



## 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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## 1. Introduction

Fluid catalytic cracking (FCC), still one of the major downstream refining operations, is responsible for the conversion of heavy feedstocks (gasolins 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<sub>2</sub>, H<sub>2</sub>O, SO<sub>x</sub> and NO<sub>x</sub> 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

related to mass transfer limitations is the accessibility of reactant molecules to the active sites located inside the catalyst particles.

The higher the zeolite crystallite size, the less amount of coke is needed in order to have a (partial) blockage of the access to zeolite pores; small crystallites present a much higher external surface area, thus limiting the effects of pore blockage. An increase of the zeolite unit cell results in a more pronounced coke forming tendency [26].

An estimation of the accessibility could be made either with selected model molecules and catalyst components [27–29] or with real feedstocks and commercial catalysts [30,31]. More important than the catalyst accessibility itself is the accessibility to the acid sites. Clearly, coke deposits can severely reduce the accessibility to the acid sites, particularly because the coke molecules tend to adsorb onto those sites [32]. The measurement of accessibility to the acid sites is a non-trivial problem, especially when coked catalysts are concerned.

The matrix may play a beneficial role by trapping voluminous molecules containing heteroatoms and contaminant metals, which indirectly reduces the amount of coke formed [31,33].

### 3.1.1. Types of coke

Coke can be defined as compounds with  $H/C = 0.3–1.0$ . There are five main types of coke identified in catalytic cracking [34–39].

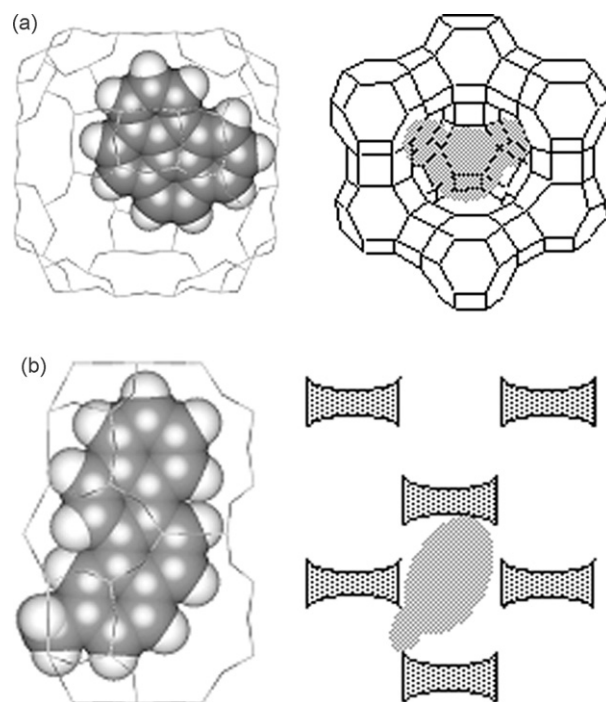
- Catalytic coke—from condensation and dehydrogenation.
- Catalyst-to-oil coke—hydrocarbons entrained in the small pores and not removed by the stripper.
- Thermal coke—formed by a free radical mechanism, it is important at high reaction temperatures and also yields hydrogen. It is less important than catalytic coke due to the low extent of thermal cracking at typical FCC conditions
- Additive coke (or Conradson coke)—from heavy molecules already present in the feed. Its amount correlates directly with the Conradson carbon residue (residue remaining after the fuel has been pyrolysed by raising the temperature to 800 °C).
- Contaminant coke—from dehydrogenation catalyzed by Ni, Fe and V.

Coke formation has a strong impact on the performance of the catalyst, modifying the conversion and product selectivity, besides playing an essential role in the heat balance of the FCC unit. Nevertheless, the different types of coke do not have the same influence on the cracking activity, e.g. depending on the feedstock characteristics, catalytic coke may have a greater influence on catalyst activity than additive coke. The time-scale in which the different types of coke are deposited over the catalyst surface may also vary, determining the change in the deactivation mode from active site deactivation to pore blockage [40,41].

Another interesting aspect observed by several authors is the presence of significant (residual) activity on the coked FCC catalysts [41–46]. Clearly, FCC catalyst deactivation is a complex phenomenon where the different variables in the process (feed composition, catalyst composition and process operation) are all inter-related [47].

Catalytic coke, the most relevant family, has its formation influenced by four factors [18]:

- Charge properties—in what regards the feed, results show that the presence of alkenes and aromatics substantially increases the rate of coke formation [48].
- Operating conditions—temperature has a determinant role both on the formation rate and on the composition of coke. At low temperatures, close to 250 °C, the  $H/C$  ratio is similar to that of the reactants and the coke molecules formed are strongly dependent



**Fig. 1.** Location of the bulkier soluble coke molecules found in the H-Y (a) and H-MFI (b) zeolites, respectively represented by methylcoronene and methylpyrene.

on the charge. On the other hand, at high temperatures (relevant case for the FCC process), coke is highly polyaromatic (low  $H/C$  ratio) and the nature of the reactants is not as important. In what concerns the pressure, coke formation reactions, due to their bimolecular nature, are favored by high reactant partial pressures.

- Zeolite acidity—the acid site density is also a relevant matter in coke formation. As the proximity of the acid sites increases, the faster will coke formation occur and, hence, will the catalyst deactivate.
- Zeolite porous structure—the pore structure is the main parameter determining the composition of coke formed with zeolites at high temperatures. Zeolites with small cages form smaller molecules like anthracenes or pyrenes, whereas zeolites with large cages allow bulkier compounds to be produced (Fig. 1).

Another relevant factor is the difference between the size of the cages (or channel intersections) where coke is produced and the pore openings of these cages [1,18,19,49,50]. If large cages, where coke is easily formed, are only accessible through small pores, the stereochemical blockage effect is severe and the deactivation is quite pronounced. These zeolites are said to have trapping cages. This fact explains the difference observed in the deactivation rate of the H-Y and the H-ZSM-5 zeolites. Moreover, for zeolites with a one-dimensional pore structure (MOR), deactivation is faster than on three-dimensional ones because if a segment of the channel is blocked, the whole channel is rendered inactive [18,51].

### 3.1.2. Coke characterization

Continuous progress in the understanding of catalyst deactivation by coke has been made in the last decades, but the characterization of coke deposits is usually poor and very rare for commercial FCC catalysts [52–57]. Several studies addressed the chemical identity of coke components by means of spectroscopic techniques such as electron paramagnetic resonance (EPR) [58], magic angle spinning  $^{13}C$  nuclear magnetic resonance ( $^{13}C$

MAS-NMR [55,57–61], ultraviolet (UV) [62,63] and infrared (IR) [14,29,68] spectroscopy, X-ray diffraction (XRD) [64] and Raman [65] spectroscopy. Most of these techniques are operated under static conditions, but the deposition of carbonaceous materials can also be followed by in situ IR spectroscopy followed by on-line gas chromatography (GC) [66–70]. Complementary information about coke location can be obtained by  $^{129}\text{Xe}$  nuclear magnetic resonance [71,72] and X-ray photoelectron spectroscopy [51,73]. However, in most instances these approaches require complete separation from the catalyst. This involves the destruction of the catalyst structure by an acidic solution followed by the dissolution of the soluble coke compounds in an organic solvent [49,74]. The heavy fraction corresponding to the insoluble coke is often only characterized by the average H/C ratio.

Despite the great number of techniques applied, the detailed knowledge of the composition of the heavy coke fraction – which is commonly the main component of commercial FCC (and RFCC) catalysts – remains a challenge [75]. The problem is aggravated because although e-cat can be easily sampled from the regenerator, the same is not true for the coked catalyst. Taking samples immediately after the regenerator implies having a special dedicated line in the FCC unit and it is not an easy procedure, since the risk of burning exists and the spent catalyst sample may be affected during the procedure. It should also be mentioned that, depending on the operating conditions, coke molecules can further react among themselves even in the absence of other reactants [76].

A detailed characterization study of commercial spent RFCC catalyst has shown that coke was mainly constituted of heavy condensed aromatic compounds, located at the mesopores of the catalyst matrix and binder [77]. The degradation of these compounds by pyrolysis liberated smaller aromatic and paraffin molecules that were previously trapped [77]. Also interesting is that despite presenting a carbon content in the range of 0.7–1.5 wt.%, commercial spent FCC catalysts still have some activity [78].

### 3.1.3. Coke formation mechanisms

Coke formation involves several consecutive reactions (Fig. 2), the mechanism being more or less complex depending on the reactant molecule [79]. Alkanes must undergo cracking to produce olefins, which oligomerize to produce  $\text{C}_6^+$  alkenes, which in turn take part into hydrogen transfer reactions, forming dienes. These latter oligomerize into naphthenes, that proceed via three other hydrogen transfer reactions forming aromatics, which are then converted into soluble coke.

On the other hand, for naphthenes the mechanism only involves the last two reactions, assuming that there are alkenes in the reactor, already produced by cracking. Lastly, for aromatics the mechanism consists only of the final step, reason why these compounds normally yield larger amounts of coke.

The same reactions transform this soluble coke, which is confined in the zeolite cages, into insoluble coke that grows and overflows onto the external surface of the zeolite crystallites [18,50]. Alternatively, the insoluble coke can overflow into the mesopores created during eventual dealumination treatments.

Much has been said in the literature about the supposed reaction of hydrogen transfer in catalytic cracking. Although both intra- and intermolecular hydrogen transfers are possible, the main focus about these reactions in relation to FCC has been on intermolecular processes. Hydrogen transfer reactions can occur between any two hydrocarbons with the condition that at least one of them is unsaturated. However, the most relevant hydrogen transfer reaction is the one between a naphthene and 3 alkenes with the production of 3 alkanes and an aromatic, which can then be easily consumed in coke formation reactions. Some authors still question whether these reactions alone can explain the large amounts

of alkanes found in the products; even so, it is widely accepted that this reaction occurs in hydrocarbon transformations over acid zeolites.

The reaction was widely studied over the years [80–96]. It is a crucial step in the catalytic cracking reaction network and it must be studied in order to understand the mechanisms of deactivation on catalytic cracking in particular, as well as on acid zeolites in general. Although some studies have shown that the density of paired acid sites has a determinant influence on the reaction rate [93,94], thus suggesting a mechanism in which two adsorbed species interact, this fact is rather difficult to rationalize. The probability of interaction between two positively charged species should be very small. In fact, Corma et al. [86] have proposed an alternative explanation for the dependency of the rate of hydrogen transfer with the acid sites density. The results of this study showed a sharp decrease in the alkene adsorption ability of the zeolite with the increase of the Si/Al ratio. This fact caused an increase of the (cracking/hydrogen transfer) ratio during gasoil and *n*-heptane cracking. This behavior can be explained by the fact that hydrogen transfer reactions necessarily involve adsorbed alkenes whereas cracking involves mainly alkanes.

One of the most accepted mechanisms [19,81] involves several consecutive steps (Fig. 3): (1) deprotonation of a cyclic “carbenium-like” species with the production of a cycloalkene, (2) hydride transfer reaction between a “carbenium-like” species and the cycloalkene with the formation of an adsorbed alkene, (3) deprotonation in which a cyclodiene is formed and a Brønsted acid site is regenerated, (4) the cyclodiene molecules exchanges another hydride ion with a surface “carbenium-like” species and, finally, (5) the protonated cyclodiene desorbs with regeneration of an acid site and production of an aromatic. Studies show that the limiting step for each hydrogen transfer step is the hydride ion transfer reaction [87].

However, this reactional path poses some issues, namely the reason why the cycloalkenes and cyclodienes exchange hydride ions instead of interacting with the zeolite Brønsted acid sites. Some studies on this subject clarified that hydride transfer is much easier for cycloalkenes than for naphthenes, mainly because the formed unsaturated “carbenium-like” species are very stable [81]. Indeed, the values determined for the hydride transfer kinetic constants were 0.045 and  $0.107\text{ s}^{-1}$ , respectively for methylcyclohexane and methylcyclohexene [81].

After the production of unsaturated molecules like aromatics and olefins, the coke formation reactions should proceed rather easily. Catalytic coke formed at normal catalytic cracking temperatures (500–550 °C) is always polyaromatic in nature, indicating that the formation of a first aromatic cycle is essential in coking reactions. Olefins alone can react to produce coke but the reaction mechanism must involve the formation of a cycle by intramolecular oligomerization and a hydrogen transfer or a dehydrogenation reaction in order to produce an aromatic. For this reason, only the mechanisms involving at least one aromatic will be presented. Therefore, two distinct mechanisms can be proposed to explain coke formation (Fig. 4).

In the first mechanism presented, aromatics can easily undergo alkylation with alkenes on the Brønsted acid sites (Fig. 4a). The alkylated aromatic then suffers two other reactions: hydrogen transfer at the side chain and cyclization. After isomerization and hydrogen transfer, a naphthalenic compound is formed. Naphthalene derivatives can then proceed via the same reactions to produce anthracenes, pyrenes, etc. An alternative mechanism involves the reaction between two aromatics (Fig. 4b). In this case, after the alkylation step, a dehydrogenative coupling step occurs, creating a non-aromatic cyclopentane cycle. After isomerization and hydrogen transfer, the resulting anthracene molecule



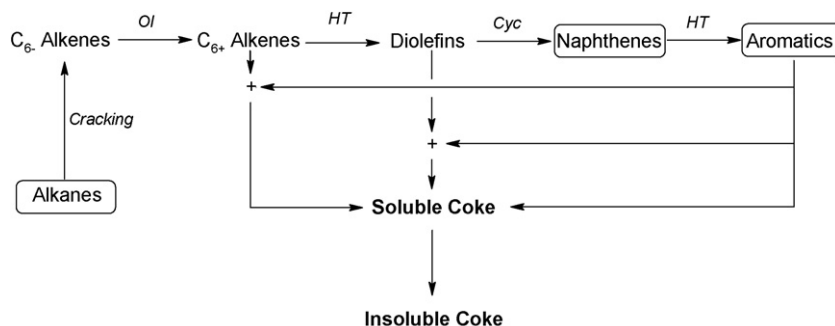


Fig. 2. Mechanism of coke formation for several reactant molecules. Oligomerization (OI), hydrogen transfer (HT) and cyclization (Cyc).

can then react as previously to produce pyrenes and bulkier compounds.

### 3.2. Molecules containing heteroatoms (N, O and S)

FCC feedstocks are composed mainly by naphthenes, aromatics and alkanes. However, apart from hydrocarbons, FCC feeds also contain non-negligible amounts of oxygen (0–2%), sulfur (0–7.5%) and nitrogen (0–0.4%). These heteroatom-containing molecules exhibit quite distinct chemical properties and will, for this reason, be analyzed separately.



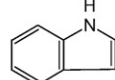
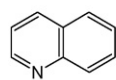
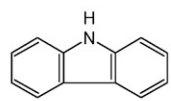
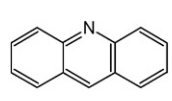
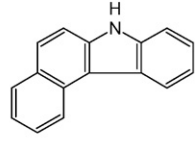
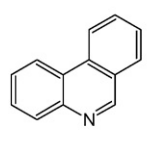
#### 3.2.1. Nitrogen poisoning

Although the damaging effect of nitrogen compounds has been known for several decades, the subject has not been studied to a great extent [81,97–110]. Recently, however, due to increasing levels of impurities in FCC feedstocks, it has come to constitute a very relevant problem. The FCC feed is mainly composed of vacuum gas oil (VGO) containing approximately 25–30% of the nitrogen existent in crude oil. Nevertheless, in the last few years, increasing amounts of vacuum residua have been added to FCC feedstocks, increasing the nitrogen content of the charge. Vacuum residue contains about 70–75% of the nitrogen present in crude oil. For the lighter fractions of crude oil, nitrogen is mainly in the form of basic compounds, while in the heavier fractions non-basic compounds are predominant.

Significant progress has been made recently in the identification and characterization of nitrogen compounds present in different oil fractions and feeds. In most cases, the nitrogen present in crude oil occurs in high molecular weight molecules containing other heteroatoms (S, O). Despite this fact, compounds of small and medium molecular weight with well-defined structures were isolated from medium distillates [111]. Basic compounds include alkyl derivatives of pyridine, quinoline, isoquinoline, acridine and phenanthridine. The non-basic ones usually include a pyrrol moiety: derivatives of pyrrol, indole and carbazole (Table 1).

Nitrogen bases are thought to deactivate FCC catalysts by interacting with the acid sites responsible for the cracking reaction, hence decreasing activity. Earlier work on this subject concluded that the deactivation affecting the catalysts depends on the physicochemical properties of the poisoning molecules [106,112]. More

Table 1  
Nitrogen heterocyclic compounds present in FCC feedstocks

Non-basic nitrogen heterocyclics	Basic nitrogen heterocyclics
	
Pyrrole MW=67 g mol <sup>-1</sup> , BP=130 °C	Pyridine MW=79 g mol <sup>-1</sup> , BP=115 °C
	
Indole MW=117 g mol <sup>-1</sup> , BP=254 °C	Quinoline MW=129 g mol <sup>-1</sup> , BP=238 °C
	
Carbazole MW=168 g mol <sup>-1</sup> , BP=355 °C	Acridine MW=181 g mol <sup>-1</sup> , BP=346 °C
	
Benzocarbazole MW=216 g mol <sup>-1</sup> , BP= 385 °C	Phenanthridine MW=181 g mol <sup>-1</sup> , BP=349 °C

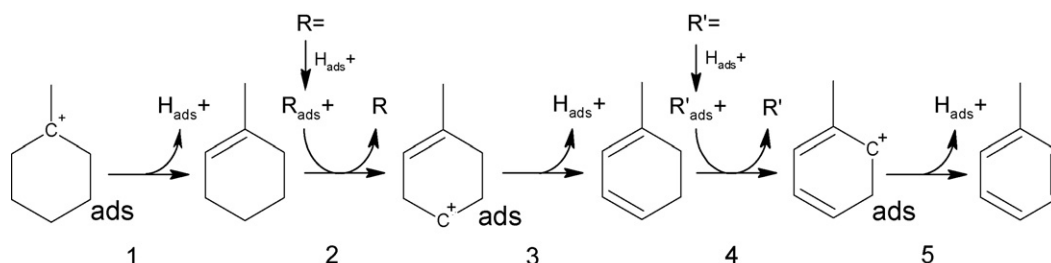
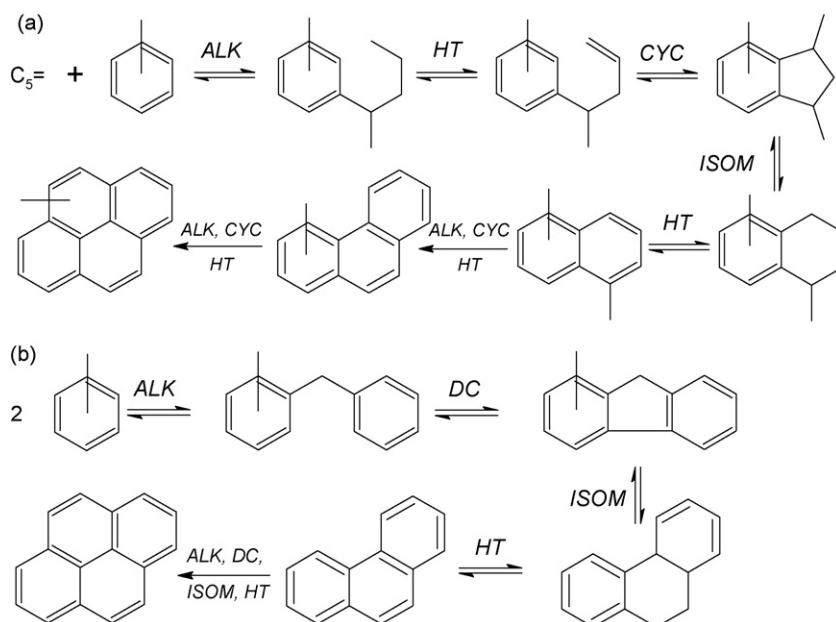


Fig. 3. Hydrogen transfer mechanism.



**Fig. 4.** Coke formation reaction from (a) alkenes+aromatics and (b) aromatics. ALK-alkylation, HT-hydrogen transfer, CYC-cyclization, ISOM-isomerization, DC-dehydrogenative coupling.

recently, Ho et al. [107] demonstrated that the higher the proton affinity (PA) of a nitrogen base is, the stronger its deactivating power will be. The measurement of PA is a good indicator of the basicity of a molecule in the gas phase.

Regarding the effect of PA, some research groups have shown that, indeed, the same amount of basic nitrogen is retained in the catalyst during the reaction with several bases presenting different PA values. Corma et al. [106] proposed an inductive partial poisoning effect (Fig. 5) of the neighboring acid sites by the stronger base, in order to explain the higher poisoning ability of 2,6-dimethylpyridine relatively to quinoline and pyridine, which present smaller proton affinity values.

2,6-Dimethylpyridine seemed to induce stronger deactivation compared to quinoline and 3-methylpyridine, which are less basic [113,114]. However, due to steric constraints, 2,6-dimethylpyridine only adsorbed on the reactive Brønsted acid sites, which could also explain its higher poisoning strength.

The size of the poisoning base molecules can also contribute to its higher poisoning ability, particularly when using smaller pore zeolites such as H-ZSM-5. Over this catalyst, pore mouth blockage caused by the bulkier nitrogen-containing molecules can explain part of the deactivation observed [115].

The acid matrix present in current catalytic cracking catalysts seems to partially prevent nitrogen poisoning. In reality, the Lewis acid sites present in the active matrix can adsorb, even if weakly, the nitrogen-containing molecules, thus preventing the interaction with the zeolite active sites. As a consequence, catalysts containing matrices with high acidity are less affected by basic molecules present in the feedstock [116].

Due to the presence of the nitrogen atom, the pyridine ring of most nitrogen bases is a  $\pi$  electrons deficient system. This means that the basic molecules are deactivated towards electrophilic substitutions and, as a consequence, they do not participate extensively in coke formation reactions, unlike other aromatics [113]. Nevertheless, substitution reactions can take place when the amount of free acid sites is low, especially for molecules containing other aromatic rings.

Several approaches can be used to minimize the harmful effects of nitrogen compounds during the catalytic cracking of high-

nitrogen feedstocks:

1. Hydrotreatment—well-known technique used to decrease the nitrogen content in feedstocks. This process requires high hydrogen pressures and temperatures. A hydrotreatment of the feed would eliminate nitrogen, oxygen and sulfur, avoiding the necessary HDS treatment of FCC gasoline. However, the amount of feedstock to hydrotreat is much higher and renders this alternative less interesting from an economical point of view.
2. Adsorption—use of acidic solid adsorbents to capture the basic nitrogen compounds. This method has been used to separate basic asphaltenes from feedstocks [117] and for syncrude denitrogenation [118].
3. Liquid/liquid extraction—use of an immiscible solvent to extract nitrogen compounds [119–121]. The method has been recommended to separate nitrogen compounds from shale oil.
4. Neutralization—using acid additives to neutralize basic nitrogen compounds. The products resulting from neutralization are subsequently separated [119].
5. Use of nitrogen-resistant FCC catalysts. The major advantage of this method is the elimination or greatly reduced cost of a pre-treatment process.

The presence of basic nitrogen molecules in the feedstock is responsible for a temporary deactivation of FCC catalysts, due to a preferential adsorption onto the acid sites [122], therefore reducing the density of acid sites. A good agreement was found between the proton affinity of nitrogen-containing molecules in gas phase and the poisoning effect over an FCC catalyst [97]. The presence of nitrogen-containing compounds was responsible for a reduction in conversion and affected the catalyst selectivity. The poisoning effect of a nitrogen-containing molecule is primarily determined by a balance between its molecular weight/size and basicity [103].

At iso-conversion and in the presence of nitrogen-containing compounds, fuel gas and coke yields are increased, whereas gasoline yield decreases [123]. In the commercial FCC unit, those changes can be explained as follows: if the refiner wants to change from a given feedstock to another one with higher nitrogen content, maintaining the conversion, in the later case the FCC catalyst

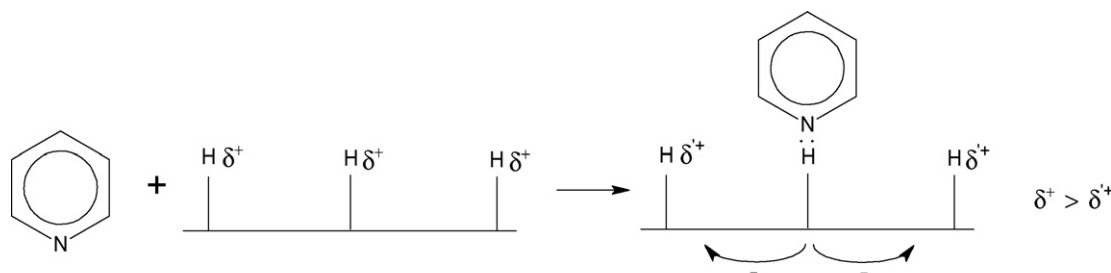


Fig. 5. Scheme of the inductive partial deactivation effect of the neighbor acid sites.

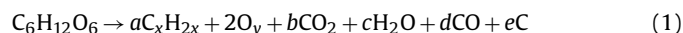
will have a lower acid sites density, thus requiring a higher catalyst circulation. The higher the catalyst circulation is, the higher the catalyst-to-oil ratio, favoring fuel gas and coke at the expense of gasoline.

### 3.2.2. Oxygen-containing molecules

The increasing price of crude oil is pressing refiners to find alternatives to this fossil resource. Nowadays, one of the possible alternatives to crude oil as a refinery feedstock is biomass. Biomass feedstocks include cellulosic biomass, sugar-based biomass and vegetable oils. Vegetable oils (triglycerides) are by far the feedstock more easily convertible, because they are already liquid and have low oxygen content [124–128].

On the other hand, cellulose-based biomass must be liquefied before conversion in the FCC process. The oils produced from cellulosic biomass are generally denominated bio-oils. These oils can be produced by pyrolysis, liquefaction or gasification followed by Fischer-Tropsch reaction [125,129–133]. These oils, although sometimes exhibiting some visual similarities with crude oil, present a completely different chemical composition. In addition, their thermal stability is quite low, requiring improvement. In some cases, bio-oils can be constituted by a mixture of more than 300 highly oxygenated compounds. Contrarily to crude oil, which commonly presents only negligible amounts of oxygenated compounds, these bio-oils are formed directly from carbohydrates, which compose approximately 75 wt.% of cellulosic biomass. These molecules can reach C-to-O ratios of 1:1. However, bio-oils present hydrophilic molecules without the appropriate combustion properties necessary to act as carburants.

A conversion step is, therefore, crucial to convert these oxygen-rich molecules into hydrocarbons, more suited to act as fuels. The catalytic cracking catalyst is quite effective in removing the oxygen atoms from biomass-derived molecules. Oxygen can be removed in the form of  $\text{CO}_x$  or  $\text{H}_2\text{O}$  through the following reaction (Eq. (1)) [134]:



Chen et al. [135] studied the transformation of carbohydrates over H-ZSM-5 zeolites. The main products were coke,  $\text{CO}_x$  and hydrocarbons. According to these authors, the main difficulty in the conversion was removing the oxygen and introducing the hydrogen atoms in order to improve the combustion properties of these carbohydrates. The conversion of bio-oils has also been investigated by other research groups using zeolites [136–143]. Each studied family presented a different reactivity. Work carried out by Gayubo et al. [141–143] disclosed the differences of reactivity between the major families of oxygenated compounds over acid zeolites. Several model compounds were tested over H-ZSM-5 and the reaction products were identified at different temperatures.

In what regards alcohols, they dehydrate at rather low temperatures (200 °C), producing alkenes that can suffer oligomerization

reactions (250 °C) and cyclization, followed by hydrogen transfer to form aromatic cycles (>350 °C) [141]. Phenol is much less reactive than other alcohols, even if small amounts of propylene and butanes could be detected at moderated temperatures [141]. 2-Methoxyphenol also displayed low reactivity, only yielding coke by thermal decomposition. Acetaldehyde reacts in a similar fashion, yielding mainly coke [142].

Acetone is less reactive than alcohols but can also suffer dehydrogenation, at slightly higher temperatures, with the formation of isobutene and  $\text{C}_{5+}$  alkenes occurring at more elevated temperatures (>350 °C). These olefins can then be transformed into gasoline-range paraffins, aromatics and alkenes.

Acetic acid can also be converted over acid zeolites, undergoing a first dehydrogenation reaction with the formation of acetone and then following the previously mentioned mechanism.

In conclusion, each oxygenated molecule presents a distinct reactivity and the nature of the feedstock can determine whether the FCC process is suitable for its conversion into more valuable hydrocarbons. Generally speaking, all oxygen-rich molecules yield large amounts of coke under typical catalytic cracking operating conditions, resulting in higher catalyst deactivation. In order to improve the yields in valuable products and limit deactivation, specific conditions must be used.

However, the existence of dedicated fluid catalytic cracking units is still far from being a reality. A possible alternative for the near future is co-feeding the biomass-derived products with petroleum-derived streams in industrial FCC reactors. Indeed, some research groups have studied this option and proved that some oxygen compounds can be added to vacuum gasoil without drastically altering the product selectivity [134].

The injection point of the biomass into the FCC riser can also be chosen in order to optimize the valorization of this feedstock. Before the injection of VGO, very severe cracking conditions are encountered (high temperatures and highly active catalyst), while near the stripper the catalyst is already partially deactivated and temperatures are lower due to the endothermic nature of the cracking reactions. As such, if the main goal is to convert the bio-oils into coke and gas, the co-feed should be injected in the beginning of the riser. On the other hand, if a mild cracking is sufficient, with the production of more liquid products, the injection point should be closer to the stripper. This decision must also account for the specificities of the oxygen-containing feedstock.

### 3.2.3. Sulfur-containing molecules

Although not so relevant for the deactivation of the FCC catalysts itself, environmental regulations state that the maximum amount of sulfur allowed in the gasoline pool will be 10 ppm. In the European Union, this limit will be imposed in 2009 by the European Parliament and Council. It is well known that from all their constituents (alkylate, reformate, isomerate, hydrocracking gasoline, catalytic cracking gasoline), the only contributor to the final amount

of sulfur is FCC gasoline. Indeed, several processes were commercialized worldwide to hydrotreat FCC gasoline in order to obtain a low sulfur product [144–146]. Another alternative is a severe treatment of VGO before the catalytic cracking reaction. However, most refiners do not select this option because, due to the amount of feedstock to be treated, the cost would be too high. This means that all the sulfur contained in the VGO will be processed by the zeolite-based catalyst.

Typically, the sulfur compounds which predominate in FCC non-hydrotreated feeds are alkylated thiophenes, benzothiophenes and dibenzothiophenes. The aromatic character of the thiophenic ring makes these compounds refractory under typical FCC conditions [147]. Pilot unit tests carried out by Collet and co-workers [148] revealed the typical distribution of the sulfur atoms after the reaction: H<sub>2</sub>S (33–55 wt.%), gasoline (2–5 wt.%), LCO (18–30 wt.%) and HCO (9–30 wt.%). The sulfur distribution in the gasoline range by family was identified: light mercaptans and disulfides (20 wt.%), thiophene and alkylthiophenes (50 wt.%) and benzothiophenes (30 wt.%). Naturally, this distribution is highly dependent on the quality of the feedstock. This distribution does not account for the fraction of sulfur that remains in the zeolite structure in the form of coke. Indeed, sulfur molecules containing unsaturated rings can easily react with aromatics through condensation reactions to form coke molecules.

Corma et al. [149] have shown that saturated compounds such as mercaptans, sulfides and disulfides are mainly converted into H<sub>2</sub>S, which means the catalytic cracking catalyst can also act as a hydrodesulfurization (HDS) catalyst. Short chain alkylthiophenes can suffer dealkylation but also isomerization [149], whereas for long chain alkylthiophenes, cyclization and dehydrogenation reactions are more probable. These latter compounds are the main responsible for gasoline sulfur content, which is not affected by polycyclic sulfur compounds present in the FCC feedstock [150].

Valla et al. [151,152] have demonstrated that the thiophene molecule is quite stable. It suffers mainly desulfurization reactions leading to H<sub>2</sub>S and the deposition of sulfur in coke. Alkylation and saturation of the thiophene ring takes place in a much lower extent.

The sulfur contained in coke can be oxidized in the regenerator with the formation of SO<sub>x</sub>, which are quite toxic and harmful to the environment. This is another problem arising from the cracking of high sulfur feedstocks.

On the other hand, benzothiophene seems to be much more reactive than thiophene and is keener to intervene in alkylation reactions, producing molecules outside of the gasoline range [151,152].

Nickel and vanadium, as it will be elaborated further on, constitute one of most relevant poisons for catalytic cracking catalysts. However, in this particular case, they may also have a positive effect, due to their ability to reduce the sulfur levels in FCC gasoline [146,153]. The presence of these metals has been proven to be one of the most successful ways to accomplish this goal.

## 4. Irreversible deactivation

### 4.1. Hydrothermal dealumination

During the reaction and regeneration steps of the FCC process, catalysts are submitted to very high temperatures in the presence of steam. As a consequence, both the thermal and hydrothermal stability of zeolites are of paramount importance for catalyst manufacturers. The standard USY zeolite, which constitutes the main active substance of the FCC catalyst, presents a framework Si/Al ratio of approximately 5. However, due to severity of the regeneration treatment (700–800 °C in presence of steam), the zeolite

rapidly undergoes dealumination. In fact, the zeolite present in the FCC equilibrium catalyst has a Si/Al ratio which can be close to 20. Obviously this change will introduce modifications in the deactivation phenomena occurring in the catalyst. Rawlence and Gosling studied the nature of the working equilibrium catalyst by blending fresh catalyst and a series of mildly and progressively more severely deactivated catalyst samples [154].

A regeneration treatment in two steps can decrease the dealumination of the catalyst. Indeed, the water generated by combustion is produced essentially in the first regenerator, where the temperature is lower (600–700 °C). In the second regenerator the amount of produced water vapor is much lower and despite the high temperatures (700–800 °C), dealumination is greatly diminished.

The presence of steam (0.5–3%) at the riser inlet is crucial in order to facilitate the atomization of the feed. The introduction of steam also causes changes on the conversion and product distribution, namely reducing coke formation.

In what concerns purely thermal treatments, zeolites can undergo various structural changes [155,156], including: (i) cell volume contraction due to the removal of water and/or organic template molecules, (ii) transformations into a more metastable phase, (iii) structural collapse, (iv) amorphization and (v) negative thermal expansion. The thermal stability of H–Y zeolites is rather small, depending on the framework Si/Al ratio. Its structure starts experiencing changes at temperatures around 450–500 °C.

The resistance to the combined effect of steam and temperature is called hydrothermal stability. As it was referred earlier on, the reaction between the zeolite hydroxyl groups and steam at high temperatures results in dealumination and loss of acid sites. After dealumination, the zeolite, although less acid, becomes more thermally and hydrothermally stable than the parent catalyst. This is one of the reasons why Y zeolites are usually steamed in specific optimized conditions before use in the FCC process [157]; the produced zeolite is generally denominated as USY (Ultra Stable Y). The USY zeolite stability is greatly affected by the presence of Na and steam.

Deactivation occurring during the catalytic cracking process is due to the dehydroxylation reaction (Fig. 6) of the Brønsted acid sites responsible for the catalytic cracking reaction [158,159]. After dehydroxylation, the system ends up in a metastable state; the Al can then be easily released from the zeolite framework, producing extra-framework Al (EFAL) species. This phenomenon is amplified by the existence of next nearest neighbor (NNN) position Al, which decreases the stability of the initial Al atom [160]. In high Si/Al zeolites, where all the acid sites are isolated, the second step is less favored. Several types of EFAL are present in zeolites structures, e.g., Al<sup>3+</sup>, AlO<sup>+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, AlO(OH), Al(OH)<sub>3</sub>, AlO(OH), ≡Si<sup>+</sup> [160,161]. The resulting framework vacancies can be refilled with Si atoms; the destruction of entire sodalite cages is a possible source of Si.

Steaming is not only important from a structural point of view; it also introduces alterations in the density, strength and nature (Brønsted or Lewis) of the acid sites [22,156,162,163]. Indeed, these modifications lead, in many cases, to an increase of the zeolite catalytic activity. However, this fact is rather surprising if one considers that dealumination is accompanied by a reduction of the acid sites density. Nevertheless, several authors [156,164–166] have reported an increase in the strength of the remaining sites, which could explain the higher activity. In addition, an activity maximum has been obtained for (Si/Al)<sub>fr</sub> ratios between 4 and 8 [167] for the catalytic cracking of heavy gasoils.

Several explanations can be advanced for this experimental observation. Firstly, a decrease in the density of the acid sites can be accompanied by an increase in acid strength. Consequently, in reactions that require strong acid sites, as it is the case of catalytic



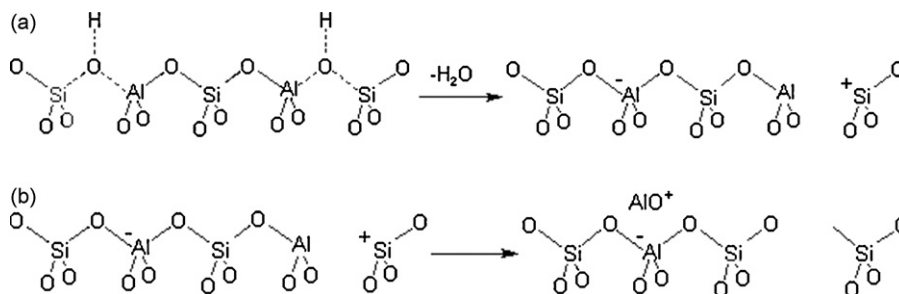


Fig. 6. Two step mechanism for the production of EFAl species. (a) Dehydroxylation and (b) Al segregation. Adapted from Kühn, 1977 [158].

cracking reactions, zeolites with isolated framework Al (Si/Al ratios of 9–10) will be more active. However, this effect seems to be relatively small because only small changes in activity are observed when the FAI content is reduced without formation of EFAl, for example by ammonium hexafluorosilicate treatment instead of steam [168]. A more consensual explanation is that the enhanced activity is due to EFAl species produced during the hydrothermal treatment and located within the sodalite cages or hexagonal prisms of Y zeolite [169]. This would increase the acid strength by charge delocalization at the framework Al (FAI) sites. On the other hand, some authors suggest that the EFAl species responsible for the increase in activity are located in the supercages [164]. Several papers also proposed that these EFAl species (Lewis acid sites) formed during the steaming treatment had a decisive role in the initiation step of the cracking reaction [170,171]. Even so, more recent studies seem to point out that the presence of Lewis sites does not seem to have a significant influence on alkane cracking reactions over H-USY [172].

Furthermore, steaming not only dealuminates the zeolite, with effects on the remaining acid site strength and distribution, but also creates mesopores that largely contribute to the increase of the catalyst activity in the cracking of VGO [33,173,174], as this latter is diffusion-limited.

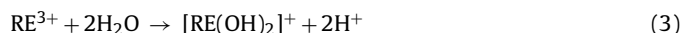
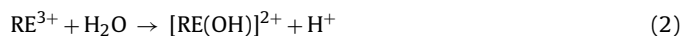
The presence of sodium in the zeolite structure can also introduce some changes in the resistance to steaming treatments. Less acidic but nevertheless thermally stable zeolites were obtained after the steaming treatment of partially proton-exchanged HNaY zeolites [175]. Indeed, the steamed zeolites exhibited large amounts of unusual OH groups with mild acidity.

In the FCC catalyst, the presence of a matrix is also responsible for an increased resistance to dealumination under severe steaming conditions and may also prevent temporary deactivation due to the presence of basic nitrogen compounds [122]. The investigation of hydrothermal ageing on a matrix-embedded lanthanum-exchanged zeolite Y by several physical techniques (IR, XRD, NMR and STEM) demonstrate that the crystallinity of LaY zeolite was totally preserved when the zeolite was incorporated into the amorphous matrix, while the same zeolite, if not embedded, lost 55% of its initial crystallinity upon steaming [176]. Furthermore, isotopic  $^{29}\text{Si}$  labelling of the matrix combined with  $^{29}\text{Si}$  MAS-NMR proved the silicon transportation from the matrix to the zeolite component with its subsequent reincorporation into the zeolite framework in the place of the expelled aluminium atoms (healing effect) [176].

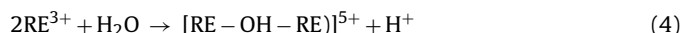
#### 4.1.1. Rare-earth stabilization on H-Y zeolites

Another form of changing the thermal stability of H-Y zeolites is through the introduction of rare-earth metals (La, Ce, Pr) [177–180]. The most accepted theory states that the observed reinforcement in stability (especially for La) is due to the formation

of coordination bonds between rare-earth cations and the framework oxygen atoms. These cations, besides conferring considerable thermal stability to the zeolite, also seem to provide an increase in its activity for moderate exchange levels. The reasons for this effect remain unclear, especially if one considers that each rare-earth cation ( $\text{RE}^{3+}$ ) replaces three  $\text{H}^+$ . One possible explanation is the formation of Brønsted acid sites via hydrolysis (Eqs. (2) and (3)).



However, even accounting for these reactions, the balance remains negative: the number of lost acid sites is greater than the amount created. The explanation may be linked to the strength of these new sites, which is thought to be greater for two possible reasons: (i) the acidity of the acid sites suffers an increase due to polarization exerted by the rare-earth cations; and/or (ii) the acid sites created by hydrolysis of the rare-earth cations are stronger than those eliminated by ion exchange. On the other hand, the activity decrease reported for high exchange degrees can be related with the formation of bridged hydroxyls (Eq. (4)) [178,179].



The industrial H-USY zeolite usually presents some rare-earth content (H-REUSY), mainly for thermal stability reasons.

The introduction of rare-earth compounds in the Y zeolite might not only affect the cracking activity but also have consequences for the hydrogen transfer properties of the catalysts, affecting their product distribution. In fact, when rare-earth elements are exchanged in the Y zeolite, the hydrogen transfer rate increases, thus favoring coke formation. This effect seems to increase in the presence of rare-earth cations and in a linear fashion as a function of the ionic radius of the element [181]. These results suggest that a certain degree of catalytic control can be exerted on these reactions through the selection of the rare-earth elements to be loaded into commercial catalysts. Other studies proved that stabilized Y zeolites with high rare-earth content exhibited improved heavy oil conversion and higher coke selectivity in addition to a higher hydrogen transfer activity [182].

#### 4.2. Metal poisoning

Depending on the crude oil source, the FCC feedstock may present different amounts of contaminant metals. The most common are vanadium, nickel, sodium and iron [183]. The presence of Ni, V and other trace elements such as Fe, Zn, Pb, Cu, Cd, Cr, Co, As, Sb, Te, Hg, Au or Ag is common in crude oils around the world. The levels found depend mainly on the crude oil source, with those from Venezuela and Mexico having the highest levels. Normally these metals are only present in the higher boiling point cuts. In fact, they are generally in the form of metal porphyrins,

that deposit themselves on the catalyst surface and act as poisons, damaging the zeolite structure and favoring dehydrogenation reactions that increase coking. Initially, crude oil contains a small amount of sodium, typically below 50 ppm. However, the presence of seawater in crude oil greatly increases the concentration of this metal.

In the case of nickel, the main effect is the increase in coke selectivity [184,185]. At low amounts (1–5 wt.%), the reduction of nickel supported on silica is affected by the presence of water and could be controlled by nucleation [186]. The alumina type and atmosphere treatment also affects the amount of nickel in tetrahedral and octahedral symmetry, which appear to control this process. The reduction of nickel spinel phases occurs only above 700 °C [187]. In the FCC catalyst, the presence of EFAL species decreases nickel mobility [188], as well as its reducibility [189]. Similarly to nickel, vanadium is also responsible for an enhancement of the USHY zeolite coke formation [190], but in the commercial FCC catalysts, in the presence of rare-earth elements, the amount of coke formed due to those metals is reduced [191,192].

Both nickel and vanadium are active in dehydrogenation reactions. While nickel is active in the metallic state for dehydrogenation, hydrogenolysis and hydrogenation [193], vanadium (V) has been used for oxidative dehydrogenation (ODH) reactions [194,195]. For V impregnated on silica, a reduction at low temperature is sufficient to form superficial  $V^{3+}$  species [196]. In the FCC catalysts, even at high temperature, a distribution of 3+, 4+ and 5+ vanadium oxidation states is observed. Among these species, studies of electron spin resonance (ESR) have shown that  $V^{4+}$  and  $V^{5+}$  have quite similar dehydrogenation activities, whereas  $V^{3+}$  or lower oxidation states present almost no dehydrogenation activity [196,197]. The ability of rare-earth elements to form vanadate species is probably responsible for keeping part of the vanadium in the +5 oxidation state [198]. It is also important to note that vanadyl species on USY are stable even at temperatures close to the regeneration step ( $\sim 700$  °C) [199].

Contrarily to nickel, both vanadium and sodium compounds present mobility over the catalyst surface [200–202]. Sodium preferentially interacts with the alumina phase and tends to migrate to the fresh particles due to the higher availability of acid sites for exchange [202]. Both vanadium and sodium are also responsible for the permanent damage of the zeolite structure in the presence of steam at high temperatures [189,192]. The existence of these metals is the main cause for the fresh catalyst addition needed to maintain the activity of the inventory.

Iron can affect the morphology of the FCC catalyst particles due to a phenomenon often referred to as *nodulation* and, above a critical iron content, the accessibility of the particles can be severely reduced [203–205]. A detailed study with different iron species evidenced that more important than its presence, is how the iron species are distributed [206]. Larger species, e.g. iron naphthenate, have proven to be more deleterious to key catalyst properties, such as crystallinity, surface area and number of acid sites [206]. Evidence that the large iron species are preferentially located at the external surface of the FCC catalyst particles was obtained applying atomic force microscopy (AFM) that revealed bright spots on the FCC catalyst surface; scanning electron microscopy combined with energy dispersive spectroscopy (SEM-EDS) confirmed the presence of iron [207].

The presence of paramagnetic iron in the FCC catalyst can be exploited to selectively discard the relatively older e-cat, with high iron content, therefore producing a higher activity/lower metal levels catalyst to recycle, that will be responsible for lower hydrogen, dry gas and coke yields and higher wet gas and octane productions [208,209].

The simulation of the deactivation by metals at laboratorial scale can be achieved by different procedures. The simplest was proposed by Mitchell and consisted of an incipient wetness impregnation of nickel and vanadium compounds followed by a hydrothermal treatment at high temperatures [210]. Despite the differences obtained for the nickel distributions over the catalyst surface, this method resulted in a good correlation between the activity of actual and simulated e-cat samples.

Attempts have been made to develop more realistic bench-scale deactivation tests, focusing on the reproduction of the physico-chemical characteristics of the e-cat. Examples of such methods are the cyclic propylene steaming (CPS), where after the deposition of metals by incipient wetness impregnation, the catalyst is submitted to reduction-oxidation cycles using propylene as the reducing medium [211,212]. Improvements to this method comprise pre-stabilization steps with reduction-oxidation cycles and changing the ratio of the time periods the catalyst spends in each environment during CPS cycles [213]. A more sophisticated approach is the cyclic deactivation (CD) procedure, where a fresh catalyst is submitted to repeated cycles of reaction with vacuum gasoil spiked with metals and regeneration [214]. This method is generally applied to study the effect of nickel and vanadium [215] but can also be applied to analyze the effect of iron [216]. It is important to note that the different methods for adding metals to the catalyst may affect not only the metal-support interaction, but the metal-metal interaction as well [217].

Another approach consists of using a mixture of artificially deactivated catalysts in order to reproduce the performance of the corresponding e-cat [218,219].

## 5. Additives deactivation

Nowadays, most FCC (and RFCC) units employ catalytic systems containing one or more additives, such as ZSM-5 for light olefin production and gasoline octane index enhancement, special matrices for Ni passivation, combustion promoters, etc. Additives deactivation, a topic that has been receiving increased attention recently will also be briefly discussed.

Besides ZSM-5 additives, it is also possible to operate the FCC unit under more severe conditions, so as to comply with the market demand for light olefins, used in the production of downstream petrochemical products [220,221].

The importance of additives in the FCC process has been increasing in the last decades [222]. The most used additives worldwide are combustion promoters [223,224], employed to favor the oxidation of CO in the regenerator dense phase, and additives based on ZSM-5 [225–228] used to favor light olefin production and improve gasoline octane number. Other additives, such as special matrices able to reduce the deleterious effect of Ni, reduce gasoline sulfur content [145,146,229], reduce the emissions of  $SO_x$  and  $NO_x$  [230–232] or enhance the catalyst mechanical properties (thus minimizing particle emissions) may also be applied.

The knowledge of how these additives are deactivated is of extreme importance for their performance in the commercial FCC unit, influencing its development and evaluation as well. Combustion promoters are based on noble metals and its deactivation depends primarily on the metal-support interaction. Under the FCC unit regenerator conditions, sintering of the active metal may occur, reducing the available metallic surface. The combination of cyclic deactivation and coke combustion assays influences the ranking of combustion-promoting additives [233].

As previously discussed in Section 3.1, ZSM-5 zeolite has a lower tendency to form coke, compared to Y zeolite, due to its narrow pores that limit the formation of bulky coke intermediates. The

main cause of ZSM-5 additives deactivation is dealumination due to the presence of steam at high temperatures, which leads to a partial destruction of its framework structure.

Several studies reported changes on the hydrothermal stability after impregnation with phosphorus over ZSM-5 zeolites [234–259] but also over FAU and MOR [251]. Even so, before the steaming treatment, the impregnation with phosphorus was said to produce several counterproductive effects: (i) reversible decrease in activity due to the interaction of P species with the protonic sites; (ii) external surface blockage; (iii) decrease in the microporous volume; and even (iv) dealumination. Despite these facts, the phosphorus impregnated samples seemed to retain their acidity and activity during the steaming treatment to a higher level than the untreated zeolite. This means that the P species formed in the treatment reinforce the zeolite structure and prevent dealumination. Optimal phosphorus contents (highest activity) were obtained by different authors [258,259], its values depending essentially on the zeolite (Si/Al)<sub>fr</sub> ratio and on the model reaction used. Corma et al. found a maximum in the *n*-decane cracking activity for P/Al molar ratios of 0.5–0.7 [258].

The fact that impregnation with phosphorus induces a stabilization of the zeolite framework is rather consensual. On the other hand, the way in which the phosphorus species interact with the zeolite is still under discussion. Phosphorus can be introduced in the zeolite by impregnation with several compounds: H<sub>3</sub>PO<sub>4</sub> [238,239,243,254,257–259], NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> [258], PCl<sub>3</sub> [251], P(OCH<sub>3</sub>)<sub>3</sub> [237,240,242,243,246,252], P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [240–242], etc. Depending on the treatment, the interaction between the zeolite and the P species may differ and some species seem to be unable to stabilize the zeolite structure. Some authors have proposed that P can replace framework Si atoms, forming (SiO)<sub>x</sub>Al(PO)<sub>4-x</sub> species [250,256], while others sustain that the only way P can interact with T atoms is by the formation of amorphous extra-framework aluminum phosphates [247,258–260]. The addition of phosphorus compounds during the zeolite synthesis step favors an interaction between phosphorus and aluminum, resulting in new species that appear as distorted tetrahedral Al atoms interacting with phosphorus on the <sup>27</sup>Al NMR spectra [247,259–261]. Those distorted species present higher hydrothermal resistance when compared to the classical framework species.

## 6. Final remarks

Although catalytic cracking is a mature subject, the aspects related to its deactivation, especially under commercial conditions are still under investigation. Fundamental studies based on pure zeolites and FCC catalyst components continue to be important for the understanding of deactivation, a complex phenomenon where the different variables in the process (feed composition, catalyst composition and operational conditions) are all inter-related. The recent advances in studies related to FCC catalyst additives deactivation prove that this field will continue to deserve attention.

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