

A Study of Eco-Friendly Disposal of the Wastes from A Fluid Catalytic Cracker

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Abstract

This is a study of fluid catalytic cracking conversion process, which is the heart of a petroleum refinery. The catalytic conversion process which is intended to provide feed stocks to innumerable plants besides this, the process also intends to produce gasoline/diesel in order to meet current demands. Keeping in-line with all these requirements, it is also necessary to meet environmental stipulation. In order to comply with the environmental standards, further research is focused on the products produced from the FCC, which can either be treated, sold out or can be used in other industries.

Keywords: Fluid Catalytic Cracker, Eco-Friendly Disposal of the Wastes

I. INTRODUCTION

The cracking of long chain hydrocarbons is the most important petroleum refining process. The method of cracking long chain hydrocarbons has evolved over the years, though the end goal remains the same. For cracking, fluid phase was very advantageous because firstly, quick heat transfer due to strong endothermic effect during cracking and secondly, strong exothermic effect in coke burning regeneration. FCC is the most important conversion process in petroleum refineries. It is a type of secondary unit operation, which is widely used to convert high-boiling, high molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases and other products.

FCC consists of two reactors, a riser and a regenerator. Feedstock is primarily vacuum gas oil, along with refinery residues. The products being- main column bottoms (used as refinery fuel oil), light cycle oil (used as a diesel blending component), heavy cracked naphtha, light naphtha, flue gas and slurry (high in sulphur, small ring and polynuclear aromatics). FCC units also produce SO_x and NO_x gases.

The process being as follows:

- 1) The vacuum gas oil feed to the unit along with recycle streams is preheated to a temperature of 365-370°C and is dispersed in the riser bottom in the form of drops through feed nozzle system, where it comes in contact with hot regenerated catalyst (temperature being 640-660°C). Finely divided catalyst is maintained in an aerated or fluidized state by oil vapors.
- 2) The catalyst section contains the reactor and regenerator. The catalyst circulates between the two. The spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process.
- 3) Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. Fresh catalyst is added and spent catalyst is removed to optimize the cracking process.

Performance of a riser and a regenerator are closely linked. Combustion of coke occurs on catalyst particles produced in the riser by cracking reactions and in the regenerator heat is generated which is needed in the riser for VGO feed vaporization and endothermic heat of cracking reaction. The intricate heat and coke balance is maintained by adjusting catalyst recirculation rate between the two. FCC riser is a complex system because of the complex interrelated hydrodynamics heat transfer, mass transfer and catalytic cracking kinetics.

The parameters influencing these aspects also change along the riser height-

Catalysts are the heart of the heart of a petroleum refinery. Several catalysts have been developed since the discovery of FCC. After many developments, it was found that zeolite catalysts possessed all the properties of a successful catalyst, activity, stability, selectivity, pore-size, resistant to fouling and low cost. Initially natural zeolites were used as catalysts then synthetic catalysts were developed further ultra-stable Y zeolites were discovered which had secondary mesopores, which facilitated diffusivity of greater molecules into zeolite crystals.

There are certain wastes which are released during the process of FCC. Treatment of these wastes is drawing attention throughout the world due to the alarming environmental issues. Few ways or methods have been devised to minimize the quantities of wastes or to reuse them.

The environmental issues caused by FCC are:

- 1) FCC is one of the largest source of air emissions, it is a substantial source of carbon mono oxide and particulate emissions in the flue gas from the regenerator.

- 2) FCC units also produce a considerable amount of SO_x and NO_x gases, which are major contributors to the greenhouse effect.
- 3) The spent FCC catalyst is though categorized as non-hazardous waste, but once its useful life is over the exhausted catalyst constitutes difficult to handle solid residue.

To control the CO emissions from the regenerator, at some places incinerators have been installed, which pose a problem of maintenance and repair besides huge capital cost. When a separate CO combustion system is taken out of line for routine or emergency repair and maintenance, there is inherent increase in CO emissions from the FCC regenerator. Therefore, in order to maintain the purity of stackgas within acceptable limits, it has been considered necessary to have back-up CO control systems or to modify the operation of the whole FCC. Another substantial progress which has been made is the increase in the air feed in the regenerator and increasing the regenerator temperature to an extent sufficient to support CO burning in regenerator. This has some beneficial effects upon some FCC operations, it permits reduction in catalyst to oil ratio and higher cracking temperature. It permits cracking feed stocks which are inherently low coke makers as burning less coke substantially all the way to carbon dioxide may generate sufficient heat to make up for smaller amount of coke. As FCC system is heat balanced by design, burning CO in the regenerator decreases the need for coke burning to satisfy the system's heat requirements. Thus, a new balance must be struck between producing little enough coke, to be burned all the way to CO_2 , to satisfy the cracking side heat requirements and also high enough coke to keep the regenerator temperature high enough to support the combustion of carbon mono oxide. This may be a very difficult balance to obtain and maintain. Further improvements have been made in carbon mono oxide burning capability of FCC regenerators with introduction of special FCC catalysts containing small amounts of platinum group metals or rhenium. These incredibly small quantities of metal have shown ability to catalyze the burning of CO in FCC regenerator without adversely effecting the selectivity of the catalyst on the cracking side of the process. The new catalysts have the capability of catalyzing the oxidation of CO in the part where catalyst particles are densely distributed, this causes the heat of CO combustion to be more readily and completely transferred to the catalyst particles rather than to flue gases. The new CO burning catalysts effectively operate to lower the temperature necessary in the regenerator to sustain CO combustion and effectively bring the combustion of CO into an area of the regenerator which contains substantial proportions of catalyst. The amount of coke produced on cracking side need only be that amount necessary to support the cracking side heat requirements and need not be concerned with maintaining an abnormally hot regenerator. One aspect of this invention resides in the modification of an otherwise substantially conventional fluid catalytic cracking system by utilizing a catalyst comprising a hydrocarbon cracking catalyst having a small proportion, up to about 50 parts per million of platinum group metal incorporated therewith and by cooling catalyst either between reactivation thereof and cracking therewith or via an internal cooling system in the regenerator or preferably by withdrawing a portion of the catalyst from the regenerator, passing it through a heat exchange cooler and returning the cooled catalyst back to the regenerator.

The heat exchange referred to may be direct or indirect. A portion of the catalyst inventory may be withdrawn from the regenerator, indirectly heat exchanged with water to produce steam and then returned at a lower temperature to the regenerator. The catalyst withdrawn from the regenerator may be directly heat exchanged with cold air in order to reduce its temperature and then cooled catalyst returned to the regenerator.

In one particularly preferred configuration, a portion of the catalyst in the regenerator is withdrawn from a lower part thereof, passed downwardly out of the regenerator, then lifted usually with air as a fluidized bed through an indirect water cooler and then reintroduced into an upper part of the regenerator. The cooled catalyst may alternatively be reintroduced into a lower part of the regenerator.

In one particular type of FCC system a regenerator having a fixed fluid bed of catalyst supported by an upward flowing stream of air, is utilized. In this system there is usually a lower, dense fluidized bed of catalyst and an upper dispersed bed of catalyst. The lower, dense bed may in fact not be a uniform bed at all but may be swirling mass of catalyst. In this type of regenerator the coked catalyst from the cracking side is introduced into the dense bed. Air is passed upwardly through and tends to support the catalyst particles while combusting the coke thereon. Lighter particles tend to be carried higher than heavier particles and are projected upwardly into the dispersed phase. The regenerated catalyst is usually withdrawn from the dense bed.

Feed is injected into the riser section of the reactor where it mixes up with the FCC catalyst and is cracked as it passes through the riser. The catalyst is deactivated by coke and feed metal. After being stripped by the steam, the coked catalyst is directed to regenerator. There the coke on the catalyst is burned off and the sulphur nitrogen in the coke originating from sulphur nitrogen compounds in the feed are transformed to SO_x and NO_x gases.

The regenerator is composed of dilute phase bed and dense phase bed. In the dense phase bed, there exists a large amount of CO resulting from the partial combustion of the coke. However, the dilute phase bed is an oxidizing atmosphere which contains an excess of O_2 . DeNO_x and DeSO_x additives are extensively used in the refineries. The mechanism of SO_x removal by DeSO_x additive involves:

- Oxidation of SO_2 to SO_3
- The chemisorption and storage of SO_3 as a sulfate in the additive and
- The reduction and hydrolysis of sulfates to H_2S which can be handled in an existing gas concentration plant.

Steps (1) and (2) occur in the dilute phase of FCC regenerator. Step 3 occurs in the FCC reactor under reducing conditions (large amounts of hydrogen and hydrocarbons). A DeNO_x additive is used to catalyze the reaction between NO_x and CO or coke in the dense phase bed of the regenerator. However, the presence of O_2 , H_2O and SO_x at higher temperature drastically

deactivates their DeNO_x activity. This poses a challenging problem for simultaneous reduction of SO_x and NO_x in the FCCU regenerator. The most ideal to solve this is to develop a multifunctional catalyst which has high NO_x reduction activity under conditions similar to the dense phase bed of the regenerator and exhibits the competence to catalyze the oxidation of SO_2 to SO_3 and effectively capture the SO_3 in the dilute phase, it must have the propensity to release the SO_x completely under FCC reactor conditions. Copper based catalysts show a high activity in the conversion of NO_x to N_2 . However, the deactivation caused by copper oxide aggregation or SO_2 poisoning is still a problem. Hydrotalcite like compounds, transformed to mixed metal oxides with high surface areas at high temperature, are potentially useful for chemisorption and storage of SO_3 as sulfate. Copper containing mixed oxides derived from hydrotalcites have been examined for the removal of NO_x using propane as a reactant, but these type of catalysts lose their activity for NO and CO reaction once SO_2 is introduced into the reaction system. Mixed solid solution spinel with cerium has been employed in many FCC units worldwide. Cerium oxide is also widely used in the automotive three way catalytic converter as an oxygen storage medium and thermal stabilizer. The addition of ceria to precious metal (Pd,Pt,Rh) could strongly improve catalyst performance.

Cu/Ce/Mg/Al/O was prepared by coprecipitation of aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ along with Deionized water is used. The metal content of the samples was determined using X ray fluorescence spectroscopy, XRFs. And the catalytic reaction tests were carried out in a fixed bed quartz reactor with a porous frit in flow conditions. X-ray diffraction patterns were obtained on a diffractometer employing $\text{Cu K}\alpha$ radiation.

The catalysts studied, the samples used all have surface area above $150\text{m}^2/\text{g}$ and a similar Mg to Al ratio. The XRD patterns of catalyst are provided. Before calcination (the precursors of catalysts), the detectable phase by XRD is hydrotalcite for Cu-cat, CeO_2 and hydrotalcite for Ce-cat and CuCe-cat. After calcination at 750°C a strong diffraction pattern of MgO with peaks at 42.9 and 62.6° is detected along with disappearance of hydrotalcite phase. It is worthwhile to note that CuO and spinel phases are observed in Cu-cat while no such phases are detected in CuCe-cat. This means that the agglomeration of CuO and formation of spinel (figure1), which are not desirable for NO reduction are strongly hindered by the presence of cerium.

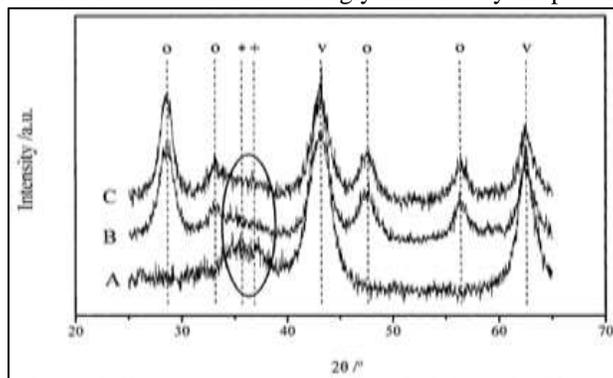


Fig. 1: XRD patterns of catalysts. A: Cu-cat, B: Ce-cat, C: CuCe-cat. o: CeO_2 , v: MgO, *: CuO, +: spinel

Oxidation states of copper in catalysts have been assigned using $\text{Cu}2p_{3/2}$ binding energy the associated shake-up satellites and kinetic energy of CuL_3VV Auger transition. The shakeup peak and higher $\text{Cu}2p_{3/2}$ binding energy are two major XPS characteristics of Cu^{2+} , while the lower $\text{Cu}2p_{3/2}$ binding energy and absence of the shakeup peak are characteristic of reduced copper. The CuL_3VV auger line is used to discriminate between Cu^+ and Cu^0 . Figure 2 shows the XPS analyses of CuCe-cat with a increase in sputtering time. With the Ar^+ sputtering (the sputtering rate $0.6\text{-}0.8\text{ nm/min}$), the relative intensity of $\text{Cu}2p_{3/2}$ shake up satellite at 943eV decreases and the $\text{Cu}2p_{3/2}$ peak position shifts toward lower binding energy. $\text{Cu}2p_{3/2}$ peak is assigned at 934 eV to CuO and peak at 932.5 eV to reduced copper. The results of CuL_3VV auger transition indicate that the low valent copper is present as Cu^+ . This means that with addition of cerium to the sample some amounts of Cu^+ ions are produced and concentration of Cu^+ increases with Ar^+ sputtering.

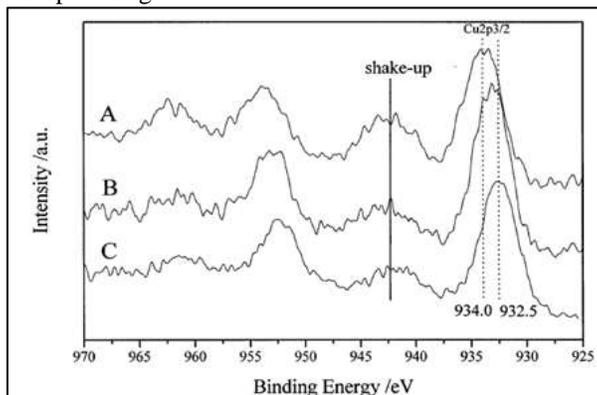


Fig. 2: Cu 2p XP spectra of (A) CuCe-cat catalyst. (B) Ar^+ sputtering 1 min. (C) Ar^+ sputtering 10 min

Figure 3 shows NO conversions as a function of temperature over Cu-cat and CuCe-cat in the absence and presence of O₂. It can be seen that for the NO+CO system, in the low temperature region <340°C CuCe-cat has a higher NO reduction activity (reaching 100% conversion at 315°C) than Cu-Cat and the difference increases with temperature within that region. At high temperatures, NO conversions over both catalysts reach 100%. The addition of O₂ to the feed produces a completely different effect on the NO conversion over Cu-cat and CuCe-cat. The presence of O₂ enhances the activity of CuCe-cat while it decreases the activity of Cu-cat.

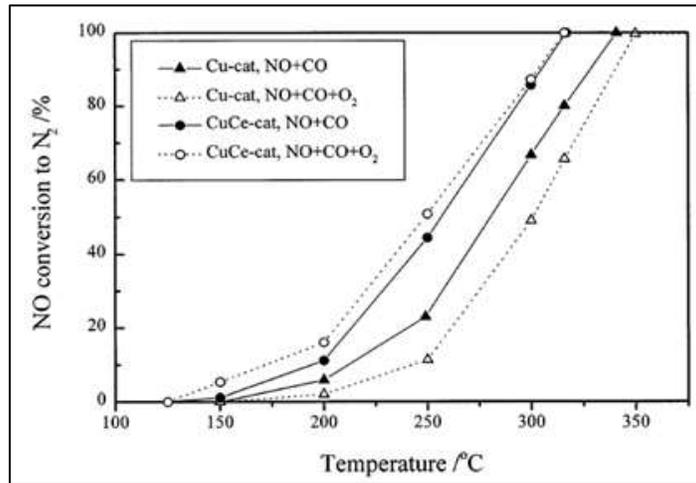


Fig. 3: NO conversions as a function of temperature over Cu-cat and CuCe-cat catalysts in the absence and presence of O₂. Reaction conditions: 600ppm NO, 1.4% Co, 0.5% O₂; total flow rate 400mL/min

The influence of the addition of water vapour into NO+CO+O₂ reaction system on NO reduction activity over these catalysts was examined and the results are presented in figure 4. The level of NO conversion was collected after a steady state of reaction was reached. At 250°C and in the absence of H₂O, CuCe-cat displays much higher activity than that of Cu-cat or Ce-cat. The same holds at 300°C.

When 1% water is introduced into the feed, Cu-cat loses its activity completely at 250°C, the activity drops at 300°C drastically. However, at the same conditions (250 or 300°C) it is interesting to note that the addition of water does enhance the activity of CuCe-cat. At higher temperatures of >550°C the presence of water has no significant effect on the NO conversion over these samples.

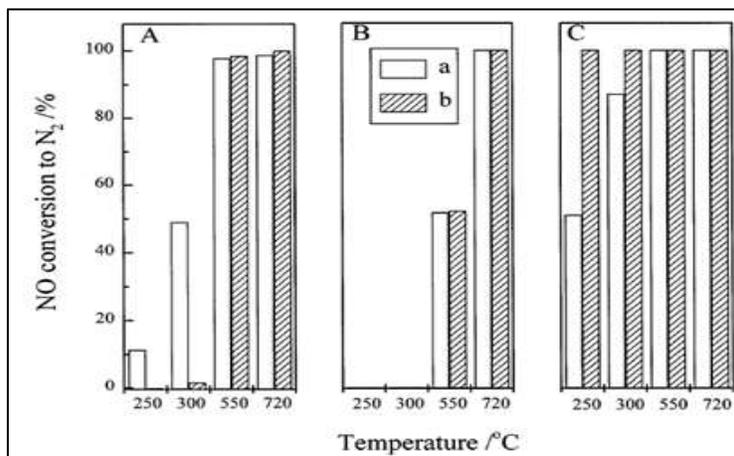


Fig. 4: Effects of the additional of H₂O to the feed on the NO conversion over (A) Cu-cat, (B) Ce-cat, (C) CuCe-cat at different temperatures. A: NO (600ppm) + CO (1.4%) + O₂(0.5%); b: NO (600ppm) + Co (1.4%) + O₂ (0.5%) + H₂O (1.0%). Total flow rate 400mL/min.

Figure 5 shows the effect of SO₂ on the catalytic activity of the catalysts for NO conversion at 720°C. It can be seen that addition of SO₂ results in drastic decline of NO conversion from 100% to 36% for Ce-cat during first 10 min. After 40 min, NO conversions over Cu-cat and Ce-cat are 31% and 16% respectively. This indicates that both of these catalysts are rapidly poisoned by sulphur di oxide. However, the presence of sulphur di oxide in the feed has no adverse effect on the NO conversion over CuCe-cat which maintains 100% conversion.

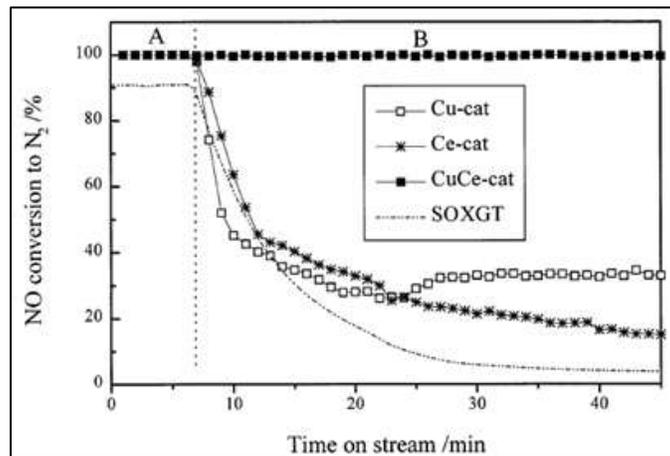


Fig. 5: Effects of the presence of SO_2 to the feed on the NO conversion over Cu-cat, Ce-cat, CuCe-cat and SOXGT. A: NO (600ppm) + CO (1.4%) + O_2 (0.5%) + H_2O (1.0%), steady state: B: adding SO_2 to the system. NO (600ppm) + Co (1.4%) + O_2 (0.5%) + H_2O (1.0%) + SO_2 (500ppm). Reaction temperature 720°C : Total flow rate 400mL/min.

CuCe, a mixed oxide catalyst containing copper and cerium simultaneously displays significantly high act for NO reduction in the presence of O_2 and excellent resistance to H_2O and SO_2 poisoning as well as good performance for CO oxidation. These promoted performances stem from the synergistic effect of copper and cerium and also addition of oxygen increases NO conversion over Cu-Ce because it oxidizes some Cu^+ ions to Cu^{2+} ions which are active for NO adsorption. Cu-Ce also displays excellent performance for SO_x adsorption in the $\text{SO}_2 + \text{O}_2$ system.

The spent FCC catalysts are classified as a non hazardous waste, the quantity is significant, so when its useful life is over, the exhausted catalyst constitutes a difficult to handle solid residue. Treatment of such wastes has drawn interest from researchers committed with environmental protection, who attempt to make rational use of these materials. Most of the waste catalysts are solidified and disposed as landfills. Several papers have reported the feasibility of reusing the spent catalysts as an aggregate in the formulation of building materials, mainly in concrete manufacture. Besides, it was demonstrated that zeolites can be incorporated as a minor component in the concrete formulation without affecting quality. Results obtained when cation exchanged zeolites were immobilized in cement mortars, this methodology is a solution of the environmental problems related to the removal of hazardous metals. Another widely used and a known method in mechanochemistry which includes treatment of different types of mill and other similar apparatus. These lead to materials with increased surface free energy, which makes them more reactive. Out of the various methods proposed, high energy ball milling proved to be of the most promising one. This technique also called HE milling produces a reduction of particle size accompanied by structural modifications of the treated solids. A gradual collapse of the crystalline structure is obtained. It was demonstrated that amorphous aluminosilicates produced in this way are very reactive product for zeolite synthesis, similar to those obtained by calcination. So it is believed that such activation could be used to attain effective modification in catalysts conversion. Depending on the synthesis conditions and activation treatments, it is possible the conversion of the exhausted catalysts in aluminium rich zeolites type A, X or their mixtures. Therefore, the proposed recycling of FCC catalysts, which normally are accumulated in petroleum refineries before a proper and expensive final disposal, constitutes a technically feasible and environmentally appropriate alternative.

II. CONCLUSIONS

- 1) In order to curb high CO emissions from a Fluid catalytic cracker, steps taken to curb them are increase the air apply, usage of special FCC catalysts containing small amounts of platinum groups or rhenium or modification of an otherwise conventional FCC system can be done by using a hydrocarbon catalyst with small proportions of metals.
- 2) CuCe, a mixed oxide catalyst containing copper and cerium simultaneously displays significantly high act for NO reduction in the presence of O_2 and excellent resistance to H_2O and SO_2 poisoning as well as good performance for CO oxidation. Cu-Ce also displays excellent performance for SO_x adsorption in the $\text{SO}_2 + \text{O}_2$ system.
- 3) High conversion of exhausted FCC catalysts to zeolitic products of commercial interest is possible and constitutes a valis alternative to disposal. On the other hand, thorough milling procedure was found to modify reactivity and characteristic s of the crystals produced. Depending on the synthesis conditions and activation treatments, it is possible the conversion of exhausted catalysts in aluminum rich zeolites type A, X or their mixtures.

Hence, improved methods can be utilized in order to minimize the emission of harmful gases into the air, it is evident from the studies that new discoveries in the field of FCC catalysts have proved highly beneficial to improved performance and is also environmental friendly.

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