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Review

# Deactivation of FCC catalysts

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ABSTRACT

Over the course of the commercial fluid catalytic cracking (FCC), catalyst deactivation occurs both reversibly, as a result of side reactions that eventually yields coke, and irreversibly, due to contaminants present in the feedstock or to the dealumination of the zeolite catalyst component. Herein, we discuss the deactivation of HY zeolite and FCC catalysts from a fundamental as well as an applied point of view. Aspects related to the various causes of FCC catalysts (and additives) deactivation under industrial conditions are also summarized.

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## Contents

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## 1. Introduction

Fluid catalytic cracking (FCC), still one of the major downstream refining operations, is responsible for the conversion of heavy feedstocks (gasoils from vacuum distillation towers or residues from atmospheric distillation towers) into lighter, more valuable products such as liquefied petroleum gases (LPG) and cracked naphtha, the major constituent of the gasoline pool. Together with the desired cracking reactions, coke formation (highly condensed hydrocarbons and/or lighter compounds dragged or retained in the pore structure of the catalyst after stripping) also occurs in these systems. The typical FCC catalyst consists of a mixture of an inert matrix (kaolin), an active matrix (alumina), a binder (silica or silica–alumina) and a Y-zeolite. During the FCC process, a significant portion of the feedstock is converted into coke. This coke temporarily deactivates the active sites of the catalyst by poisoning, pore blockage or both [1–4], resulting in an important activity loss. In order to recover the activity, the FCC catalyst continuously circulates between the riser (FCC reactor) and the regenerator vessel. In the regenerator, coke is converted into CO, $CO_2$, $H_2O$, $SO_x$ and $NO_x$ compounds.

Conventional FCC units operate in heat balance. The heat produced by the combustion of coke is used in various ways: (i) to heat the feed to the reaction temperature, (ii) to provide energy for the endothermic cracking reactions, (iii) to heat the combustion air and (iv) the coke on the spent catalyst to the regenerator temperature, (v) to supply the heat lost from the reactor/regenerator and (vi) to heat the steam to the exit temperature [5].

The new discoveries of heavy oil deposits have favored many FCC units to begin processing feedstocks with a higher tendency to form coke. This is particularly true for residue fluid catalytic cracking (RFCC) units, which are designed to convert 100% residue from the atmospheric distillation tower. The excess coke produced in RFCC units results in a surplus of energy during the burning at the regenerator. In order to maximize the profitability of those residue FCC units, part of the heat produced by the combustion of coke is recovered by means of catalyst-coolers that control the regenerator dense phase temperature and produce steam.

Due to the cyclic nature of the process, the catalyst particles may break, producing fines that will result in particulate emissions. In order to cope with the loss of fines because of catalyst attrition [6] and maintain catalyst activity, fresh catalyst make-up is frequently needed. For some FCC units processing feedstocks with a high level of metals, it is also common to remove a portion of the inventory and increase the catalyst make-up to accelerate the replacement of catalyst by fresh portions and, thus, keep contaminant metals at an acceptable level. The fresh catalyst addition needed to maintain the activity of the inventory (1400 t/d for 350 FCC units worldwide) is responsible for making the FCC process the most important market for catalysts [7,8].

As a consequence, the catalyst that effectively participates in the cracking reactions has an age distribution [9,10], i.e., it is composed of a mixture of young (low metal concentration, high activity) and old (high metal concentration, low activity) particles. This mixture of young and old catalyst from an industrial FCC unit is called equilibrium catalyst (e-cat).

Many studies have been carried out in the recent decades with the intent to better understand the deactivation phenomena taking place during hydrocarbon transformations over acid zeolites and industrial FCC catalysts. The aim of the present work is to review the state-of-the art regarding these topics.

## 2. Modes of deactivation

Deactivation in heterogeneous catalysis is due to two types of causes: physical and chemical. The first include phenomena such as sintering, occlusion, loss of active surface, among others. However, industrially used zeolites are normally sufficiently stable to avoid these processes in the operating conditions for which they were designed. The same happens with cracking catalysts: their physical stability would allow continuous operation during several months. Indeed, chemical causes are the main problem and can be subdivided into three categories:

- Chemical degradation–reaction of a compound with the catalytic phase, causing its destruction or loss of reactivity. The main agents are alkaline metals which neutralize the acid sites, steam that causes dealumination and V which destroys the zeolite framework. The effects of V on the performance of cracking catalysts are well known.
- Poisoning—it expresses the irreversible adsorption of impurities on the catalyst active sites. This leads to a permanent reduction of the activity. In the FCC process, the main poisons are basic nitrogen compounds and coke. Both are discussed in detail below.
- Fouling—under this designation we find all phenomena of coke deposition and other inorganic materials such as metals and its composites. These compounds block the porous structure and the access to the active sites [11]. In catalytic cracking this type of deactivation occurs almost exclusively due to coke deposition.

A different type of classification can be established according to other criteria, for example based on the possibility of restoring the activity of the catalyst using a regeneration treatment, i.e., whether the deactivation is reversible or irreversible. In FCC processes, regeneration is achieved by combustion with air and, consequently, all the relevant deactivation phenomena taking place during catalytic cracking can be grouped in two categories: those that can be removed by combustion (reversible) and the ones that force the replacement of the catalyst after a certain number of cycles (irreversible).

## 3. Reversible deactivation

### 3.1. Coke

The deactivation of zeolite-based catalysts by coke is caused either by poisoning of acid sites or by pore blockage [3]. In the former case, one coke molecule blocks one active site, affecting the activity linearly, and may also affect the reaction selectivity [11–14]. The deactivating effect is much more pronounced in the case of pore blockage, with one coke molecule blocking the access of reactants to, on average, more than one active site [2,4,15–19]. Acidity–activity correlations have shown that the Brønsted acid sites located in the supercages are the primary active sites throughout cracking reactions. During coke formation, a linear correlation was found between the activity of the USY zeolite and the amount of Brønsted acid sites accessible to pyridine in the supercages [20]. Prior to pore blockage, coke molecules can be heterogeneously distributed over the zeolite crystallites and more concentrated at the external surface (pore mouth). If this is the case, the effective pore diameter is reduced and the diffusion resistance of reactants in the crystallites increases [21,22]. For higher coke contents, the heavier coke molecules can accumulate on the outer surface and locally block the access of reactant molecules to the pore openings.

Diffusive mass transport plays a key role in catalytic cracking under commercial conditions [23–25]. An important parameter