concentration of C, Si, Ni, Fe and V contaminants in different parts of the FCC-PT catalyst bed.

Catalyst performance in FCC-PT is limited by reaction conditions and the actual conditions in terms of e.g. pH<sub>2</sub>, pH<sub>2</sub>S, pNH<sub>3</sub> and temperature change throughout the reactor. In general, the temperature is too low to remove all N, which is the main HDS inhibitor, but too high to hydrogenate aromatics to a significant extent. That is why coke formation is very important. With decreasing hydrogen availability and increasing bed temperature from reactor top to bottom, an increased coke formation is usually observed in the bottom part of the reactor (Fig. 1b). Compared to metal deposition and coke formation, deactivation due to active phase sintering and segregation is less important under the FCC-PT conditions. This is related to the lower reaction severity, i.e. lower reaction exotherm, in FCC-PT as compared to e.g. HC-PT.

### Significance

Thorough understanding of the catalytic processes and deactivation mechanisms under the FCC-PT reaction conditions is the necessary prerequisite for the development of more active and stable FCC-PT catalysts. The analysis of used catalysts is an important part of the FCC-PT catalyst development.