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Development of heavy metal passivators in residue fluid catalytic cracking process

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ABSTRACT

The advancement of residual fluid catalytic cracking (RFCC) is significantly influenced by the development of heavy metals passivation technology. Resids often include larger concentrations of heavy metals (Ni, V, and Fe) than gas oils, primarily in the form of porphyrin complexes and salts of organic acids. Under cracking conditions, metals, especially Ni and V in residues and gas oil deposit on the cracking catalyst and induce adverse dehydrogenation reactions. The catalyst's zeolite component is destroyed by these metals. While reducing the yield of gasoline, active metals increase the yields of coke and hydrogen. Because most cracking FCC units can only tolerate limited amounts of coke and hydrogen, the level of heavy metals on the catalyst needs to be kept under control in order to achieve maximum productivity and profit. Metal passivation enhances catalytic activity and/or selectivity to more desired products by minimizing the detrimental effects of contaminating metals. In this study, we will review heavy metals deactivation mechanism in RFCC process and the potential technological solutions to the catalyst deactivation concern.

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1. Introduction

Fluid catalytic cracking (FCC) is an important process in oil refineries, which transforms low-value hydrocarbons into higher value-added

products, like propylene and gasoline [1]. The first step in the FCC process involves injecting preheated gas oil into the riser reactor, following by vaporizing and short contact with the preheated FCC catalysts. At the next step, the coke-deactivated spent catalyst is separated from the products and sent to the regenerator, where the activity of catalyst particles

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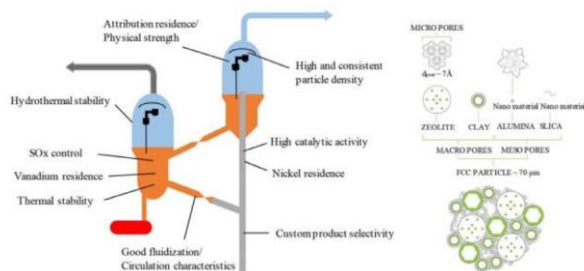


Fig. 1. A typical schematic representation of the FCC process and its catalyst [8].

is recovered by burning the coke at high temperatures in an airflow [2].

The conventional FCC catalyst consists of four main components: zeolite Y, matrix, filler, and binder. These fine particles typically range in size from 60 to 80 µm. To create microspherical catalyst particles, all ingredients are combined and spray-dried [3]. For special objectives, additives may be added during preparation. Examples include ZSM-5, an olefin enhancer [4-6], a hazardous metals trap, a CO combustion promoter, or SO and NO scavenger additives [7].

The most active component of FCC catalyst is zeolite, which regulates its activity and product distribution. The matrix effectively plays a supporting role in the catalyst by giving it attrition resistance, mechanical strength, and the ability to lessen the undesirable impacts of contaminants [9-12]. In particular, the most common matrix type is the active matrix, which is usually porous silica-alumina in the FCC catalysts. [10].

The filler, typically considered an inert component of the matrix, acts as a transfer medium and a heat sink and gives no or little activity to the catalyst. The fillers provide the mechanical strength required for the FCC catalyst to fluidize in the unit [13].

Zeolite, matrix, and filler are held together primarily by the binder, offering great attrition resistance. The binder can sometimes improve the coking properties and serve as a toxic species trap [14-16]. A typical FCC catalyst microsphere is shown in Figure 1.

Industrial FCC uses a variety of feedstocks, including atmospheric residue and vacuum gas oil which contain undesired contaminants like Ni, V, Ca, Fe, and Na [17]. Metals tend to gradually poison the surface of the FCC catalyst, reducing its activity and increasing coke production, in contrast to hydrocarbon molecules, which convert to useful products when they come into contact with the catalyst. Because the petroleum refiner uses the FCC process, the actions of these metals cause difficulty and raise the cost of refining [18].

Academic and industrial researchers have conducted numerous studies to determine the damaging impact of heavy metals, such as V, on the stability of FCC catalysts. The creation of metal passivating agents has been the focus of numerous efforts. It was discovered that the majority of previous reviews in this field of study mainly concentrated on issues like the evaluation of FCC catalyst testing units, FCC catalyst deactivation, FCC catalyst deactivation methods, and the FCC unit, with little focus on the effects of feedstock contaminants, which are crucial in the FCC process. Although numerous researchers have looked into how contaminants affect FCC catalysts, there has not yet been a thorough analysis of the research findings.

2. Deactivation mechanism of RFCC catalyst by heavy metals

The poisoning of the FCC catalyst by feedstock metals, i.e., organic porphyrins, is one of the issues the FCC process has faced. Various metal compounds such as V and Ni are among the different pollutants present in FCC feedstocks (mostly residues). These metals poison the catalyst and reduce its activity in cracking reactions [19, 20]. The FCC catalyst

can be poisoned by the deposition of these metals, which affect the selectivity and product yields [21].

Feedstock contamination might include non-metallic substances such as nitrogen and organic sulfur. As heavier feedstocks are now more prevalent and fairly priced for refiners, their entry into the cracking unit has become a common procedure. As a result, additional coke is formed, increasing the regenerator's operating temperature to an unacceptable level and altering the selectivity and activity of the FCC catalyst [22].

Unlike N₂, sulfur, and coke deposition, inorganic metal accumulation over the catalyst can not be generated by oxidation, which makes the FCC catalyst permanently deactive [15, 23-25].

Other elements like Fe and Ca do not have the same negative effects on FCC catalysts as V and Ni but lead to excessive coking and textural disorder [26, 27].

The metals content (also known as the metals factor) in feedstock has been referenced by scholars over the years in a variety of ways [1, 28, 29], as listed below:

- Metal factor(Fm) = ppm Iron+ ppm Vanadium + 10(ppm Nickel + ppm Copper)
- Mobile Index= ppm Nickel + ppm 0.25Vanadium
- Davison Index=ppm Nickel + ppm Copper + 0.25Vanadium
- Shell Index= ppm 1000(14Nickel +14Copper + 4Vanadium + Iron)
- Jersey Nickel equivalent index =ppm 1000 (Nickel + 0.2 Vanadium + 0.1Iron)

A feed with a Fm larger than 2.5 is regarded as hazardous for FCC based on the relationships presented above [28]. For instance, according to the Mobil index, the most widely used Fm: Nickel + 0.25Vanadium or 4Nickel + Vanadium, Ni produces four times more hydrogen than vanadium. These metal parameters correspond with metal activity because they increase coke formation and encourage dehydrogenation processes (i.e., coke and hydrogen yields). Typically, the FCC catalyst becomes permanently deactivated due to the contamination of metal impurities from the feedstock. Understanding the corresponding physicochemical properties changes in the FCC catalyst and how these alterations impact the behavior of the catalyst is, therefore, crucial [22].

2.1. Iron

Fe in E-cat (equilibrium catalyst) may be generated from a variety of sources, such as FCC feedstock, a corrosion byproduct, or the deterioration of storage equipment [30]. Fe contamination of the cracking catalyst limits the catalyst's efficiency by preventing reactants from reaching the active sites and reducing bottom conversions [31]. Fe is the slowest mobile element compared to V and Na. Results from SEM-EDS and XPS techniques revealed that Fe concentration on the catalyst surface was significantly higher than Na, showing that the majority of the accumulation of Fe was retained on the catalyst particle's surface [30, 32]. Additionally, XPS results demonstrated that Fe on the E-cat presents in the form of Fe³⁺, but the riser or regenerator did not contain iron in this oxidation state. Any reduced Fe found in the E-cat catalyst collected from the FCC process will probably be converted to Fe³⁺ in the atmosphere [32].

There are two ways that iron reduces catalyst activity. While pore blocking occurs at greater concentrations, deactivation at lower concentrations results from poisoning acid sites [33]. Iron not only reduces accessibility and contaminates acid sites, but also directly exchanges ions with the active sites of a cracking catalyst, which results in a loss of activity. When Fe is deposited on FCC catalyst particles, it catalyzes the dehydrogenation processes that increase coke selectivity and may disrupt with fluidization of the catalyst in the FCC process[34].

These deposited compounds are composed of magnetite crystals (Fe₂O₃), which readily combine with H₂S in the riser to generate FeS,

which then oxidizes to magnetite in the reactor, releasing sulfur and oxygen. The matrix layer on the surface of the particle surface, which reaches a depth of several microns, is melted due to the extremely rapid reaction and a large amount of heat released. As a result, a thick coating of iron oxide is created, acting as a surface barrier to the diffusion of hydrocarbon molecules [32]. The iron-enriched rings' blockage of the surface pore structure protected the interior of the catalyst made with silica-based binders, but also reduced its activity and reduced bottom conversion. Even with large Fe concentration, the catalysts with an alumina binder demonstrated strong resistance to Fe deactivation and preserved high bottom cracking performance and high activity [32]. Fe precursors play a significant role in the distribution of iron artificially deposited on the surface of the catalyst. The poisoning of the FCC catalyst by Fe was mostly brought on by larger molecules, like $C_{22}H_{14}FeO_4$, which produced iron-enriched clusters on the catalyst's surface. Because of the uniform distribution of iron, small iron species like $FeCl_3$ had minimal effect on the performance of the catalytic process. The physiochemical parameters, such as variations in crystallinity, pore volume, and surface area, were similarly linked to decreased catalytic performance [35].

The textural properties of the poisoned catalyst with Fe do not change by hydrothermal treatment, which indicates Fe has no additional impact on hydrothermal instability, opposite of vanadium [22]. Additionally, oxidized Fe (Fe_2O_3) could probably oxidize some feedstocks to CO_2 via chemical looping combustion, which is also undesired in cracking reactions [36-38].

2.2. Vanadium

Certain crudes from Mexico and Venezuela are among the major natural sources of vanadium. However, practically all crudes include some amount of vanadium. Porphyrin complexes or naphthenate make up most of the vanadium compounds in crude oil. Under 525–530 °C, naphthenates are completely decomposed [39]. It is well acknowledged that V is deposited on the catalyst particle due to the size of the porphyrin molecule and the polar character, whether or not complete decomposition happens through riser cracking or burning in the regenerator.

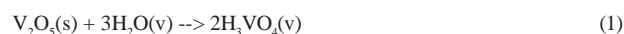
A part of the vanadium on the catalyst is oxidized to V^{+5} due to introducing the coked catalyst into the FCC regenerator. Vanadium is only present in the +5 valence state, according to Electron spectroscopy for chemical analysis (ESCA) of equilibrium and metal-impregnated fresh catalysts [40]. According to another study, about 5 wt.% of the V is found as VO^{+2} species on a steamed Y zeolite. However, it is commonly acknowledged that the predominant vanadium species is V^{+5} following steaming. The source of vanadium contained in the crude has no influence on the V oxidation state. Vanadium undergoes continuous valence shifts between +5 and +4 oxidation states when the cracking catalyst carries it from the regenerator to the riser and back. Under typical FCC reactor settings, V^{+5} does not easily decrease to a +3 valence once generated in the regenerator [40].

The FCC catalyst suffers a significant decrease in activity and surface area due to V deposition. Since the zeolite part has the maximum surface area, a decrease in surface area is principally linked to zeolite crystallinity loss. Although induced by zeolite acid site poisoning or zeolite destruction, contamination by Na or V similarly affects catalytic activity [41]. According to reports, vanadium is less harmful to the zeolite when nickel is present. [18, 42]. Vanadium deposited on the catalyst's surface slowly moves from the surface of the matrix to the zeolite structure, where it conducts a destructive reaction.

The procedure by which zeolite is destroyed by V is a controversial subject. Some literature published in early 1980 proposed that zeolite and V O interact and form a mixture with a low-melting tempera-

[41] established that an oxidative environment is required to destroy zeolite. Thus, it is typically thought that a V^{+5} species is responsible for the destruction of zeolite. Most of the zeolite damage is believed to happen in the regenerator. Another piece of evidence is that hydrogen can be used at high temperatures as a reducing agent to lessen the harmful effects of vanadium. These situations are believed to decrease the V^{+5} species and mitigate its impact on the zeolite [41].

There was no zeolite damage without steam condition. Vanadic acid was suggested as the V species necessary for zeolite destruction by Wormsbecher, Peters, and Maselli in 1986. In the FCC regenerator, the following reaction would result in the formation of the acid H_3VO_4 [43]:



This theory took into account the need for both steam and oxygen. Vanadic acid is a strong acid that is comparable to H_3PO_4 . Therefore an acid attack on the zeolite through decomposing the SiO_2/Al_2O_3 structure looked probable. Zeolites are widely known for being vulnerable to acid attacks. This explanation, however, failed to explain why catalysts with high sodium concentrations were even less vanadium-tolerant than those with low concentrations. It would be predicted that Na ions would have a balancing impact and increase vanadium tolerance. Vanadium was discovered to be equally damaging when introduced to the catalyst by physical V_2O_5 powder combination or naphthenate impregnation.

For steaming catalysts exposed to V by physical mixing or impregnation, X-ray absorption spectroscopy (XAS) experiments discovered that the V adsorption edges were similar, showing the same coordination geometry and oxidation state [44]. Following steam treatment, vanadium was found to be dispersed throughout the catalyst particle, according to electron microprobe investigations. According to Wormsbecher, a volatile species must be involved in a small amount of vanadium oxide powder to have the same destructive effects as vanadium impregnation [43]. The deactivation caused by small amounts of V_2O_5 powder cannot be attributed to solid-state interaction or liquid wetting. Transport tests were performed in a flowing tube reactor to show that volatile species is responsible for zeolite destruction. In these tests, a supplier of V_2O_5 powder was physically removed from the zeolite catalyst. In flowing air, high-temperature water was injected above the V_2O_5 . Even though the catalyst and vanadium supply were not in direct touch, the zeolite eventually lost its crystallinity after several hours. Therefore, H_2O vapor and V_2O_5 must exist in the precursor for vanadium poisoning; the resultant species must be volatile. Vanadium compounds with oxidation levels less than +5 were not considered because they were not present under the FCC regenerator. Pine [45] investigated vanadium oxidation using a solid-state kinetics methodology. He suggested that V^{+5} only acts as a catalyst for zeolite to be destroyed by steam.

It was discovered that the vanadium concentration directly correlated with the crystallinity loss reaction rate. That would be true regardless of whether vanadium served as a catalyst or a reactant. However, a catalytic role is more compatible with the reality that extremely little concentration of V significantly impacts reaction kinetic without being consumed. The rate constants acquired with V were extrapolated to zero concentration by Pine [45], who discovered agreement with the rate constants obtained without vanadium.

The rate constant for silicalite, CREY (Calcined rare-earth-exchanged Y), and USY (ultrastable Y) with or without V was calculated to comprehend more clearly the vanadium's site attack in the zeolite. It was discovered that silicalite had a low vanadium tolerance. Despite CREY having roughly five times more framework aluminum atoms per unit cell, CREY and USY were found to have the same vanadium tol-

erance. These results concluded that the Si-OH bond was a more likely target for attack. This was in line with the smaller particle Y zeolite's reduced steam stability, which would have a higher SA-to-volume ratio.

Additionally, in contrast to prior research [41], it was discovered that Na and V each had the same catalytic properties for the zeolite destruction by steam and that when combined, they had a synergistic effect. Pine concluded that both components speed up the pace at which steam reacts with a zeolite based on kinetic measurements. Pine omitted a description of the synergistic effect's mechanism.

Characterizing textures consequences of the hydrothermal process of zeolites showed that the ZSM-5 framework had greater resistance to V poisoning in comparison to zeolite Y at more V concentration because of the stability of the crystalline structure due to the smaller pore diameter of the ZSM-5 and, more critically, the smaller amount of Al content [46]. With increasing vanadium concentration in the catalysts, the micropore volume of ZSM-5 and Y-zeolite reduced.

V provides the disappearance of micropores in ultra-stable Y with the formation of mesopores in the presence of steam, as demonstrated by Etim et al. [21]. Accelerated dealumination is the reason why non-intracrystalline mesopores with an average pore diameter higher than 25 nm form. Vanadium had the least impact on the micropore volume when no steam was present, but it reduced the zeolite cracking activity and changed the product distribution during the FCC process. In contrast to coke and nitrogen, V deactivation typically results in permanent deactivation. The negative effects of vanadium significantly affect the textural aspects of FCC catalysts and other characteristics [21].

According to Cristiano-Torres et al., vanadium can penetrate a catalyst's surface in a dry environment and neutralize strong acid sites [47]. With increased V dosage, the density of sites of bronsted acidity, as determined by the C_3H_9N breakdown, reduced. It was discovered that the first step in zeolite destruction is the neutralizing of acidity sites in the regenerator unit [48].

Pimenta et al. investigated the impact of V contamination on the deactivation of zeolites by using $n-C_6H_{14}$ as a probe molecule over a model cracking reaction. The lowered $n-C_6H_{14}$ conversion indicated that V elements poisoned acid sites and facilitated the extraction of Al from the zeolite structure. Vanadium also greatly impacts the XRD patterns of V-contaminated catalysts by shifting the Bragg's angle, which reduces the catalyst's unit cell size and d-spacing characteristics [46]. Factors that vanadium deactivates FCC catalyst, such as vanadium's oxidation state, high temperatures, and the presence of steam, are well understood, even though the level of knowledge is still inadequate from an academic standpoint

2.3. Nickel

Ni is a dehydrogenation catalyst that produces significant yields of H_2 and coke when used in an FCC reactor. The amount of dehydrogenation is influenced by the Ni concentration, Ni age, and type of FCC catalyst. Research has indicated that Ni-containing catalysts create more HCO, which is suggestive of a lower capacity to crack the heavier feed components, even though Ni is not thought to be a major contributor to the loss of catalytic activity. Ni poisons both the weak acid sites on the catalyst matrix and the strong acid sites on the zeolite outer surface because heavy oil conversion is often linked to the catalyst matrix [40].

Reynolds [27] provides the mechanism of how Ni deactivates FCC catalysts: (1) In the initial deactivation stage, Ni deposits on the surface of the catalyst, possibly in an amorphous form, blanket the surface and locally deactivating it; (2) Over time, the surface layer thickens and forms crystalline sulfides that move inside the porous structure. The catalyst pores are finally destroyed and become inactive by these sulfides.

Reynolds claims that this two-step mechanism enables these catalysts to tolerate significantly larger concentrations of Nickel and Vanadium without fully deactivating [27].

This hypothesis would be consistent with where Ni was found on commercial catalysts (external to zeolite) by secondary ion mass spec-

troscopy (SIMS) [40]. Additionally, Ni possesses catalytic activity in the regenerator that generates significant amounts of CO_2 [49]. Processing heavy Ni feed may result in decreased unit throughput because the oxidation of C to CO_2 generates around 3.5 times the heat of the oxidation of C to CO. Commercial FCC catalysts differ in their vulnerability to Ni poisoning, just like other metals. ESCA demonstrate that Ni occurs as Ni^{+2} and Ni^{+3} on E-Cat [49].

The nickel interacts with the clay and gel ingredients of the FCC cracking catalysts to create $NiAl_2O_4$ surface species, according to X-ray photoelectron spectroscopy (XPS) experiments. SiO_2 is shown to move to the surface of steam-aged catalysts where, in the presence of nickel, it forms inert $NiSiO_3$ -like species. The catalyst's resistance to nickel will depend on a catalyst matrix's (non-zeolitic component's) capacity to reduce Ni distribution or a clay's capacity to produce inert Ni species. When nickel reacts with Al_2O_3 or extraframework material in modified zeolite, the most active nickel species are created [50]. On various supports, varied nickel dehydrogenation activities were observed. Effective studies of nickel interactions have been performed using a variety of laboratory approaches.

Studies using temperature-programmed reduction (TPR) have been beneficial in examining these various nickel species. The reduction of nickel on alumina proved to be challenging. With increasing Ni concentration [51] and higher reduction temperature [52], the amount of Ni reduction on alumina-supported catalysts increased. Because of the less contact with the support, the reduction for Ni-silica catalysts was often greater than that for alumina-supported systems [51]. Based on these aspects, it was discovered that the active Ni species producing coke and hydrogen varied on the FCC catalyst.

On catalysts having alumina species that may interact with the Ni, nickel was typically more active. According to imaging SIMS, Nickel tended to get immobilized after being deposited on the surface of the catalyst. Palmer and Cornelius used data from E-Cat that they separated using gradient density separation to link catalyst age with Ni content. It was discovered that the amount of nickel deposited equaled the sum of the feed rate, feed Ni content divided by the unit's inventory over time. By dividing the measured Ni content by the nickel deposition rate, it is possible to calculate the catalyst's average age in the unit using this connection. Nickel loses dehydrogenation activity as it ages, which decreases the amount of passivation agent needed [53].

3. Control of metal contamination

Many methods have been devised to alleviate the negative effects of metals, particularly V and Ni. These include passivation agents [54], operational improvements to vary the oxidation states of metals [55], and hydro treatment to eliminate heavy metals from the residual feedstock [56]. According to the amount of metal impurity in the feed, fresh catalyst addition is often adjusted to maintain the FCC unit's activity [57]. When feed metal levels rise, the amount of new catalyst added rises. When working with feeds that contain more metals, just adding more fresh catalysts may not be an efficient catalyst management method since doing so will not lessen the influence of contaminant metals and will negatively damage the stability and activity of the catalyst. Therefore, having a suitable catalyst composition that can efficiently trap metal impurities is crucial. Through a process known as metal passivation, the metal trap technology captures the volatile and mobile metal impurities, primarily vanadium, to create a catalytically inactive and stable compound [58].

3.1. Metal passivator

Manufacturers have been attempting to improve the metals tolerance of FCC catalysts for years and have successfully created several mod-

ified catalysts. Including diluents with the ability to specifically sorb metal impurities has been used to achieve these advancements. These metal traps may be incorporated directly into the catalyst particle during synthesis or added to the FCC catalyst as separate particles. Usually, the physical mixing is made at the plant before being shipped. The literature identifies a wide range of substances as metal traps. These trap elements, usually inorganic oxides, are less harmful to the environment than other substances. Some of these inorganic oxides are minerals that are found in nature. The dual-function cracking catalyst is initially less active (due to dilution effects) when a metal scavenger is added to the FCC catalyst. The vanadium trap picks out the V contamination and immobilizes it. Microscopic observation of a poisoned catalyst demonstrates that nickel traps can lead to Ni agglomeration or incorporation within the trap. As the metal content in the feed increases, FCC catalysts with metal traps deactivate at a much slower pace than the typical FCC catalyst. Changes in the formulation of the catalyst, as well as the addition of separated particle metal traps, might increase the metal endurance of cracking catalysts.

The addition of active substances or elements to the catalyst matrix is one example of how the formulation of the catalyst has changed. These components interact with the arriving metal atoms to form inert compounds on the surface of the matrix, which makes the metal inactive as a catalyst for the formation of coke and hydrogen. V bound on the matrix outside of the zeolite cage framework is immobilized.

These additives are typically added to incorporate ion catalysts by slurring with the other catalyst ingredients, such as zeolite, active matrix, binder, clay, and similar substances, and then spray drying into

Table 1.

Summary of metal traps introduced in the literatures

3-Challenges and perspective

powders. The passivation components may be precipitated or impregnated on the catalyst for in-situ cracking catalysts produced using pre-formed particles. The additive, in particular, prefers to bind to the particle's outer surface [59].

3.1.1. Vanadium Trap

Vanadium is the contaminating metal that will cause the FCC catalyst significant damage, costing the refiner much money to replace the catalyst. Because of this, scientific research has been increased to produce an efficient V passivation agent. Only tin additions are readily available commercially, despite the fact that several compounds have been mentioned in the literature for vanadium passivation [60]. For oil-soluble Ti and rare earth elements, data are available from laboratory research or brief commercial trials [60]. Before the incoming V can damage the zeolite, these vanadium passivation agents are introduced into the cracker feed stream dissolved in a solvent.

Meanwhile, much work has gone into creating V passivating agents, and the usage of basic oxides has received much attention in this regard. Alkaline earth oxides, such as magnesium oxide, seem to work well when added [61]. However, in regeneration, it is frequently unable to passivate V. Later, as passivating agents, rare earth compounds were added to FCC catalysts [58, 62]. In order to increase the hydrothermal stability of zeolites and reduce the impact of V as metal passivators in the cracking catalysts, RE elements, primarily La and Ce, have been utilized [63]. Depending on their kinds and introduction methods, they can reduce zeolite destruction by reducing vanadium mobility [64-66].

Trap	Precursor	Heavy metal	Method of trap introduction	Catalytic Improvement	Ref.
B ₂ O ₃	B ₂ O ₃	7000 ppm Ni	Physical mixing	-2.09 % coke reduction -1.77 increase in gasoline yields	[77]
LaUSY	LaCl ₃	2000-6000 ppm V	Precipitation	In decreasing order, zeolites' vanadium resistances were: La-PO-USY > Ce-USY > La-USY > USY	[72]
CeUSY	CeCl ₃				
LaPOUSY	LaCl ₃ and (NH ₄)-3PO ₄				
Y-MgO	Y(NO ₃) ₃ ·6H ₂ O and MgO	7500 ppm V	Doping	-26% activity increasing -Increase yield of desired products	[73]
RE ₃ +La, Gd, Lu	RE tri-acetylacetonate	10000 ppm V	Impregnation	-Inhibition of the vanadium attack and avoiding zeolite destruction	[82]
La ₂ O ₃	La(NO ₃) ₃	6000 ppm V	Ion Exchange	Physical mixing showed: - High crystal retention	[83]
La ₂ O ₃	La ₂ O ₃	6000 ppm V	Physical mixing	- Higher-level cracking performance	
MgO CaO CeO ₂ MgTiO ₃ CaTiO ₃ Li ₂ Ti ₂ O ₇ ZnTiO ₃	-	4800 Ni 5800 V	Physical mixing	-Mixtures of CeO ₂ and MgO were known best vanadium trap -Increasing conversion and coke reduction	[61]
La-USY	LaCl ₃	3000 ppm V	Three different methods: Precipitation, Ion exchange, and Impregnation	The impregnation method showed better trap respect to the other two methods: -High tolerance to V -Lower zeolite damage	[64]

Since rare earth oxides like La_2O_3 are naturally basic, they can neutralize vanadic acid to create rare earth vanadates [61, 67-69], which stop the zeolite framework from rapidly hydrolyzing. Eq. (2) illustrates the reaction of rare earth (RE) with acidic vanadium chemicals to produce vanadates, where RE_2O_3 stands for the rare earth oxide that produces stable vanadium compounds [70].



In general, lanthanum is preferentially found in the cages and super-cages of zeolite made via ion exchange [71] as opposed to the surface of the precipitation-derived zeolite. Due to V combining with La in La-Y zeolites to create lanthanum vanadate, RE-zeolite becomes unstable due to the loss of La-Oxygen bonding stabilizing in the zeolite channels [72].

The zeolite's thermal and hydrothermal stabilities are strengthened when RE ions are positioned in the small cages, but its V tolerance decreases [72]. For example, Feron investigated the impact of and lanthanum octoate and samarium naphthenate on V deactivation found that by co-impregnated $\text{C}_{44}\text{H}_{28}\text{O}_8\text{V}$ and soluble RE-elements, more than 90% of the crystalline structure could be retained [69]. Including ion-exchange methods, impregnation, and precipitation, Moreira showed the impact of the La incorporation procedure on V deactivation and discovered that none of using methods could stop the unexpected mobility of lanthanum ions into the zeolite framework [64]. Recently, Du et al. used Rietveld refinement to confirm the rare earth ions' migration behavior and noted that LaO_4P would be a preferable choice for V deactivation due to the lanthanum ions' poor migration [58].

Additionally, alkaline earth oxides, like magnesium oxide or calcium oxide, have a high vanadium resistance [43]. Alkaline earth metals do a good performance of passivating contaminants, but there are still issues; silicate formation decreases the contaminated metal's activity. According to Eq. 3, magnesium oxide and silicate combine to form crystalline magnesium silicate.



By adjusting the MgO slurry to keep the bulk MgO intact, it is possible to control the production of crystalline metal silicate [73].

To increase the vanadium tolerance of the catalyst, magnesium silicate components and anionic clays can also be added to the matrix of FCC. However, even those acidic centers that can neutralize alkali hardly exhibit metal-cracking abilities. As a result, the cracking activity initially lowers when commercial FCC is added [72].

3.1.2. Nickel Trap

By enhancing the FCC catalysts' diffusion capabilities, certain material types, like porous alumina, are frequently employed as a matrix to enhance the FCC catalyst's tolerance in front of Ni poisoning [74, 75]. However, these specialized matrix materials not only have the potential to affect the properties of the synthesized FCC catalyst but also raise their price, making them challenging to use in actual applications [76]. Two factors must be considered to boost the anti-Ni deactivation performance of catalysts following the aforementioned Ni-contamination mechanism. In order to reduce the production of coke and dry gas by limiting the coking reactions and over-cracking, one feature, the acidity of catalysts, must be properly tuned. To stop NiO from have been converted to NiO species and lessen the reactions of dehydrogenation carried on by NiO species, FCC catalysts must also have high Ni-trapping abilities [77].

To increase the tolerance of industrial cracking catalysts, alumina is frequently utilized. When a low surface area of large crystal alumina is added to the matrix of the catalyst, Ni can agglomerate into the

low surface area of Ni crystals, increasing nickel tolerance. The large Ni crystals leave significantly fewer active surface locations for dehydrogenation processes.

The low surface area alumina can be made directly or by back-filling with silica, which effectively reduces the surface area of the alumina by blocking its pores. Nickel may also be bound by encapsulation into a dormant Ni-alumina tetrahedral spinel structure, according to Lam et al. study [60].

The findings of commercial testing of Katalistiks International's nickel trap-containing catalyst in high resistance, moderate Conradson carbon unit were published [78]. The feed nickel amount almost doubled from 6 to 10 ppm throughout the new catalyst's use, increasing the E-Cat Ni content from 3000 to 6000 ppm. Throughout the trial's first phase, antimony was still charged as the supply of catalysts that included traps increased.

Before the antimony addition was completely stopped for three months, the antimony concentration on the catalyst could fall from a high of 2000 ppm shortly after introducing the new catalyst to a low of 700 ppm. Conversion maintained within the base range and was roughly steady over time with the catalyst that contained a trap [39].

3.2. Addition of Passivation Components Method

Passivators were introduced into the FCC catalyst structure using various methods, including precipitation, ion exchange, and impregnation [66]. There are various ways to incorporate metal traps into the structure of catalysts, such as the hydrothermal method, which introduces metal into the catalytic structure during the process of synthesis [79].

The catalyst carrier is impregnated by immersing in a solution containing an active metal precursor salt. In this situation, the carrier offers a large area, making the impregnation process more effective. When no anion or cation is exchanged with the active phase, impregnation is achieved. Ion exchange is based on exchanging ions from the carrier with the active metal. By exchanging alkali or alkaline earth cations, cations are introduced into the catalyst using this approach [80, 81].

According to some reports, introducing lanthanum and cerium using an ion-exchange method is less effective than incorporating them through precipitation [66]. Additionally, it has been demonstrated that the incipient wetness impregnation (IWI) approach of introducing cerium avoided damage of zeolite by vanadium more effectively than other ways and that this method also impacted the catalyst's resistance to hydrothermal deactivation [79]. On the other hand, the hydrolysis of the RE cations or the ionic fields inside the zeolite may affect the activity of the FCC catalysts when rare-earth ions are added by ionic exchange. In this regard, a correlation between the radius and the acidity of the RE ion has been discovered in NaY zeolite that has been exchanged with various rare-earth ions. The introduction technique may impact how a rare earth ion changes concerning acidity and activity [66].

Different metal traps have been applied for controlling the heavy metals in the FCC feedstock. The metal traps have been introduced through various methods, which have resulted in different catalytic performances. The corresponded traps and the introduction methods are summarized in Table 1.

Metal pollutants can cause damage in an FCC unit through obvious paths. Since the amount of metals derived from the crude oils treated is expected to rise, it is important to comprehend how these metals affect the selectivity and activity of FCC catalysts so that more efficient mitigation measures may be created. Recognizing metal mobility is essential to comprehending metal effects and has provoked many discussions. There are few reliable and organized quantitative techniques for calculating mobility. To precisely assess metals deposition behavior and phenomena, a method for examining FCC catalyst images that are both clear and consistent is required. Although a method previously created

and published, Peripheral Deposition Index (PDI), for quantifying intra-particle mobility, it was very time-consuming, expensive, and unreliable because of the operator's requirement for close attention.

Accurate knowledge of the mobility and distribution of contaminant metals in a specific FCC unit can be used to evaluate the effectiveness of metals-passivators, identify the effects of metals on various catalysts and additives, and provide guidance for experimental studies at the laboratory scale. Contaminant metals can arise from feed, catalysts, or additives.

Consequently, the development of quantitative visual characterization methods will increase knowledge of the catalysts and contaminants in fluid catalytic cracking and will also lead to the advancement of new catalyst technologies.

On the other hand, it is crucial to establish a clear correlation between the microscopic world and the larger world of catalyst testing and real-unit performance. The industrial performance occurs at scales several orders of magnitude bigger than those used by the current microscopic and spectroscopic instruments, which typically only analyze a few FCC catalyst particles. It is necessary to close this gap, and appropriate tools must be created. We can adjust the catalyst performance with these insights to meet the demands of the broad trends in raw material availability and product demand.

4. Conclusion

We have reviewed recent advancements in the FCC procedure in this assessment. The FCC catalysts and processes, despite being close to 80 years old and highly developed unit, is one of the most important petrochemical processes.

The FCC feedstock impurities generally have the following effects on the cracking catalyst: blockage of catalyst pores, the collapse of the structure, acidic sites neutralizing, deterioration of the surface area, and dealumination of the aluminum framework.

In general, non-metallic contamination is reversible, whereas metallic pollutants result in permanent deactivation. The study of all stages of a catalyst performance has recently been made possible using modern characterization instruments, which give valuable information for commercial units. This has allowed researchers to understand better the mechanisms by which contaminating metals deactivate FCC catalysts. Most recent research using cracking catalyst particles has revealed details about the localization and distribution of heavy metal contamination within the catalyst particle, which may be useful in developing catalysts with modifying matrix and structure to offer the greatest tolerance to metal poisoning.

Vanadium has been demonstrated to be the most destructive metal to the FCC catalyst in petroleum feedstock. Destroying the zeolite structure through dealumination process reduces the activity of the catalyst. This causes the catalyst framework to collapse and some acid sites essential for cracking reactions to disappear. Dehydrogenation is accelerated by Ni, a known FCC catalyst poison, which catalyzes dehydrogenation reactions. Ni's impact on the catalyst framework and catalytic behavior has not received as much attention as vanadium and is instead only limited to coke production tendencies and the dehydrogenation process. By clogging the catalyst pores, iron significantly lowers the diffusion of reactant hydrocarbons to the catalyst's active sites.

Most earlier research has been concentrated on only zeolites, which are very different from FCC catalysts. For further research, especially in the case of nickel presence, all components of FCC catalyst, which include zeolite, matrix, filler, are necessary. More research is needed on interactions among the different elements of FCC catalysts to understand the functions of the distinct components in cracking reactions. To supplement experimental findings, theoretical research on the processes of contaminant metal-induced FCC catalyst deactivation is advised. This

might make it possible to understand catalyst deactivation at the molecular level.

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