



## Hydroprocessing catalyst deactivation in commercial practice

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### ABSTRACT

Hydroprocessing catalysts are susceptible to deactivation by several mechanisms, e.g. coke formation, metals deposition and active phase sintering, in their life cycle. Typical examples of catalyst deactivation are presented, showing the phenomena that may be encountered in commercial hydroprocessing units. Spent samples of hydroprocessing catalysts were obtained from various commercial units, as well as pilot plants. The cause(s) of deactivation were identified by analyzing spent catalyst samples for coke and metal content, pore size distribution and the distribution of metals (by SEM-EDX and STEM-EDX). Catalysts applied in the hydroprocessing of light feeds (middle distillates) mainly deactivate due to coke deposition and possibly sintering. Poisoning by metal deposition becomes significant during hydroprocessing of heavy feeds (like VGO and residue) as well as upgraded streams (e.g. coker products). Once the possible causes are known, deactivation mitigation strategies can be defined, which comprise optimizing the catalyst properties, catalyst loading and reactor operation.

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### 1. Introduction

Hydroprocessing is a key technology for the production of clean fuels in today's refinery operations. It comprises a wide variety of reactor systems (fixed bed, moving bed, and ebullated bed), feeds (middle distillates, vacuum gas oil, residue) and operating conditions (gas/liquid phase, low and high temperatures, low and high pressures). Although this process is over 70 years old, it is still subject to continuing changes [1]. Over the years, refineries have been processing heavier and more sour feeds, due to shifting crude diversity and sources. These crudes contain more contaminants and require a higher conversion level, which has led to the development of improved hydroprocessing catalysts tailored for such applications. The catalysts, which are mostly based on Ni, Co, Mo and W sulfides, are susceptible to several deactivation mechanisms during their life cycle [2]. Catalyst deactivation will become more and more critical, due to the ongoing trend in increasing hydroprocessing severity and maximizing catalyst performance.

Catalyst deactivation plays an important role in process design and operation within the petrochemical industry. Various chemical reaction engineering solutions can be applied depending on the typical lifetime of the catalyst. A classical example is the fluid catalytic cracking process. The FCC catalyst must be continuously regenerated due its very short lifetime [3]. In most hydroprocessing applications, the life of the catalyst is long enough to enable the use of fixed-bed reactors. This implies that the process needs to be

periodically taken offline to replace the spent catalyst. The loss of unit availability is often minimized by combining the moment of catalyst change out with the periodic maintenance of the unit [4]. Consequently, the ability to control the catalyst life cycle length is crucial for refinery management.

The HPC catalyst life cycle is strongly influenced by the type of application. Fig. 1 shows typical catalyst deactivation curves for different classes of feeds. The processing of heavier feeds requires higher operating temperatures (and pressures), which is generally accompanied by a faster deactivation rate of the catalyst. This results in a shorter cycle length, although the higher pressure somewhat alleviates the deactivation. The intrinsic mechanisms of catalyst deactivation can be classified into three basic types of processes: chemical, mechanical and thermal [5]. In hydroprocessing, each class is represented respectively by the following deactivation mechanisms: active site coverage by strongly adsorbed species and deposits (coke and metals), pore mouth constriction/pore blockage and sintering of the active phase [6]. A better understanding of deactivation could extend catalyst life and thus have enormous economic benefits.

Ideally, catalysts should be studied under industrially relevant conditions. It is however difficult to mimic these conditions in laboratory experiments, because the deactivation of hydroprocessing catalysts takes place on a very long time scale. That is why the investigation of samples withdrawn from an industrial or pilot reactor can provide information of great value [7]. The aim of the present study is to show the deactivation behavior of commercial hydroprocessing catalysts under typical industrial conditions. Spent hydroprocessing catalysts were retrieved from several commercial and pilot units and a series of samples was selected for

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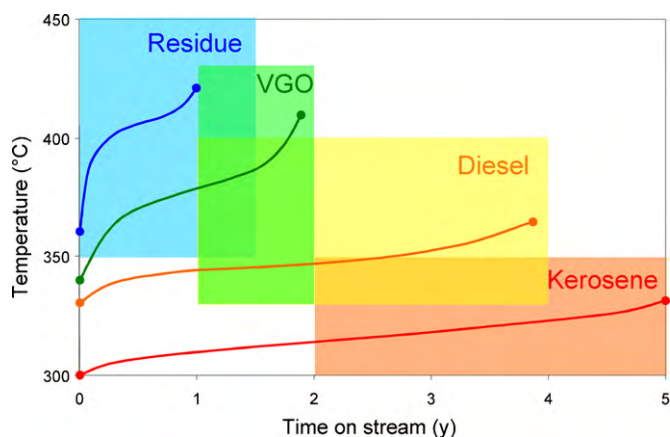


Fig. 1. Typical catalyst deactivation curves and operating cycle limits of hydroprocessing applications.

further investigation. These catalysts represent typical cases of catalyst deactivation in commercial practice. Using advanced analysis techniques, the mechanisms responsible for the deactivation of the catalysts can be identified, and options to mitigate catalyst deactivation can be defined.

## 2. Experimental

### 2.1. Spent catalyst samples

Several spent catalyst samples used in the hydroprocessing of diesel, vacuum gas oil (VGO) and vacuum residue were obtained from various industrial hydroprocessing reactors and/or pilot plants. Further details regarding the origin of the sample will be given in Section 3. Any remaining oil was removed from the catalyst particles by Soxhlet extraction with toluene, prior to further analysis.

### 2.2. Elemental analysis, thermogravimetric analysis and porosimetry

The elemental composition of the spent catalysts was determined by XRF analysis using a Philips PW 2400 X-Ray fluorescence spectrometer, after calcining the samples at 450 °C. The total carbon content was measured using a LECO CS-200CSH apparatus. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo SDTA851 apparatus coupled with a Nicolet iS10 infrared off-gas analyzer. Nitrogen porosimetry measurements were performed using a Micromeritics GEMINI-V apparatus, after drying the samples under N<sub>2</sub> at 120 °C for 1 h. Mercury porosimetry measurements were performed using a Micromeritics AutoPore IV 9520 system.

### 2.3. Electron microscopy

The samples were evacuated for at least 2 h at 150 °C and subsequently vacuum impregnated with the standard mixture Ultra Low Viscosity Kit, hard version (Polaron Instruments Inc.). The mixture with catalyst was transferred into a polyethylene capsule (BEEM) and mixed with fresh embedding medium. The epoxy embedding medium was hardened at least 48 h under N<sub>2</sub> (2 bar, 60 °C).

For STEM-EDX analysis, sections of about 60 nm thickness were prepared using a Leica Reichert Ultracut-S ultramicrotome, collected on a water surface and transferred to a slightly etched (Ar plasma) Cu grid and dried. The thin sections on the TEM grid were covered with a thin layer of carbon to prevent charging during TEM analysis. Shortly after preparation, the sections were investigated with a JEOL JEM-2010F-HR TEM, with a 200 kV electron

beam (Field Emission Gun, FEG), equipped with a STEM unit and a Thermo Noran EDX system. The active phase dispersion was studied by high resolution TEM imaging under slightly underfocussed conditions (−48 nm). The distribution of active metals was studied by STEM-EDX spectral imaging under analytical probe (1.0 nm) conditions.

For SEM-EDX analysis, a cross-section of an individual embedded extrudate was made using a diamond knife. The cross-section was mounted on a stub with conductive carbon cement (Leit C). A conductive carbon coating was deposited by a Balzers MED10 apparatus to avoid charging in the SEM. Micrographs were made by a Tescan analytical SEM and a LEO 1550 high resolution SEM. EDX spectra were obtained with an Oxford INCA system.

## 3. Results and discussion

### 3.1. Diesel HPC spent catalysts

In middle distillate applications (kerosene and diesel), the catalyst is typically very stable due to the relatively mild process conditions and light feedstock, with a typical boiling range between 220 and 350 °C. As a consequence, cycle length is usually very long (up to 5 years, Fig. 1). The most important factor involved in the catalyst deactivation is active site coverage by nitrogen compounds and coke [8]. Nitrogen-containing compounds are the most common poisons for hydroprocessing catalysts. Because of their basic nature, they adsorb reversibly or irreversibly on catalyst acidic sites, depending on reaction conditions. Irreversibly adsorbed species may eventually be converted to coke [9]. Coke deposition occurs in virtually all hydroprocessing applications. However, coke build-up increases with the boiling range and/or aromaticity of the processed feed [10]. Deactivation by coke is strongly influenced by operating conditions (temperature, partial pressure of hydrogen, % aromatic saturation and H<sub>2</sub>/oil-ratio). Typically, coke is rapidly formed in the initial stage of the operation; then the coke level reaches a near steady-state, and increases again at the end of the cycle [11]. The catalyst may retain a substantial portion of its original activity in spite of the rapid initial coke deposition [12].

Two spent catalyst samples were selected from a commercial HPC unit and a pilot reactor processing ultra low sulfur diesel (ULSD). One catalyst was applied in a normal operating cycle, while the other was exposed to extreme process conditions, i.e. high temperatures, low pressures and high conversion levels, in order to accelerate the deactivation process(es). Aim of this artificial aging procedure was to compare the deactivation phenomena with a normal life cycle, by analyzing the spent catalysts. The catalyst deactivated more in the normal cycle than during the artificial aging run (about 25 °C difference). Options to measure coke deposition in a spent catalyst pellet on a detailed scale are limited [13], however, the properties of coke can be analyzed using conventional methods [14]. Fig. 2 shows the coke characterization using TGA-IR. The major part of the weight loss occurs in the region 250–550 °C where coke is combusted, as is apparent from the CO<sub>2</sub> signal. Both samples feature a peak maximum around 425 °C, in agreement with other reports [14,15]. The sample from the normal cycle shows the highest weight loss and CO<sub>2</sub> evolution in this region. Furthermore, the temperatures of the onset and completion of the coke combustion is about 50 °C higher for this sample as compared to the sample from artificial aging. Hence, it can be concluded that the spent sample from the normal cycle contains more coke, and that this coke is more refractory (i.e. more difficult to combust), which is in line with the observed difference in deactivation. This illustrates that time on stream is an important factor in the coking mechanism [11]; the relatively short artificial aging procedure results in

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