# RECOVERY OF METALS FROM SPENT CATALYSTS 1. CATALYSTS MANAGEMENT AND SPENT CATALYSTS SOURCES

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**Abstract:** Catalysts are indispensable in many chemical processing industries for routine production of ammonia, nitric acid, sulfuric acid, methanol, formaldehyde, gasoline, diesel fuels, jet fuels, heavy oil hydrocarbons, petrochemicals and plastics. During processing, catalysts will become contaminated with impurities and become deactivated. When that happens, they are usually sent for regeneration where contaminants are removed. Ultimately, they will be contaminated in a manner and at a level that makes regeneration impractical. At this stage, catalysts are considered "spent" and they may pose significant environmental problems, as landfill disposal is no longer accepted as best practice. The paper provides an overview on the spent catalyst sources, level and potential hazard, highlighting the actual trends in catalysts management.

**Keywords:** spent catalysts, metals recovery, recycling, scrap, chemical industry, oil refining.

## 1. INTRODUCTION

The importance of catalysis to chemical processes is enormous. An estimated 90% of the chemical production processes are based on catalytic technologies [1], encompassing four major market sectors: fuel refining, polymerization, chemical production, and environmental remediation. Reasons for the widespread use of catalysis are both economically and environmentally compelling: catalytic processes have, as a rule, lower operating costs and yield higher purity products with fewer size-products – hence fewer environmental hazards – compared to non-catalytic processes [2].

The earliest recognition of a catalytic phenomenon is credited to *Sir Humphrey Davy*, who reported, in the early 19$^{th}$ century, the incandescence of metals in contact with mixtures of air and combustion gases [3]. The word ***catalysis***, coined by *Berzelius* in 1836 to describe some enhanced chemical reactions [4] is now used popularly in a non-technical way. Practical applications of catalysis long preceded a conceptual understanding of the process. The first patent for a catalyst was granted to *Philips* in 1831, for the oxidation of $SO_2$ over Pt. The industrial scale version of this process was implemented in 1875, in order to generate sulfuric acid. Another milestone in catalysis development was the synthesis of nitric acid by catalytic oxidation of ammonia, achieved by *Ostwald* in 1901. The industrial plant, built in 1908 produced 3 tones of diluted nitric acid (53%) per day [5]. Coupled with the discovery by *Haber* in 1909 of the Fe-catalyzed ammonia synthesis from elements industrially tested in 1913 at Oppau, Germany by *BASF* [6], the stage was set for the production of synthetic fertilizers and explosives which changed the course of the 20$^{th}$ century.

Heterogeneous catalysis found early applications both in organic and inorganic chemical technology. In 1902 *Sabatier* discovered the catalytic effect of nickel on hydrogenation of unsaturated hydrocarbons. The process is

still used for the production of margarine by the selective hydrogenation of triglycerides from vegetable oils. In the 1940s, catalytic cracking of petroleum hydrocarbons on acidic aluminosilicate clays was set, opening new ways in fuel production. In the 1950s, the *Ziegler – Natta* catalysts were introduced for the polymerization of α-olefines in a great variety of commodity polymers.

## 2. CATALYST AGING AND DECAY

Catalysts are frequently defined as "materials which accelerate chemical reactions without themselves undergoing change". As the manager of any plant using a catalytic process knows, this is too optimistic a definition: the properties of all real catalysts do change with use [7]. A more realistic definition, which is found in nowadays textbooks, describes a catalyst as "a substance which, without appearing in the final products, changes the rate of a chemical reaction" [3].

The good catalyst has three cardinal virtues: activity (ability of the catalyst to convert feedstock to products), selectivity (ability of the catalyst to give the desired product, out of all possible products) and life (time for which the catalyst keeps a sufficient level of activity and/or selectivity). A loss of either activity or selectivity can be sufficient to necessitate catalyst discharge or reactivation. Wide variations in catalyst life occur in practice, dependent on the process, as shown in Tables 1 and 2.

Table 1. Typical lives of some catalysts used in the manufacture of ammonia, nitric and sulfuric acids, methanol and formaldehyde [7, 8]

| Process and typical conditions | Typical catalyst | Life [years] |
|---|---|---|
| Ammonia synthesis:<br>$N_2 + 3H_2 \rightarrow 2NH_3$ ; 450 – 550 °C; 20 – 50 MPa | $Fe/Al_2O_3/CaO/K$<br>granules | 5 – 10 |
| Methanation:<br>$CO/CO_2 + H_2 \rightarrow CH_4 + H_2O$ ; 250 – 350 °C; 3 MPa | Supported Ni<br>pellets | 5 – 10 |
| Sulfuric acid:<br>$2SO_2 + O_2 \rightarrow 2SO_3$ ; 400 – 600 °C; 0.1 MPa | V/K sulfates/$SiO_2$<br>extrusions | 5 – 10 |
| Methanol synthesis:<br>$CO + 2H_2 \rightarrow CH_3OH$ ; 200 – 300 °C; 5 – 10 MPa | $Cu/ZnO/Al_2O_3$<br>pellets | 2 – 8 |
| Low temperature CO shift:<br>$CO + H_2O \rightarrow CO_2 + H_2$ ; 200 – 250 °C; 3 MPa | $Cu/ZnO/Al_2O_3$<br>pellets | 2 – 6 |
| Natural gas desulphurization:<br>$R_2S + 2H_2 \rightarrow 2RH + H_2S$ 300 – 400 °C; 3 MPa | Co/Mo sulfides/$Al_2O_3$<br>extrusions | 2 – 8 |
| High temperature CO shift:<br>$CO + H_2O \rightarrow CO_2 + H_2$ ; 350 – 500 °C; 3 MPa | $Fe_3O_4/Cr_2O_3$<br>pellets | 2 – 4 |
| Natural gas steam reforming:<br>$CH_4 + H_2O \rightarrow CO + 3H_2$ ; 500 – 850 °C; 3 MPa | $Ni/CaO/Al_2O_3$<br>rings | 2 – 4 |
| Methanol oxidation:<br>$CH_3OH \rightarrow CH_2O + H_2$ ; $CH_3OH + 0.5O_2 \rightarrow CH_2O + H_2O$ ;<br>500 – 600 °C; 0.1 MPa | Silver<br>granules | 0.3 – 1 |
| Ammonia oxidation:<br>$2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O$ ; 800 – 1300 °C; 0.1 – 1 MPa | Platinum alloy<br>gauze | 0.1 – 0.5 |

During a catalytic operation, various factors can cause a temporary or permanent aging of the catalyst. There are three main different causes of catalyst decay: physical causes, poisoning by impurities and poisoning by reactants or products.

Physical changes on a micro- or macro-scale in a catalyst can lead to decay in performance. Agglomeration of the crystallites of the active phase (sintering) leads to loss of active surface and, consequently, a decrease in activity [9]. On a larger scale, the break-up of catalyst pellets (Fig. 1) will hinder gas flow through the catalyst bed, with greater pressure drop, and so will also give a decreased output from the reactor.

Table 2. Typical lives of some catalysts used in oil refining and the petrochemical industry [7, 8]

| Process and typical conditions | Typical catalyst | Life [years] |
|---|---|---|
| Distillate oil hydrodesulfurization:<br>300 – 400 °C; 0.5 – 10 MPa | Co/Mo sulfides/$Al_2O_3$<br>extrusions | 1 – 2 T<br>2 – 8 P |
| Residual oil hydrodesulfurization:<br>250 – 400 °C; 10 MPa | Co/Mo sulfides/$Al_2O_3$<br>extrusions | 0.5 – 1 P |
| Heavy oil hydrocracking:<br>250 – 400 °C; 10 – 20 MPa | Ni/W sulphides/$Al_2O_3$ + $SiO_2$/$Al_2O_3$<br>(Pd/zeolites) extrusions | 1 – 5 T<br>1 – 10 P |
| Catalytic reforming:<br>450 – 550 °C; 0.5 – 5 MPa | Pt/Re/$Al_2O_3$/$Cl^-$<br>spheres, extrusions | 0.01 – 0.5 T<br>2 – 15 P |
| Fluid catalytic cracking:<br>500 – 600 °C; 0.1 – 0.3 MPa | Zeolite/$SiO_2$ – $Al_2O_3$ matrix<br>microspheroids | $10^{-8}$ – $10^{-9}$ T<br>0.1 P |
| Ethylene oxidation:<br>$C_2H_4 + 0.5O_2 \rightarrow CH_3\text{-}CHO$;<br>200 – 300 °C; 1 – 2 MPa | Ag/α-$Al_2O_3$/promoters<br>rings | 1 – 4 P |
| Benzene oxidation to maleic anhydride:<br>$C_6H_6 + O_2 \rightarrow C_4H_2O_3$; 350 °C; 0.1 MPa | V/Mo oxides/promoters/ α-$Al_2O_3$<br>rings | 1 – 2 P |
| Reduction of aldehydes to alcohols:<br>$2RCHO + H_2 \rightarrow R\text{-}CH_2\text{-}OH$;<br>250 – 400 °C; 10 – 30 MPa | Cu/ZnO<br>pellets | 0.5 – 1 T<br>2 – 8 P |
| Acetylene hydrogenation:<br>$C_2H_2 + H_2 \rightarrow C_2H_4$; 30 – 100 °C; 5 MPa | Pd/support | 0.1 – 0.5 T<br>0.2 5 – 10 P |
| Ethylene oxychlorination:<br>$C_2H_4 + 2HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_2O$;<br>250 °C; 0.1 – 1 MPa | Cu chlorides/$Al_2O_3$<br>microspheroids | 0.2 – 0.5 P |

P – permanent loss of catalyst performance;
T – temporary loss of catalyst performance, recoverable (at least partly) by regeneration.

(a) (b)

Fig. 1. Natural gas steam reforming catalyst: (a) initial rings; (b) broken and crushed rings after discharge

Poisoning by impurities (in feed or catalyst) occurs when their interaction with the catalyst is stronger than that of the feed [10]. The types of impurities which can act as poisons depend on the chemical nature of impurity and active site, since strong chemisorption is the main feature of the poisoning action. Significant poisons for some industrial catalysts are given in Table 3. The list is not complete, but nevertheless the pattern is clear: strong interaction, usual related directly to the chemistry of the bulk states, between poison and catalyst is present [7].

Poisoning by reactants or products is encountered in those catalytic processes that use organic reactants that form carbonaceous deposits on the catalyst. These are usually described as “coke”. Coking is by far the most common encountered poisoning, and it was studied especially in relation to oil-refinery processes [10].

Table 3. Some typical poisons of industrial catalysts [7]

| Poison | Catalysts | Processes |
|---|---|---|
| CO, $CO_2$, $H_2O$, $C_2H_2$ | Fe | Ammonia synthesis |
| CO | Pd, Pt | Hydrogenation |
| $H_2S$, $AsH_3$, $PH_3$ | Co, Ni, Pd, Pt, Cu | Hydrogenation, steam reforming, catalytic reforming, methanol synthesis, low temperature CO shift |
| $H_2S$ (high levels) | $Fe_3O_4$ | High temperature CO shift |
| Na, $NH_3$, organic bases | $SiO_2/Al_2O_3$, zeolites | Catalytic cracking, hydrocracking |
| V, Ni | $SiO_2/Al_2O_3$, zeolites, Co/Mo sulfides | Catalytic cracking, hydrocracking, hydrodesulphurization |
| Fe, Ni carbonyls | Ag | Methanol oxidation to formaldehyde |
| Pb, Hg, Zn | Most transition metals | Many |

Aging and catalyst decay are complex phenomenon. There are also frequent interactions between the factors that produce premature aging of catalysts.

## 3. SPENT CATALYSTS MANAGEMENT

Until the 1970s, catalysts used in most chemical processes had a very simple life cycle: they where either used for one production cycle until exhaustion of their catalytic properties or otherwise they were used for a few cycles, with some in-situ regeneration between cycles. Disposal, in a more or less acceptable environmental way was the last step. Under those conditions, there was a rather limited need for off-site services.

The situation has changed drastically, more recently as off-site regeneration of many catalysts, and particularly hydroprocessing catalysts, has become widely accepted and preferred by the industry. This is due to a number of reasons, including safety and time considerations and better catalyst activity recovery. Furthermore, spent catalyst disposal is evolving towards more environmentally acceptable recycling schemes.

In improper disposal conditions, waste catalysts are chemically and mechanically degraded by natural factors. Fine catalyst dust is taken by the air currents and spread over large areas. Acidic rain, formed nearby chemical and petrochemical plants due to the $SO_x$ and $NO_x$ emissions, is leaching the heavy metals from catalyst framework. The formed ions are passing into the soil and from here, by diffusion they may migrate into the groundwater and surface waters. Due to the improper disposal, spent catalysts are simultaneously polluting the air, the soil, the waters, and the vegetation (Fig. 2) [11].

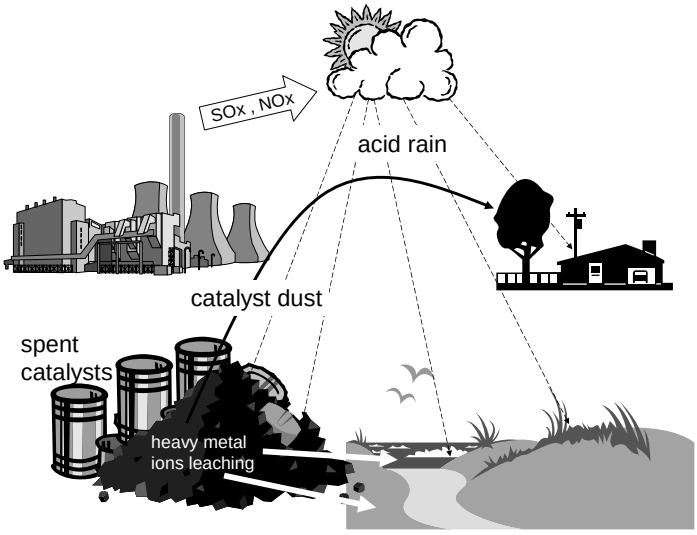


Fig. 2. Complex environmental pollution due to the improper disposal of spent catalysts

Safe disposal of spent catalysts is a significant environmental problem as landfill disposal is no longer generally accepted as the best practice. In many cases, the spent catalysts have been classified as hazardous waste material and are subject to stringent disposal guidelines. Most major refinery, chemical and petrochemical companies have set up special disposal practices and only allow authorized waste collectors and processors to dispose the catalyst waste. The Basel Convention classifies into the "hazardous wastes" category, subject to trans-boundary movement, the following metal containing wastes (including spent catalysts): chromium wastes (HW21), copper wastes (HW22), zinc wastes (HW23), mercury wastes (HW29), lead wastes (HW31), and

nickel wastes (HW46) [12]. Excepting catalysts based on Al, Si, Co, Mo, Mn, V, Fe, Ag, and Platinum Group Metals (PGM) – all other catalysts have to be treated as hazardous wastes.

Although landfilling is still widely practiced, increasingly restrictive environmental regulations regarding hazardous wastes and risks of future liabilities are inducing most refiners and chemical plants to turn to more environmentally sound options. The non-availability of a "universal" recycling company, capable of handling all types of spent catalysts, makes it sometimes difficult for the user to find the appropriate outlet for the spent materials. In addition, legislation and transportation regulations often vary between geographical regions and countries. The presence of many brokers or other intermediators does not always guarantee a safe and environmentally acceptable recycling process. Many plants prefer to deal with a well established company which has developed its own hydrometallurgical process, a unique expertise and a network of partner companies to assist the user in finding the optimal recycling solutions appropriate to his need [13].

Nowadays, specialized companies are available to provide ex-situ or on site services to chemical and petrochemical plants and oil refineries, in relation to their catalyst operations [14].

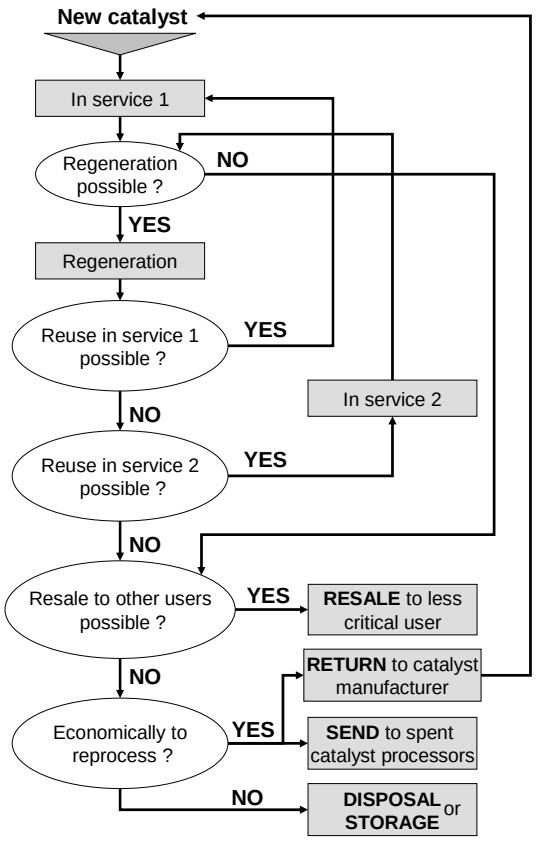


Fig. 3. Catalyst life cycle

The life cycle of a catalyst can be illustrated as in Fig. 3. At the end of the life cycle there still are several options. Depending on the spent catalyst chemical composition, recycling or recovery of valuable compounds is preferable. If recycling and/or recovery are economically unattractive, safe disposal or landfilling are the remaining options, depending on the hazard degree of each type of catalyst.

## 4. SPENT CATALYSTS MARKET

The worldwide market for solid catalysts reaches around 2 billion US$/year [3]. The greatest catalyst consumers are oil refining and petrochemical industry. It is difficult to give an estimate on the quantity of spent catalysts resulted from process industries, but recent studies indicate an estimate for refinery spent catalysts (Table 4).

Table 4. Estimation for spent catalysts evacuated yearly from oil refineries [15] and ammonia plants

| Plant | Type of catalyst | Quantity [t/y] |
|---|---|---|
| Oil refinery | Fluid catalytic cracking | 393,000 |
| | Hydrotreating | 87,500 |
| | Hydrodesulphurization | 297,500 |
| Ammonia plant | Feedstock desulphurization | 1,150 |
| | Natural gas steam reforming | 4,150 |
| | High temperature CO shift | 14,300 |
| | Low temperature CO shift | 24,200 |
| | Methanation | 970 |
| | Ammonia synthesis | 15,700 |

In ammonia production, based on the total world capacity of 135.835 Mt/y (as nitrogen), and on an average 80% capacity usage in 2005 [16], and considering the spent catalyst evacuation at the level of BAT [17], the estimation for spent catalysts is that presented in Table 4.

## 5. CONCLUSION

Recovery of valuable compounds from spent catalysts is an option due to the environmental constraints. In many cases, spent catalysts are richer in metals than the exploited mineral ores, making the process viable and attractive.

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