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PHYSICAL -CHEMICAL CHARACTERIZATION OF SPENT AUTOMOTIVE CATALYSTS

Radmila T.Marković
Ljiljana J.Mladenović **Ljiljana R.Avramović**
Radojka J. Jonović **Nevenka B.Petrović**

MMI, Mining and Metallurgy Institute, Zeleni bulevar 33, 19210 Bor, Serbia

ABSTRACT
This paper presents the results of the chemical and physical-chemical characterization of spent automotive catalysts samples. The results of chemical analysis for twelve different samples are pointed out that first group of samples (6 samples), as catalyst metal contains only Pt in a range from 0.18 to 0.79 wt %, second group of samples (2 peaces) contains Pd+Rh as catalysts metals group, third group witch contain Pt+Pd as catalysts metals group, fourth group with one sample witch contain Pt+Rh and fifth group with Pt+Pd+Rh, as a catalytic .metals group.
Results of the physico-chemical characterization are presented for the composite sample obtained by mechanical treatment of twelve different samples by grinding in ball mill. The chemical characterization of the composite sample is pointed out that the Pt content is the highest – 0.195 wt %, Pd content is lower - 0.034 wt % and Rh content is 0.004 wt %.
The results of sieve analysis of composite samples after grinding in a ball mill during the period of 15 min have shown that content of particle size finer than 38 μm is more than 50 wt%. The value for apparent density of this sample is 1.118 g/cm^3, density value is 2.87 g/cm^3 and acidity 7.08.
Keywords: *physic-chemical characterization, automotive spent catalysts, Pt, Pd, Rh*

1. INTRODUCTION
Today's way of life just determined that we must have some kind of motorized vehicle. Many people in urban and smaller communities have the same thinking about this topic. However, when many vehicles are found on a small surface area leads to the fact that air is becoming poisoned and blight.
Aim to reduce emissions and harmful gases in the atmosphere, the engine manufacturers had to come up with some ways that toxic gases from the engine exhaust do neutral or continue them, but in much smaller quantities.

Vehicle exhaust contains a number of harmful elements. These elements could be controlled by the platinum group metals in autocatalysts. The major exhaust pollutants are:
- carbon monoxide
- oxides of nitrogen
- hydrocarbons
- particulate

The role of autocatalysts is to convert the harmful elements. The percent of conversion of hydrocarbons, carbon monoxide and oxides of nitrogen from gasoline engines into less harmful carbon dioxide, nitrogen and water vapour is over 90 per cent. Autocatalysts also reduce the pollutants in diesel exhaust by converting 90 per cent of hydrocarbons and carbon monoxide and 30 to 40 per cent of particulate into carbon dioxide and water vapour.

In 1975 the United States, following the lead of the Californian Air Resources Board, and Japan applied clean air legislation which led to autocatalysts being fitted to light duty vehicles. Many other countries with large vehicle markets have followed since then, including South Korea (1987), Mexico (1989), the member states of the European Union (1993), Brazil (1994) and China (2000). Today, over 85 per cent of all new vehicles sold globally each year are fitted with catalytic converters [1].
An automotive catalytic converter is one of the several elements of an exhaust system that reduces the emission of harmful pollutants, such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x). The catalytic function of the converter will activate certain oxidation and/or reduction reactions, which transform these harmful pollutants into carbon dioxide (CO_2), water (H_2O) and nitrogen (N_2). Current generation automotive catalyst material consists of a ceramic or metallic substrate coated by an aluminium oxide (Al_2O_3)-based wash coat. The most commonly found converters contain a ceramic substrate (cordierite: $2Al_2O_3.2SiO_2.5MgO$) coated with a precious metal containing washcoat. It is a commonly known fact that converters on a ceramic substrate cover about 95% of the total market. This wash coat contains a combination of platinum group metals (Pt, Pd, Rh) with other rare earth oxides such as CeO_2, ZrO_2, etc. and provide for the catalytic function. PGM is a commonly used denominator for the precious metals platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os) [2].
The aim of this study was to determine physical -chemical characteristics of samples of spent catalyst of unknown origin as well as to form one composite sample that will used in the further process in order to valuate precious metals.

2. EXPERIMENTAL PART

Experimental investigations were focused on the characterization of spent autocatalyst removed from different cars. Chemical characterization is subject to all the 12 samples and the method of selection of random samples from each of these groups of materials. The X-ray fluorescent analysis - XRFA [3] on apparatus NITON XL3t-900 according to the program mode Mining AutoCat file is used for the chemical analysis. In order to prepare the composite sample that could be subjected to further process aim to valuation the precious metals, 12 existing samples were grinding in ball mill. Standard methods verified by relevant institutions are used for the physical characterization of composite sample. The system of sieves, Tyler MPIF Standard 05, last verified 1998th was used for the sieve analysis. The specific weight was determined using a glass pycnometer.

3. RESULTS AND DISCUSSION

Chemical characterization of the sample referred to the definition: the composition of individual samples and the composition of the composite sample.
Physical characterization was aimed to determine the following characteristics of the composite sample:
1. Sieve analysis content
2. Apparent density
3. Specific mass

Samples of spent automotive catalysts which have different content of Pt, Pd, Rh in the starting materials are classified based on the results of chemical analysis and the results are shown in Tables 1 and 2-

Table 1 Chemical composition of spent catalysts of the samples from Group I: Pt as a carrier of the catalytic activity and other elements

	Group of samples: I					
	Sample No. 1.	Sample No 2.	Sample No 3.	Sample No 4.	Sample No 5.	Sample No 6.
Element,	wt. %					
Pt	0.18	0,43	0.79	0.25	0.21	0.2
Si	36.15	37.76	5.05	6.01	10.65	14.71
Al	2.05	2.23	15.19	11.57	10.65	11.98
Sr	3.40	-	-	-	-	-
Zr	-	0.55	1.96	-	1.95	-
Cr	-	-	-	-	-	0.03

Pb	-	-	-	-	0.11	0.06
Fe	-	-	0.23	0.47	0.76	0.60
V	-	-	-	0.41	-	-
Zn	1.24	0.55	-	-	-	0.05
Ce	-	-	-	-	-	-
Ca	-	-	-	0.24	-	0.05
Mg	-	-	-	< 1.2	-	< 0.9
Ti	0.14	-	-	0.15	-	0.44

Results from Table 1 show that the samples 1 and 2. and samples 3 and 4 belong to the same group of catalyst. Different Pt content in samples from the same group of catalysts is a consequence of unequal time using them and the absence of legislation regulative.
Group II: Pd + Rh as carriers of catalytic activity and other elements
Group III: Pt + Pd as carriers of catalytic activity and other elements
Group IV: Pt + Pd + Rh as carriers of catalytic activity and other elements
Group V: Pt + Rh as carriers of catalytic activity and other elements

Table 2 Chemical composition of spent catalysts of the samples from different group based on elements as carriers of catalytic activity

	Group of samples: II		Group of samples: III	Group of samples: IV	Group of samples: V
Element	Sample No.1, wt. %	Sample No. 2 wt. %	Sample No. 1, wt. %	Sample No. 1, wt. %	Sample No. 1, wt. %
Pd	0.45	0.08	0.002	0.35	-
Rh	0.01	0,06	-	0.004	0.02
Pt	-	-	0.54	0.004	0.13
Si	2.26	3.74	12.41	4.60	6.41
Al	7.44	8.12	8.86	14.77	18.20
Sr	-	-	-	-	-
Zr	1.65	2.09	-	-	2.32
Cr	-	0.97	-	0.09	1.27
Pb	1.04	-	-	0.097	0.12
Fe	0.44	0.40	0.35	0.68	0.41
V	3.03	1.28	-	0.19	-
Zn	-	0.04	-	0.31	-
Ce	6.92	4.47	-	-	-
Ca	-	0.21	-	0.95	-
Mg	-	< 0.9	< 0.9	< 0.9	-
Ti	-	-	-	0.32	-

Chemical characterization of the composite samples showed that the Pt content in the sample is the highest: 0.195 wt%, the Pd content is 0.034 wt%, while the Rh content is the lowest: 0.004 wt%. The contents of other components in the composite material is CaO - 1.35 wt. %, MgO - 4:28 wt. % SiO_2 - 54.50 wt. % and Al_2O_3 - 22:46 wt. % .

Sieve analysis
The method for defining sieve analysis content depends on the size and type of the samples. Accordingly, the sieve analysis method was used, in range from 300 to 37 µm. The results are shown in Table 3.

Table 3 Sieve analysis content of the composite sample

Size class, mm	W (%)	R (%)	D (%)
-0.300 +0.212	3.50	3.50	100.00
-0.212 +0.106	12.00	15.50	96.50
-0.106 +0.075	6.00	21.50	84.50
-0.075 +0.053	9.50	31.00	78.50
-0.053 +0.038	12.00	43.00	69.00
-0.038	57.00	100.00	57.00

The results show that approximately 78% of the sample was below 75 µm, and that the largest part of single fractions was 57% of the fraction finer than 38 µm.

Apparent density and density

The apparent density was calculated by the following formula:

$$\Delta = \frac{m_2 - m_1}{V}, \ (kg/m^3)$$

where: V- vessel capacity, m^3 ; m_1 - mass of vessel, kg ; m_2 - mass of vessel with sample, kg.
Apparent density of the dry sample, average value is 1.118 g/cm^3.
The density of the treated sample was 2.870 g/cm^3.

4. CONCLUSION

The chemical characterization of the composite sample is pointed out that the Pt content has the highest value of 0.195 wt %, Pd content value is lower - 0.034 wt % and Rh content is 0.004 wt %.
The results of sieve analysis of composite samples after grinding in a ball mill during the period of 15 min have shown that content of particle size finer than 38 µm is more than 50 wt.%. The value for apparent density of this sample is 1.118 g/cm^3, density value is 2.87 g/cm^3 and acidity 7.08.
The results of physical-chemical characterization of composite sample could be used for choose the suitable process in order to valuate precious metals.

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