Catalyst Deactivation and Regeneration

Santosh Walke[1*], Sagar Kambale[2]

[1,2]Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering
Navi Mumbai, Maharashtra, India
*Corresponding Author Email address: santosh.walke@bharatividyapeeth.edu

Abstract: In this article a study about catalyst regeneration is been put forward. A study of how catalyst regeneration is done, why there is a need of regeneration and also about catalyst deactivation mainly in refinery processes. Catalyst Regeneration is widely used in many industries by in-situ or ex-situ methods as an economical beneficial technique for processes. In this article I have also shared some important test done on catalyst before they are used in a specific process. Catalyst Regeneration is mainly seen where the spent catalyst is costly.

Keywords: Regeneration, Deactivation, in-situ, ex-situ, Poisoning

I.   Introduction

Catalyst regeneration entails the processing of spent catalysts in order to make them reusable. This is done by reinstating chemical properties of spent catalysts and thereby increasing their efficiency through a process called catalyst regeneration. Catalyst deactivation, the loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern in the practice of industrial catalytic processes. Costs to industry for catalyst replacement and process shutdown total billions of dollars per year. Time scales for catalyst deactivation vary considerably; for example, in the case of cracking catalysts, catalyst mortality may be in the order of seconds, while in ammonia synthesis the iron catalyst may last for 5–10 years. But it is inevitable that all catalysts will decay. Typically, the loss of activity in a well-controlled process occurs slowly. However, process upsets or poorly designed hardware can bring about catastrophic failure. For example, in steam reforming of methane or naphtha great care must be taken to avoid reactor operation at excessively high temperatures or at steam to hydrocarbon ratios below a critical value. Indeed, these conditions can cause formation of large quantities of carbon filaments which plug catalyst pores and voids, pulverize catalyst pellets, and bring about process shut down all within a few hours. While catalyst deactivation is inevitable for most processes, some of its immediate, drastic consequences may be avoided, postponed, or even reversed. Thus, deactivation issues (i.e. extent, rate and reactivation) greatly impact research, development, design and operation of commercial processes. Accordingly, there is considerable motivation to understand and treat catalyst decay. Indeed, over the past three decades, the science of catalyst deactivation has been steadily developing, while literature addressing this topic has expanded considerably to include books; comprehensive reviews; and proceedings of international symposia. A significant fraction of this literature addresses mechanisms of deactivation. This area of research provides a critical understanding which is the foundation for modelling deactivation processes, designing stable catalysts, and optimizing processes to prevent or slow catalyst deactivation. This review summarizes the present state of knowledge regarding mechanisms of catalyst decay. Areas of mechanistic research in which further investigations are needed are also addressed.

I. NEED OF REGENERATION

The major advantage of catalyst regeneration is that it costs less than fresh catalysts. Catalyst regeneration is a chemical process that is used to convert naphtha into reformates, which contain high-octane gasoline. Catalytic processes are used in crude oil refining to convert the high boiling point fictions of the crude (atmospheric and vacuum residual oil fi-actions and asphalt pitch) into lower boiling materials that become fuel oil, gasoline, diesel, and jet fuels. However, applying these catalytic processes is complicated by relatively high concentrations of heavy metals (i.e., vanadium and nickel) in the oil. These metals affect the lifetimes and behaviour of the catalysts during refinery operations and also become a factor in disposing of spent catalysts. Some spent catalysts are used in asphalt, as road-base, or in manufacturing cement but there are limits on the metals content in these applications. (Higgins 1996). Others that have typically been sent to a metal reclaimed or to a landfill have recently been listed as hazardous wastes by the U.S. Environmental Protection Agency (EPA) (Oil& Gas Journal 1998). Consequently, various alternatives are being considered for meeting stricter disposal regulations, reducing costs, and improving catalyst performance.

II. VARIOUS METHODS

A. *In-situ Method*

In-situ vapour phase catalytic upgrading of fast pyrolysis vapours combines direct liquefaction of biomass by pyrolysis and pyrolysis vapour upgrading in the same vessel. In-situcatalytic pyrolysis has the potential to reduce costs associated with upgrading conventional fast oil to a hydrocarbon by producing a lower-oxygen-content intermediate phase with lower associated water. Hydrogen consumption during final upgrading to a hydrocarbon will also be reduced.
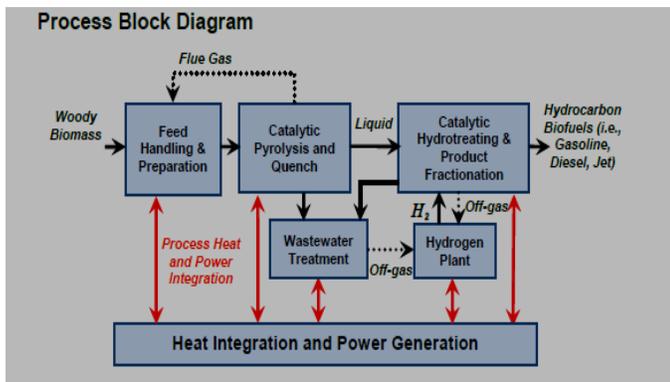
Figure 1. Process Block Diagram of an In-situ Catalyst Regeneration.

The addition of the vapour phase upgrading catalyst to the same reactor that pyrolyze the biomass eliminates the external vapour phase reactor (ex-situ vapour phase upgrading), thus likely reducing capital and operating costs. The upgraded vapour's lower reactivity may allow use of extended surface heat exchangers to recuperate heat and reduce the cooling water load when the vapours are condensed.

B. *Ex-situ*

In the ex-situ catalytic fast pyrolysis pathway, biomass is rapidly heated in a fluidized bed reactor containing a catalyst to yield vapours, which are catalytically modified and condensed into a partially stabilized and deoxygenated liquid bio-oil. This stable bio-oil is subsequently upgraded to produce hydrocarbon bio fuel blend stocks.
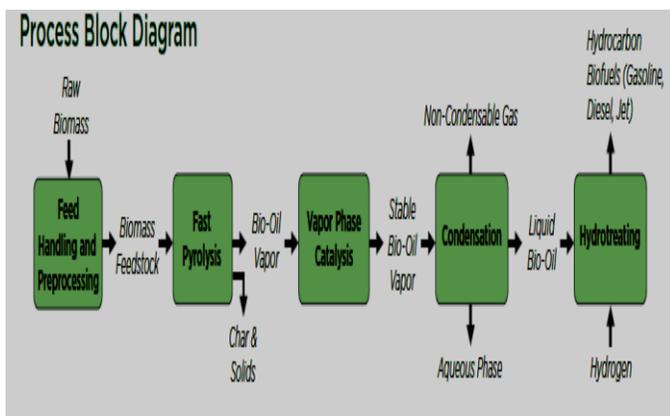
Figure 2. Process Block Diagram of an Ex-situ Method of Catalyst Regeneration.

C. *Continuous Catalytic Regenerator*

The Continuous Catalyst Regeneration (CCR) process is part of a process used in the petroleum and petrochemical industries, which produces aromatics from naphthenes and paraffin's commonly used as motor fuel. In this process, hydro-treated naphtha is combined with recycle hydrogen gas, heated to the desired
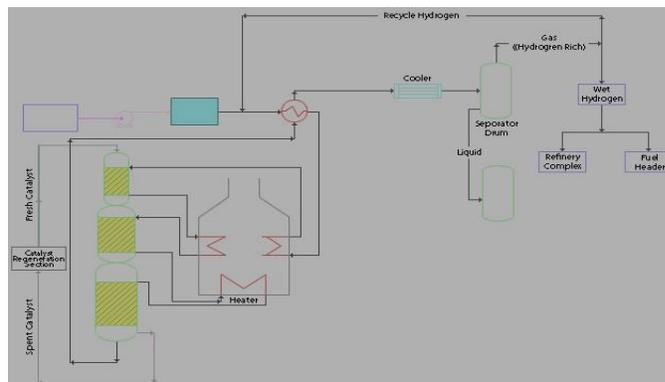
Figure 3. Process Flow Diagram of a Continuous Catalytic Converter.

reaction temperature (925 – 975 ^{0}F) and sent through a series of reactors (vertical or side by side). Because the reaction is endothermic, inter stage heaters are required between each reactor section to attain the required reaction temperature. In order to attain the desired reactions and high product yield, a metal catalyst such as platinum is used. The catalyst moves from reactor to reactor and the feed mixture flows radially across the catalyst beds.

IV. FCCU

PRODUCTS	EX-SITU	IN-SITU
YIELD OF OLEFINS	17.4%	5.4%
AROMATIC HYDROCARBONS	18.9%	26.1%
RESIDUE	18.6%	31.3%

Table 1. Comparison of Ex-situ and In-situ

Fluid catalytic cracking unit (FCCU) is one of the most important conversion processes used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefin gases, and other products. The reactor and regenerator are considered to be the heart of the fluid catalytic cracking unit. The preheated high-boiling petroleum feedstock (at about 315 to 430 °C) consisting of long-chain hydrocarbon molecules is combined with recycle slurry oil from the bottom of the distillation column and injected into the catalyst riser where it is vaporized and cracked into smaller molecules of vapour by contact and mixing with the very hot powdered catalyst from the regenerator. All of the cracking reactions take place in the catalyst riser within a period of 2–4 seconds. The hydrocarbon vapours "fluidize" the powdered catalyst and the mixture of hydrocarbon vapours and catalyst flows upward to enter the reactor at a temperature of about 535 °C and a pressure of about 1.72 bars.

The reactor is a vessel in which the cracked product vapours are:

(a) Separated from the so-called spent catalyst by flowing through a set of two-stage cyclones within the reactor and

(b) The spent catalyst flows downward through a steam stripping section to remove any hydrocarbon vapours before the spent catalyst returns to the catalyst regenerator. The flow of spent catalyst to the regenerator is regulated by a slide valve in the spent catalyst line.

Since the cracking reactions produce some carbonaceous material (referred to as catalyst coke) that deposits on the catalyst and very quickly reduces the catalyst reactivity, the catalyst is regenerated by burning off the deposited coke with air blown into the regenerator. The regenerator operates at a temperature of about 715 °C and a pressure of about 2.41 bar, hence the regenerator operated at about 0.7 bar higher pressure than the reactor.

The combustion of the coke is exothermic and it produces a large amount of heat that is partially absorbed by the regenerated catalyst and provides the heat required for the vaporization of the feedstock and the endothermic cracking reactions that take place in the catalyst riser. For that reason, FCC units are often referred to as being 'heat balanced'.

The hot catalyst (at about 715 °C) leaving the regenerator flows into a catalyst withdrawal well where any entrained combustion flue gases are allowed to escape and flow back into the upper part to the regenerator. The flow of regenerated catalyst to the feedstock injection point below the catalyst riser is regulated by a slide valve in the regenerated catalyst line. The hot flue gas exits the regenerator after passing through multiple sets of two-stage cyclones that remove entrained catalyst from the flue gas.

The amount of catalyst circulating between the regenerator and the reactor amounts to about 5 kg per kg of feedstock, which is equivalent to about 4.66 kg per litre of feedstock. Thus, an FCC unit processing 75,000 barrels day (11,900 m^3/d) will circulate about 55,900 tonnes per day of catalyst.
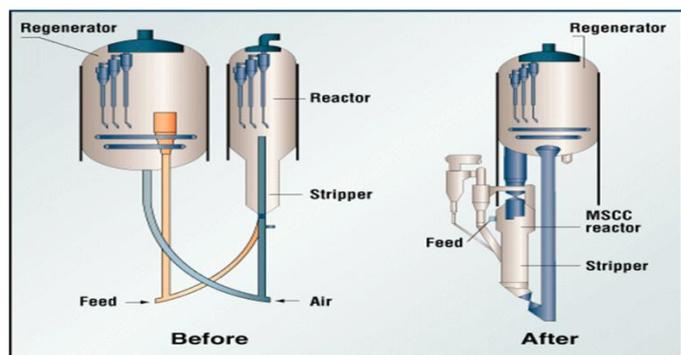
Figure 4. Different Configurations of FCCU

There are two different configurations for an FCC unit: the "stacked" type where the reactor and the catalyst regenerator are contained in a single vessel with the reactor above the catalyst regenerator and the "side-by-side" type where the reactor and catalyst regenerator are in two separate vessels.

V. CATALYST DEACTIVATION/POISONING

Catalyst poisoning refers to the partial or total deactivation of a catalyst caused by exposure to a range of chemical compounds. Poisoning may be desirable when it results in improved selectivity (e.g. Lindlar's catalyst) but may be undesirable when the catalyst is rendered ineffective (e.g. Lead in catalytic converters). Poisoning refers specifically to chemical deactivation, rather than other mechanism of catalyst degradation such as thermal decomposition or physical damage.
The poisoning reaction should be viewed like any other chemical reaction between a gas phase reactant and the solid surface, where the poisoned sites are distributed throughout the catalyst pore structure as a function of poison diffusion into the catalyst and the rate of the poisoning reaction.

Poisoning involves compounds which bonds chemically to the active surface sites of a catalyst. This may have two effects: the total number of catalytic sites or the fraction of the total surface area that has the capability of promoting reaction always decreases, and the average distance that a reactant molecule must diffuse through the pore structure before undergoing reaction may increase. Poisoned sites can no longer accelerate the reaction with which the catalyst was supposed to catalyze. Large scale production of substances such as ammonia in the Haber–Bosch process includes steps to remove potential poisons from the product stream.The poisoning reaction should be viewed like any other chemical reaction between a gas phase reactant and the solid surface, where the poisoned sites are distributed throughout the catalyst pore structure as a function of poison diffusion into the catalyst and the rate of the poisoning reaction. At the two extremes, this gives rise to two scenarios. First, when the poisoning reaction rate is slow relative to the rate of diffusion, the poison will be evenly distributed throughout the catalyst and will result in homogeneous poisoning of the catalyst. Conversely, if the reaction rate is fast compared to the rate of diffusion, a poisoned shell will form on the exterior layers of the catalyst, a situation known as "pore-mouth" poisoning, and the rate of catalytic reaction may become limited by the rate of diffusion through the inactive shell.

A. FACTORS CAUSING DEACTIVATION
i) High temperature exposure: automobile catalytic converter, close to 1000℃
ii) Poisoning: exhaust or process contaminants adsorbing onto or blocking active sites
iii) Attrition and erosion of the wash coat from the support.
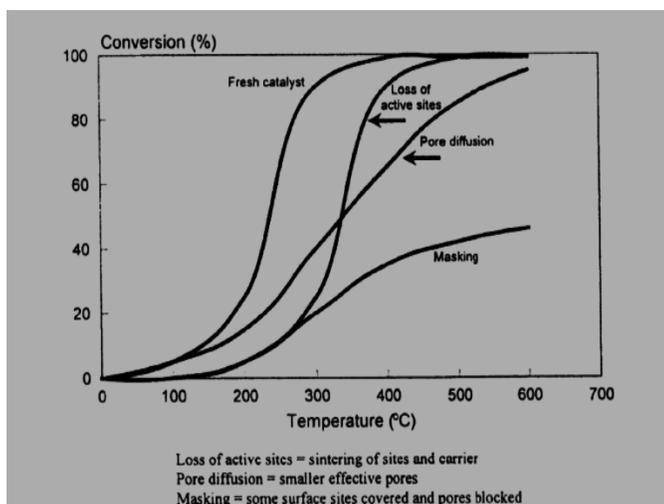
Figure 5. Relative Changes in Conversion-Temperature profile for various deactivation models.

B. *TYPES OF POISONING*

  i)   SELECTIVE-POISONING
       A chemical directly reacts with the active site or the carrier, rendering it less or completely inactive.
  ii) NONSELECTIVE-POISONING
       Deposition of fouling agents onto or into the catalyst carrier, masking sites and pores, resulting in a loss in performance.
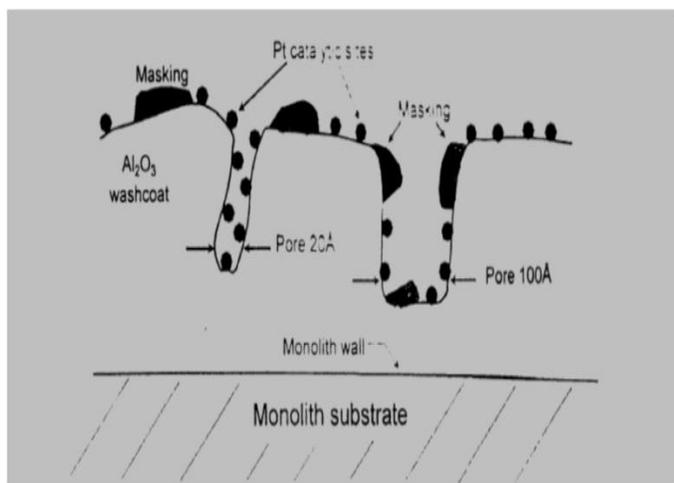
Figure 6. Deactivation of Catalyst due to masking of wash coat.

Masking refers to blocking of surface area of catalyst surface due to which activity or efficiency of the catalyst decreases. Such cases are seen where fouling of vessel occurs in inner part and the inner surface peel from the walls. Such type of poisoning is termed as Selective poisoning where in active sites on catalyst are blocked or poisoned for reducing the reaction rate or rendering it.
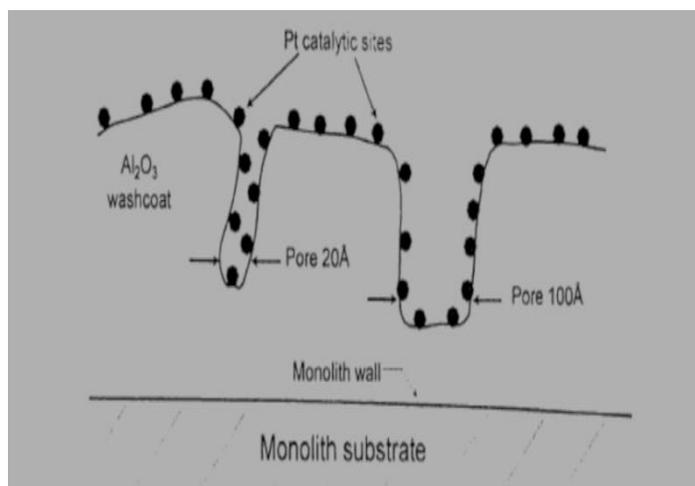
Figure 7. Ideal impregnation of a Pt on Al_2O_3 base.

Pictorial view of an ideally impregnated Pt catalyst on Al_2O_3 base which provides the necessary surface area for Pt for its overall efficiency.

VI. CATALYST ANALYSIS

ASTM's catalyst standards are instrumental in the testing and chemical analysis of the various forms of catalysts and catalyst carriers used to increase the rate of specific chemical reactions. These standards are helpful in allowing laboratories and other chemical facilities to examine and assess catalysts to ensure their safe handling and use. The test methods and techniques presented in these catalyst standards include hydrofluoric/sulphuric spectroscopic analysis, potentiometric titration method, micro activity test, volumetric vacuum method, static volumetric measurements, mercury intrusion porosimetry, electronic counting, laser light scattering, nitrogen adsorption by continuous flow method, ammonia chemisorption, X-ray powder diffraction (XRD), X-ray fluorescence spectrometry (XRF), and elemental analysis by inductively coupled plasma atomic emission spectroscopy.

A. *What is XRD?*

   X-ray diffraction is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

Figure 8. X-ray Diffraction Unit

In a single-crystal X-ray diffraction measurement, a crystal is mounted on a goniometer. The goniometer is used to position the crystal at selected orientations. The crystal is bombarded with a finely focused monochromatic beam of X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup.

B. *What is XRF?*

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology.

Figure 9. X-ray Fluorescence Unit

When materials are exposed to short-wavelength X-rays or to gamma rays, ionization of their component atoms may take place. Ionization consists of the ejection of one or more electrons from the atom, and may occur if the atom is exposed to radiation with energy greater than its ionization potential. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom. The removal of an electron in this way makes the electronic structure of the atom unstable, and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved.

Thus, the material emits radiation, which has energy characteristic of the atoms present. The term fluorescence is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy (generally lower).

VII.   MARKET ANALYSIS

The catalyst regeneration market was estimated around $3.6 Billion in 2013, with the highest share of more than 60% held by the Europe and Asia-Pacific together. The global market is projected to grow at a CAGR of 5.5% from 2014 to 2019 to reach $5 billion by 2019. The highest growth is forecasted to be in the Asia-Pacific due to the rising refinery capacity and increasing use of catalyst regeneration process, especially in China.

From 2010 to 2014, expansion was observed as the most important growth strategy adopted by the major catalyst regenerators, accounting for a share of 33% of the total strategies adopted by the players. Europe was close behind in terms of catalysts regenerated. The region was followed by North America and Rest of the World (RoW).The market for regenerated catalyst, in terms of value, is estimated to reach $5002.47 Million by 2019, witnessing a CAGR of 5.54% between 2014 and 2019. In 2012, Asia Pacific accounted for the highest market share, followed by North America. Countries in Asia Pacific have peak catalyst demands with increasing popularity of offshore application for this market.

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