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DISSOLUTION OF METAL SUPPORTED SPENT AUTO CATALYSTS IN ACIDS

Metal supported auto catalysts, have been used in sports and racing cars initially, but nowadays their application systematically increases. In Metal Substrate (supported) Converters (MSC), catalytic functions are performed by the Platinum Group Metals (PGM): Pt, Pd, Rh, similarly to the catalysts on ceramic carriers. The contents of these metals make that spent catalytic converters are valuable source of precious metals. All over the world there are many methods for the metals recovery from the ceramic carriers, however, the issue of platinum recovery from metal supported catalysts has not been studied sufficiently yet. The paper presents preliminary results of dissolution of spent automotive catalyst on a metal carrier by means of acids: H₂SO₄, HCl, HNO₃, H₃PO₄. The main assumption of the research was the dissolution of base metals (Fe, Cr, Al) from metallic carrier of catalyst, avoiding dissolution of PGMs. Dissolution was the most effective when concentrated hydrochloric acid, and 2M sulfuric acid (VI) was used. It was observed that the dust, remaining after leaching, contained platinum in the level of 0.8% and 0.7%, respectively.

1. Introduction

Catalytic converter is an essential element of any modern car. Its task is to convert toxic compounds such as CO, NO_x C_xH_y into non-toxic compounds CO₂, H₂O, N₂ [1,2]. Currently ceramic and metal supported catalysts are mainly used on the market. Metal Substrate converters (MSC) were originally used in sports and racing cars, where low exhaust back pressure and operational reliability with continuous heavy load were required. Metal catalysts are still a small group among all auto catalysts used currently in vehicles - approx. 4%. However, the metal carriers begin to be used more because of the numerous advantages. Metallic substances provide a lower resistance to air flow and require less heat to warm up because the corrugated metal roll allows gases to flow through almost 90% of the total front area while still providing more surface area than the ceramic monolith [3,4].

Metallic catalytic converters are made of heat-resistant Fe-Cr-Al foil, with a thin film of PGM on the surface, wrapped in a manner that allows to maximize the contact area with the catalyst substances. The content of PGM in these type of devices is similar to those on the ceramic monolith - usually no more than 2-3 grams [5].

In the literature there is a lack of information regarding the recovery of precious metals from automotive catalysts on metal carriers. The only company processing metal catalytic converters on industrial scale is Umicore Precious Metals Refining - one of the world's leading precious metal recycling

facilities. They have highly automated lines for metallic catalytic converters shredding in Maxton (USA) [6].

The first stage in the recovery of PGM from metallic catalysts is mechanical separation of different parts of the catalyst, including those containing PGM [5]. Through to specialized process of catalysts dismantling, initial selection is made on the fractions containing precious metals. Then fraction containing PGM is homogenized. The metal carrier is shredded using one or more different types of shredders. During the crushing process dust, rich in precious metals, is produced and carefully collected, in order to avoid additional losses during the process. Fractions of steel scrap (can-fraction, foil-fraction) are practically devoided of valuable metals and are recycled for reuse [7].

Hydrometallurgical treatment of MSC might be an alternative way to the currently applied - mechanical pretreatment and pyrometallurgical process. Previously various leaching agents (hydrochloric acid, nitric acid and sulfuric acid) were usually used to separate precious metals from different types of metal-bearing wastes, as well as from spent catalytic converters [1]. Hydrometallurgical process is one of the most often employed (including leaching step), however it has been mostly studied in various conditions and applied for ceramic monoliths, instead for MSC.

Due to the lack of reports in the literature concerning processing capabilities (dissolution) of metal automotive catalysts in acid solutions, preliminary studies have been undertaken to determine the susceptibility of metal catalyst carrier by leaching. The main aim of the research was the

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dissolution of base metals (Fe, Cr, Al) of metallic carrier of catalyst, and avoiding dissolution of PGMs, using basic oxidizing and non oxidizing acids as lixiviant: sulphuric acid, hydrochloric acid, nitric and phosphoric acid.

2. Experimental method

The spent Metal Substrate Converters (MSC) were used in experiments (Fig. 1).



Fig 1. Metal Substrate Converter with corrugated FeCrAl foils, applied in experiment

Material was cut and subjected to leaching experiments in 10-20 mm particle size fractions.

Concentrated and 2M acids solutions of H₂SO₄, HCl, HNO₃ and H₃PO₄ in the volume of 50 ml were used. Prepared samples (3.0 g) were left for 24 hours leaching process and were stirred periodically in ambient temperature. Next, samples were filtered and residues (in the form of insoluble dust and foil) were rinsed with distilled water. The content of metals (Fe, Cr, Al, Pt) was determined by the atomic absorption spectrometry (AAS, Solar M6). Raw MSC was analysed by using scanning electron microscope (SEM), equipped with a Hitachi S 4200. Microanalysis of

the chemical composition was performed by EDS method (Energy Dispersive Spectrum). Structure of the raw MSC, its chemical composition together with EDS analysis have been presented respectively in Fig. 2, in Table 1 and in Fig. 3. Next to Fe, Cr and Al a significant part represents alumina, an intermediate layer, which plays the role of a carrier for catalysts substances.

TABLE 1
Chemical analysis for the sample of raw catalytic converter (points marked on Fig. 2)

Weight %				
	Base(3) pt1	Base(3) pt2	Base(3) pt3	Base(3) pt4
Cr	-	-	1,3	1,1
Fe	0,9	1,2	4,2	3,5
Pt	-	0,4	0,3	0,4
O	70,6	70,3	63,7	65,4
Al	25,8	28,1	30,5	29,3
Si	-	-	-	0,3
Zr	1,6	-	-	-
Ba	1,2	-	-	-

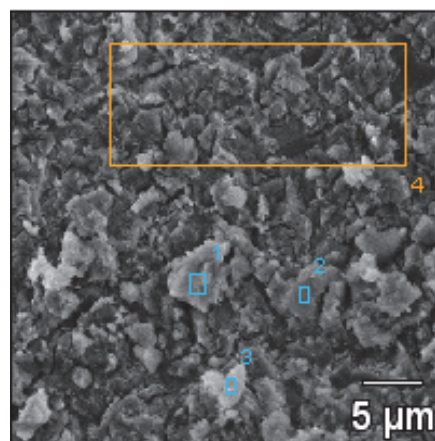


Fig. 2 Structure of catalytic converter sample with marked selected areas for X-ray energy spectra

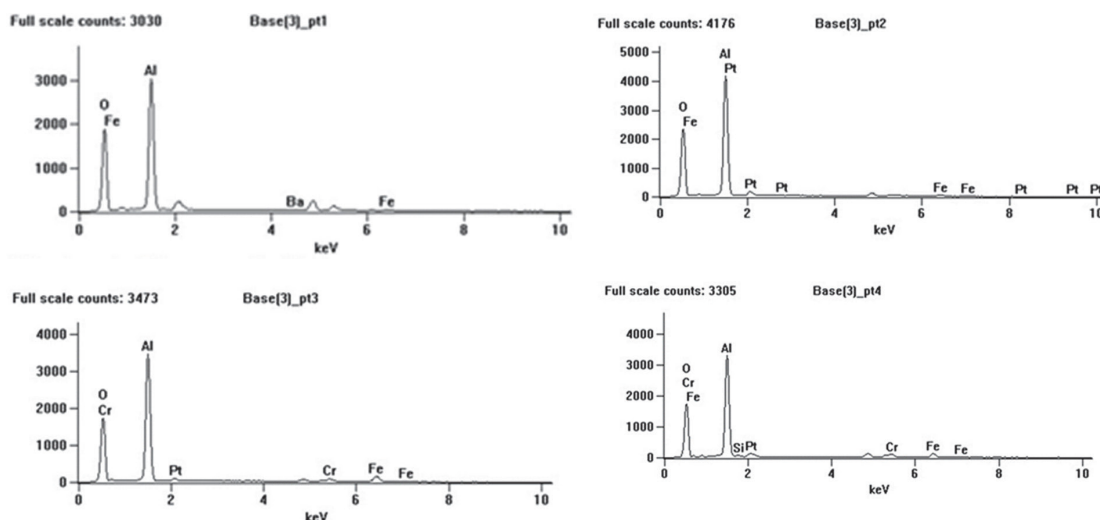
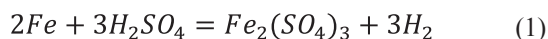


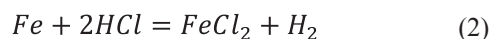
Fig. 3 Microanalysis of the chemical composition by EDS method (pt1-pt4)

3. Results and discussion

In samples containing concentrated H_2SO_4 gas evolution was observed. In the case of 2M H_2SO_4 the gas release was much more intense. There was a reaction in which iron reacted with dilute sulfuric acid (VI), whereby the evolution of H_2 proceed according to the following reaction [8]:



When concentrated HCl acid was used intense reaction with gas evolution and colour change to green was observed. While in the sample with 2M HCl gas evolution was slower. HCl reacts with Fe, and as a consequence H_2 was produced. The reaction product $FeCl_2$ causes green colour, characteristic for most compounds, wherein the iron is on the + II oxidation number, according to the reaction:



In systems with a 2M HNO_3 , solution became turbid, due to the reaction (3). In a concentrated acid Fe was passivated [8].

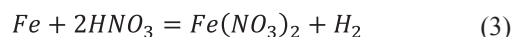


Table 2 shows the results of dissolution of the metal carrier of spent autocatalyst and the extraction of metals (Fe, Cr, Al) from a solid phase into solution in the presence of the most widely used oxidizing and nonoxidizing acids: H_2SO_4 , HCl, HNO_3 and H_3PO_4 .

The results confirmed the assumption that the iron in the presence of a dilute acid (H_2SO_4 , HCl, HNO_3) would be dissolved. Concentrated nitric acid (V) and sulfuric acid (VI) did not dissolve chromium and iron, since it was the passivation reaction [8]. Aluminium was dissolved in acid with hydrogen evolution, with the exception of nitric acid (V), where passivation took place. Platinum did not occur in solution after leaching, or its content in liquid phase was low in

trace level, which was in line with expectations. Dissolution of PGMs is only possible and performed with strong oxidants: in widely known mixtures of HCl/ HNO_3 , in alternative chloride precursors such as $AlCl_3$, alone or mixed with HCl, using HNO_3 as oxidant or in other common leachant mixture like HCl/ H_2O_2 or HCl/ Cl_2 [9-11].

Depending on used acids, solid residue after leaching was in the form of undissolved (in a sufficiently large extent) metal foil FeCrAl or dust - containing a significant amount of platinum. Analysis showed the highest content of platinum in the dust, remaining after filtration of the sample containing concentrated HCl (0.8%). A high value of Pt was obtained as well, in the filter dust for the sample after dissolution of carrier in 2M sulfuric acid (VI) (0.7%). With the exception of nitric acid (V), the aluminum content in the solutions was at a similar level (approx. 4.8%). The content of Cr and Fe in solid residues was higher for samples treated with concentrated oxidizing acids where passivation reaction took place.

4. Conclusion

The paper presented preliminary results of dissolution of spent metal substrate converters using concentrated and 2M solution of basic acids as lixiviant: sulphuric acid, hydrochloric acid, nitric and phosphoric acid. The main aim of the study was dissolution of base metals of metallic carrier (FeCrAl) of spent automobile catalysts, avoiding dissolution of PGMs as well as determining the susceptibility of the catalyst components (Fe, Cr, Al) to the effect of concentrated acids and their 2M solutions. Dissolution was the most effective using concentrated hydrochloric acid, and the 2M sulfuric acid (VI). It was observed that the dust, remaining after leaching, contained platinum in the level of 0.8% and 0.7% respectively. Iron and chromium were dissolved most effectively in diluted acids, while in oxidizing concentrated acids were passivated. Aluminium reacted similarly, in concentrated nitric acid (V) it was also coated with the passive layer, preventing further reaction.

TABLE 2
Content of metals in solutions and in insoluble MSC residue after leaching

Sample	Content %							
	Solution				Residue			
	Pt	Fe	Al	Cr	Pt	Fe	Al	Cr
Before solution	-	-	-	-	0.084	57.5	5.0	19.7
H_2SO_4 conc.	-	0.303	4.921	0.001	-	58.138	4.616	19.034
H_2SO_4 2M	0.003	41.97	4.881	19.03	0.7033	9.767	4.656	0.01
HCl conc.	0.002	9.593	4.837	17.325	0.8328	1.102	3.623	0.04
HCl 2M	0.0001	74.391	4.832	15.372	0.3874	33.351	3.604	0.04
HNO_3 conc	0.0008	0.028	0.007	0.301	0.0125	61.755	4.984	18.22
HNO_3 2M	-	0.115	0.041	18.435	-	58.941	4.954	0.02
H_3PO_4 conc	-	0.998	4.776	16.436	-	49.498	1.334	0.01
H_3PO_4 2M	0.003	0.112	4.767	16.867	0.0029	67.043	0.987	0.03

conc. – concentrated acid

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