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Industrial catalysts as a source of valuable metals

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ABSTRACT

Purpose: Catalyst are used in all sector of the chemical industry: in basic chemistry (synthesis of sulfuric and nitric acid, ammonia, methanol and aromactics; in petrochemistry; in polymerization chemistry; in refining, in reactions of fluid catalytic cracking (FCC), resid fluid cracking catalyst (RFCC), hydrodesulfurization (HDS) and hydrotreatment; in auto industry for reduce of pollution, for removal of NO, CO and hydrocarbons in exhaust emissions; in variety of industrial processes. Recovery of metals and precious metals from spent catalysts has been an important topic not only from economic aspect but also for recycling rare natural sources and reducing the catalyst waste to prevent the environmental pollution. Various methods for recovering metals form spent auto catalyst, petroleum reforming and other industrial catalysts are reviewed.

Design/methodology/approach: The article presents the methods used in the world for metals recovery from spent industrial catalysts.

Findings: To recover precious metals from spent catalysts many hydro- and pyrometallurgical methods are used. But none of these methods is an universal method that can be used to recover all type of spent catalysts. These recovery methods have also some disadvantages: pyrometallurgical methods require special equipment, reaching the desired temperature, and they are not only expensive but also highly energy consuming. The application of hydrometallurgical methods requires to solve the problem of harmful waste solutions generated during the process.

Practical implications: The paper presents the possibilities of industrial catalysis as a source of valuable metals.

Originality/value: The present work is a review about industrial catalysts as a source of valuable metals.

Keywords: Catalyst; Recycling of catalyst; Reforming; Recovery of metals

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1. Introduction

The word "catalysis" comes from the Greek word "katalein", which means decompose. This concept was introduced and explained in 1835 by Jöns Jacob Berzelius [1]. The phenomenon of catalysis is associated with a change of chemical reaction rate in addition of a chemical compound, called a catalyst. Catalysts are used widely in the chemical industry and nowadays it is hard to find a proper field that is used in chemical reactions are not accelerated by catalyst. Without the participation of biocatalysts does not work any life process and without the industrial catalysis is not possible to obtain fuels from raw material, the production of sulfuric and nitric acids, ammonia or car exhaust getting more "friendly" environment. By applying appropriate catalytic converters is possible to avoid the formation of harmful byproducts in the process of desulfurization and denitrification of vehicle exhaust gases and waste disposal. Thus, given the enormous importance of catalysts, for the functioning of biological organisms, chemical industry and cost-effectiveness of using the catalysts, the production of catalysts for different purposes is tremendous. The worldwide market for catalysts used in chemical, pharmaceutical and polymers is estimated at about $ 1.5 billion and global demand will grow 9-10% per year [2].

With the huge number of catalysts of different application, introduced on chemical, petrochemical or automotive market, the number of used or withdrawn from service catalysts (because of damage or defects in materials) is still increasing. The catalysts used in the past left in landfills. Nowadays air pollution and the environmental regulation caused that these waste has become a serious global problem. Some of them can be classified as hazardous, toxic waste, and therefore require special treatment and monitoring of their transport and storage. Such reactors pose a major threat to the environment due to the variety materials used in their production but also they are a valuable source of various kinds of metals (Mo, Ni, V, Ag, Pt, Pd, Rh). The metals such as nickel, cobalt, molybdenum, vanadium from the spent refinery catalysts can be recover. From the catalysts used in the food industry - silver and from automotive catalysts - platinum, palladium and rhodium can be recover. Thus, recycling of spent catalysts brings tangible benefits for both ecology and economy. This is due to limiting the amount of waste on landfilled, savings the natural resources or to reduce energy consumption and emissions in comparison to technologies obtaining metals from raw materials.

2. Metals applied in industrial catalysts

Catalyst are used in all sector of the chemical industry [3,4]

- in basic chemistry (synthesis of sulfuric and nitric acid, ammonia, methanol and aromactics);
- in petrochemistry ,
- in polymerization chemistry,
- in refining, in reactions of fluid catalytic cracking (FCC), resid fluid cracking catalyst (RFCC), hydrodesulfurization (HDS) and hydrotreatment,
- in auto industry to reduce of pollution by removing NO, CO and hydrocarbons in exhaust emissions,
- in variety of industrial processes.

Precious metals and especially Platinum Group Metals - PGM (platinum, palladium, rhodium and iridium, ruthenium and osmium) are widely applied in many industrial areas such as: electronics sector (hard disks, multilayer ceramic capacitors, integrated circuits), production of liquid crystal displays, jewellery or as catalysts in chemical industry [5].

The sector of automotive is still leading one demand for PGMs (especially Pt, Pd and Rh). The data concerning demand and global use of platinum, rhodium and palladium in various industries in the years 2008-2010 are summarized in Tables 1-3.

Precious group metals (PGM) from spent catalysts used in other kinds of chemical and petrochemical industries are also recovered. Heavily-diluted organic platinum and rhodium solutions comes from homogeneous catalytic processes from the chemical industry. Catalysts containing platinum are also used to oxidize ammonia (containing Fe) and in the process of gasoline reforming. Platinum catalysts are important also for silicone production. Rhodium is principally needed for catalytic converters for the automotive industry, but also finds widespread application in the chemical industry because of its outstanding catalytic properties. Homogeneous catalytic processes using rhodium play an important role in the production of special chemicals (plasticizers, acetic acid, acetic anhydride, and pharmaceutical agents) [6].

Also metallic silver and some of its compounds show good catalytic properties and are used for oxidation of organic substance. As catalytic converter silver can be used in its pure form as well as electrolytical coarse powder, and silver compounds: AgO, Ag_2O, $AgNO_3$, AgSiF, AgClO.

Pure silver is used as catalytic converter in production of:

- formaldehyde form methanol,
- ethylene from ethylene oxide (ethylene oxide is a basic material for production of solvents, detergents and dyes),
- in synthesis of nitryle form aldehyde and ammonia.

As a catalytic converters powder of silver can also be used. Due to economical reasons it is deposited on bauxite or alumina oxide Al_2O_3. This technology can be used in desulphurization of petroleum distillate [4].

Metallic powder of silver on copper oxide carrier is used as catalytic converter in reactions [4]:

- detonation of air-acetylene mixture,
- oxidation of carbon (II) oxide,
- alcohol oxidation to aldehyde and acids,
- Ethylene glycol production.

The data concerning demand and global use of silver in various industries in the years 2008-2010 are summarized in Table 4.

Transition metals such as nickel, cobalt, molybdenum, cobalt and vanadium are applied in catalysts for petrochemical industry. These metals are used in the an oxide form of carrier of alumina or aluminum silicate. Spent and unfit for the regeneration catalysts become waste. Management of spent catalysts is a challenge because of their form (fine-grained and high porosity), a complex chemical composition and content of hazardous substances, including compounds of transition metals, hydrocarbons and sulfur phase [7].

Table 1.
Demand and use of platinum in 2008-2010 divided into branches of industry (in tones) [3]

Industry branch	Platinum		
	2008	2009	2010
Auto catalysts	103.6	61.9	84.6
Electro	6.5	5.3	6.3
Invest	15.7	18.7	12.3
Jewellery	58.4	79.6	68.6
Glass	8.9	0.2	10.3
Medicine	6.9	7.0	7.2
Chemistry	11.3	8.2	12.7
Others	15.0	11.3	12.0
Use	**226.5**	**192.6**	**214.3**
Recycling	51.8	39.6	52.1
Net consumption	174.6	152.8	162.1
Stocks	6.2	18.0	8.2

Table 2.
Demand and use of palladium in 2008-2010 divided into branches of industry (in tones) [3]

Industry branch	Palladium		
	2008	2009	2010
Auto catalysts	126.5	114.8	146
Electro	38.8	36.0	39.8
Invest	11.9	17.7	18.9
Jewellery	27.9	21.9	17.8
Medicine	17.7	18.0	17.5
Chemistry	9.9	9.2	10.9
Others	2.1	1.9	2.2
Use	**235.0**	**219.7**	**253.4**
Recycling	45.7	40.5	52.3
Net consumption	189.2	179.1	201.1
Stocks	18.0	22.1	1.2

Table 3.
Demand and use of rhodium in 2008-2010 divided into branches of industry (in tones) [3]

Industry branch	Rhodium		
	2008	2009	2010
Auto catalysts	21.7	17.5	20.6
Electro	0.08	0.08	0.1
Glass	0.9	0.5	1.6
Chemistry	1.9	1.5	1.8
Others	0.6	0.5	0.5
Use	**25.4**	**20.2**	**24.8**
Recycling	6.4	5.3	6.7
Net consumption	18.9	14.9	18.0

Table 4.
Demand and use of silver in 2008-2010 divided into branches of industry (in tones)

Industry branch	Silver		
	2008	2009	2010
Industrial application	13976.3	11481.6	14174.8
Photography	2863.3	2239.6	2041.2
Jewellery	4507.6	4535.9	4734.4
Silverware	1615.9	1672.6	1445.8
Coin and medals	1842.7	2239.6	2806.6
Use	**24805.9**	**22169.3**	**25231.1**

To recover precious metals from spent catalysts many hydro- and pyrometallurgical methods are used [8]. But none of these methods is an universal method that can be used to recover all type of spent catalysts. These recovery methods have also some disadvantages: pyrometallurgical methods require special equipment, reaching the desired temperature, and they are not only expensive but also highly energy consuming; application of hydrometallurgical methods requires to solve the problem of harmful waste solutions generated during the process.

3. Recovery of metals from spent catalysts used in petrochemical industry

Since January 2009, the Polish market, as well as other European Union countries, force the EU regulation, which allows to sell of fuel with a sulfur content not exceeding 10 ppm (10 mg per kg). This regulation reduces permitted sulfur content of fuels five times. Such tightened requirements allow to produce only low sulfur fuel, however it requires complex technological operations, because the major oil contamination are the organic compounds of sulfur. Their content varies depending on the origin of the material [9].

Growing demand for high purity, free of sulfur and aromatic hydrocarbons motor gasoline, was the reason why a lot of technological operations restricting the content of these compounds had to be applied. Two basic operations in today's refineries suppling gasoline components to compose gasoline, are catalytic cracking and reforming. The main objective of the catalytic cracking is to split hydrocarbons of high molecular weight into fragments of a suitable volatility, enabling their use as fuels. Products obtained from this process does not hav sufficiently high octane number, required high compression for engines and it is necessary to subject them to catalytic reforming, high-temperature heating of light petroleum fractions or cracking under pressure [10,11]. However, such systems, used for crude oil, are a constant source of spent catalysts, which are formed by aging and deposition of inorganic contaminants, petroleum coke and carbon-containing compounds and sulfur on the catalyst surface. Spent catalysts in the refinery processes are classified as hazardous waste: they are flammable, explosive, toxic, corrosive, they also emit toxic gases in contact with the environment [12].

Table 5.
Available methods applied in recovery of metals from spent catalytic converters in petrochemical processes [4]

Type of catalytic converter	Applied method
Bimetallic reforming catalysts (for eq. $Pt/Re/Al_2O_3$ and $Pt/Ir/Al_2O_3$)	Precious metals on bimetallic reforming catalysts are recovered by dissolving them with an oxalic acid ($H_2C_2O_4$) solution buffered at ph>3 with ammonium oxalate ($(NH_4)_2C_2O_4$. The spent $Pt/Re/Al_2O_3$ catalyst is calcined and mixed with hot H_2SO_4 to dissolve Re and most of Al_2O_3. Next step is filtration to separate Pt and undissolved Al_2O_3. Then Re is eluted by a mixture of $HClO_4$ and C_2H_5OH.
The spent catalyst containing Pt, Pd, Rh and Fe alloy	These kinds of spent catalytic converter are recovered by leachning with chloride solution mixed with a small amount of HNO_3. The solution is reducing by powdered Fe after that dissolving the precious metals with HCl and an oxidizing agent selected form Cl_2, H_2O_2, O_2 and air. Pd is extracted with a series of organic extracting agents such as dihexylsulfide for recovery of Pd, and extracting Pt and Rh with tributylophospate for their recovery.
The spent catalyst sieve containing Pt and Rh	The spent catalyst sieve containing Pt and Rh is dissolved in aqua regia, and the concentrated solution is converted to chlorides with HCl. This solution is treated with aqueous saturated by NaCl solution, and contacted with an acidic cation exchanger to separate common elements. Residual solution after the ion exchange is treated with aqueous 25% NH_4OH to pH 9 to obtain NH_4-salts of hexachlorocomplex. The salts are reduced with hydrazine hydrate. After filtration, the resulting Pt-Rh powder is washed with water and dried at 110°C.

Reforming and hydrogenation catalysts can be processed by dissolving a ceramic base in sodium hydroxide or sulfuric acid. Before leaching, excess amount of coal and hydrocarbons is burned.

Recovery of platinum from this type of catalysts is complicated and there may be a need to repeat the particular stages of the process to achieve the required purity. Their number and sequence also depend on the type of discharged pollutants. Many methods of metal recovery require the application of cyanide, chlorine, hydrochloric acid and nitric acid. These reagents are used again in these processes, but ultimately they require oxidation or neutralization with caustic soda and lime. Sludge from wastewater treatment is analyzed for the content of recycled metals [13].

Disposal of spent catalysts is a challenge because of their form (fine-granulation and high porosity), complex chemical composition and content of hazardous substances: compounds of transition metals, hydrocarbons and sulfur phase. Technologies of roasting processes, hydrometallurgical and pyrometallurgical processes to separate the various metals are mainly used for this purpose [14]. The recovery of metals such as Mo, Ni, Co, V from spent catalysts of petroleum is possible, however, for economics of this process influences of prices metals, the content of this metal, transport costs and the purity of the recovered metal [3, catalysis]. The demand for petrochemical catalysts, FCC and RFCC on the basis of Ni and V is increasing and is projected to increase in global demand for them is estimated for 6.3% per year [15].

4. Recovery of metals from spent automotive catalysts

Spent automotive catalysts are a valuable source of important non-ferrous metals such as platinum, palladium, rhodium and aluminum.

Car engine during the fuel combustion process emits many compounds which are harmful to human health and natural environment. To reduce emission of these compounds companies started to install catalytic converters in cars. The main aim of catalytic converters is to limit emission of such compounds: nitrogen oxides (NO_x), hydrocarbons (CH) and carbon monoxides (CO). They are converted into harmless nitrogen, carbon dioxide and water.

Table 6.
Available hydrometallurgical processes applied in PGM metals recovery from the used auto catalytic converters [4,16-20]

Hydrometallurgical processes
In the hydrometallurgical methods PGM contained in the used auto catalytic converters are dissolved in an aqueous solution of chlorate, perchloric acid, Cl_2, H_2O_2, bromate, nitrate and aqua regia. As a result PGM metals are mostly in the form of chloro-complex (MCl_6^{2-}). The obtained solution contains PGM metals, but their concentration is low. So the next stage is to concentrate the solution and extract them from this solution. However, in hydrometallurgical methods liquid wastes can be created in large numbers. Such wastes might be very dangerous to the environment.
Examples
Segregation method
During the grinding process the small addition of KCl and NaCl is used, heating is applied to concentrate the solution; in consequence part of the solution is evaporated; during the platinum extraction oxygen blow is used.
Chlorination method
Used auto catalytic converters are chlorinated in high temperature. The temperature must be higher than 1200 °C to evaporate the metallic fraction.
Aqua regia method
Catalytic converter is dissolved in aqua regia (mixture of HNO_3 and HCl in the 3:1ratio). As a result H_2PtCl_6 is obtained. Then this solution is precipated, by the Al/Zn powder. The last stage is platinum refining process.

Catalytic converter is built from metallic or ceramic carrier with porous structure, covered by the layer of PGM metals. Catalytic carrier is wrapped by fibrous material and closed in stainless steel shell. It has the porous structure of the honeycomb (the dense net of square holes). Such construction increases the active surface that is the contact zone of precious metals with fumes.

Content of precious metals depends not only on the structure and utilization of auto catalytic converters (on the average 2 grams of platinum metals) but also on the car manufacturer. Catalytic converters should be periodically regenerated and after some time replaced. Therefore the number of catalytic converters stored at scrapyards increases. They are both the ones replaced and the ones not used any more.

Recovery of metals from spent automotive catalysts can be divided into four basic stages: homogenization, compaction, dissolution and separation of metals and their purification. The last stage is the final refinement, which allows to obtain metal of relatively high purity, but it is very expensive. Methods often used for final purification are very different: calcination, ion exchange, solvent extraction, hydrolysis, oxidation and reduction, or precipitation. Spent catalysts are processed pyrometallurgically or hydrometallurgically or using mixed methods. In these technologies deal with a number of intermediate operations, aiming at extracting pure metal.

Table 7.
Available pyrometallurgical processes applied in PGM metals recovery from the used auto catalytic converters [4,16-20]

Pyrometallurgical processes
In pyrometallurgical methods broken-up carriers covered by the PGM metals are melted with the addition of other metal which has a special function - to be a liquid matrix. PGM metals pass into the alloy, while carriers are separated and scrapped. Obtained metal is rich in PGM metals, so the next stage is the PGM metals purification.
Examples
Rose method
Grinded (milled) catalytic converter is melted in the electric furnace with copper oxide, coke, calcium, iron oxide and silica. After melting, copper with platinum and slag are obtained. Slag consists of ceramic carrier, calcium, silica and iron oxide. The alloy is processed in oxidaizing furnace where copper is oxidized and platinum (which does not react with oxygen) is separated. Obtained product contains 75 % of metal and goes to refining section.
Melting method
The catalytic converters are melted with iron in temperature higher than 2000 °C. Slag from the metallic phase is separated due to the difference between its densities. Obtained metallic phase is leached in the H_2SO_4. As a result iron is removed from the platinum solution. In the lower temperature other metal can be also used for collecting platinum. The obtained slag is less aggressive and the conditions are less reactive.

5. Conclusions

An appropriate economic development is possible not only due to correct use of natural resources but also due to suitable utilization of renewable (air, water, wind) and non-renewable (coal, gas, petroleum) natural resources. However the world economy faces the big problem of limited sources of natural materials especially non-renewable ones. Some of them, for example coal or petroleum, might be completely used during the next few decades. This situation forces many countries to take some actions in order to decrease irreparable losses. They try to replace non-renewable materials by renewable ones. Another way is to use parts of materials again, so the consumption of natural resources gets limited and the amount of wastes is reduced Thus, environmental protection, waste reduction, use of precious materials and secondary raw materials are certainly requirements of our times.

Recycling of other metals, especially the precious ones, also remains in the area of interest; however it is not so easy. Copper, silver, gold and the PGM metals (Platinum Group Metals) such as platinum, palladium, rhodium, etc. belong to the group of PGM metals. These metals, because of their chemical reactivity, can be found in natural form or in the impurities of copper, zinc and nickel ores. They are rare metals, so the amount in earth crust is small. This is why their production process is expensive and energy-consuming. The great demand for PGM metals has been caused by the development of chemical industry and especially processes which need catalytic converters. Demand for PGM metals will be still increasing as the amount of produced cars is high and might be even higher in the future [21].

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