



A SEM-EDS study of new and used automotive catalysts

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Abstract

Automotive catalyst deactivation by inorganic contaminants originating in engine oil and fuel is discussed. Scanning electron microscopy images and energy dispersive spectroscopy analysis were used to characterize the variation of contaminant relative concentrations in various types of used monolithic catalysts. The major contaminants were calcium, phosphorus, sulphur, lead, iron and zinc. All contaminants seem to have a cumulative time dependent effect, acting more as foulants than as poisons. Valuable information about the washcoat composition were derived. A preliminary acetic acid leaching test showed that a significant quantity of the contaminants may be easily removed from the catalyst surface.

Keywords: Scanning electron microscopy; Energy dispersive spectroscopy; Automotive catalysts; Inorganic contaminants distribution; Rejuvenation

1. Introduction

Automotive catalysts are generally available in the form of monoliths. Monolithic catalysts employ a washcoat on the top of a honeycomb structure. The latter is composed of magnesium cordierite $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. The washcoat consists of γ -alumina as a substrate for the valuable metals (mainly platinum and rhodium) and a variety of additives to improve the catalytic action and to stabilize alumina and active metals at the operation conditions [1].

After a certain time period, depending on catalyst operating conditions, the catalyst is deactivated. There are four basic mechanisms of catalyst decay [2]:

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poisoning, fouling, thermal degradation and loss of catalyst mechanically or through formation and escape of vapours. Poisoning and vapour formation are basically chemical phenomena; fouling is mechanical; thermal degradation (sintering or washcoat and active metals transformation) is naturally thermal.

The main effort of this research is to study the accumulation of inorganic contaminants on the catalyst's active surface, which either by poisoning or fouling causes catalyst deactivation. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) analysis techniques were used. Scanning electron microscopy and energy dispersive spectroscopy are extensively used in catalyst characterization and especially in the study of contaminants accumulated on the catalysts surface [3,4]. A preliminary effort was also carried out to remove these contaminants from the catalyst surface. The latter is important for three reasons:

- Storage of spent catalysts in open areas may cause leachate problems.
- If the contaminants are easily removed from the surface and they are the main cause of catalyst deactivation a rejuvenation procedure may be established.
- The preliminary removal of the major quantity of the contaminants will simplify a hydrometallurgical or pyrometallurgical PGM recovery procedure by minimizing elaborate and costly purification procedures.

The most detrimental contaminants are those originating from fuel and engine oil [5,6]. Most lubricating oils for engine use contain additives designed to improve such properties as lubricity, detergency, oxidation resistance and viscosity. The common lubricating additive zinc dialkyldithiophosphate is the main contributor of phosphorus, zinc and partially sulphur contaminants. Other possible contaminants originating from engine oil are barium, calcium, magnesium and boron. Although the presence of sulphur and lead in automotive fuels was minimized the last decades due to environmental restrictions [7], the presence of small quantities is unavoidable. So the fuel is a potential contributor of such contaminants. The engine and exhaust system construction material can also contribute harmful contaminants, i.e. iron, copper, nickel and chromium. Iron is the major component of the debris retained by the catalyst; nickel and chromium are usually components used to fabricate high-temperature resistant materials such as engine parts and the exhaust system itself; copper may originate in engine bearings or in the copper lines used for air injection.

2. Experimental

The characterization of new and used automotive catalysts, which includes the examination of the contaminants accumulated in the catalysts, uses a variety of modern analytical techniques. Complete characterization of used or deactivated catalysts, of course, requires much more than chemical analysis. For example, the interaction of poisons with catalyst constituents and with each other by X-ray

Table 1
Origin and operating life (expressed in accomplished kilometers) of the monolithic catalysts used in this study

| Origin | Kilometers |
|----------------------|------------|
| Opel (Germany) | 200 000 |
| Lancia (Italy) | 200 000 |
| Alfa-Romeo (Italy) | 80 000 |
| Citroen (France) | 45 000 |
| Volkswagen (Germany) | 40 000 |
| Volvo (Sweden) | 40 000 |
| Nissan (Japan) | 40 000 |
| Opel | New |
| Volkswagen | New |

diffraction and by electron microscopy, the morphology of the contaminant deposits by optical methods, the distribution within the catalyst and washcoats, and the distribution of contaminants on the surface of the active metals are required.

The scope of this study is to use a part of the abilities of SEM and EDS to study the inorganic contaminants accumulation and distribution on new and used automotive catalysts of various origin. The instrument used was a JEOL 840-LINK AN10S equipped with a Be window.

In SEM [8] a spot-focused electron beam rasters over the sample surface. The resulting backscattered beam electrons (BSEs), secondary electrons (SEs), and emitted X-rays are scanned synchronously with the beam, giving television-like images. Best image resolution is about 5 nm.

EDS [9] is accomplished by using a semiconductor crystal that absorbs X-rays, thereby exciting the crystal's electrons into the conduction band, producing an electric pulse proportional to the energy of the X-rays. These pulses are then counted and sorted in a multichannel analyzer, and a display of intensity of the signal versus its energy gives the desired spectrum.

Used commercial catalysts of various origins and operating life were used. The origin and the active life are shown in Table 1. Nine cores from each catalyst were used for the subsequent procedure. The samples were selected to give a more representative figure of the washcoat composition. Previous studies had shown a negligible variation from the axis to the periphery of the monoliths, while the contaminants concentration decreases considerably longitudinally (upstream to downstream) [5,6]. The same happens in the catalysts under examination as shown in Fig. 1 for the main contaminants. So the nine samples were derived as follows:

- three from the upstream edge,
- three from the centre,
- three from the downstream edge,

Three different surfaces from each sample were analyzed by EDS and the data presented are the average of 27 measurements for each element. The presented % w/w concentrations are relative (normalized) concentrations since oxygen, hydro-

gen and carbon are not detectable by EDS. In order to examine the contaminants distribution in the washcoat, cross sections as shown in Fig. 2 were used.



Fig. 1. Detail of a monolithic catalyst showing washcoat deposited on a substrate.

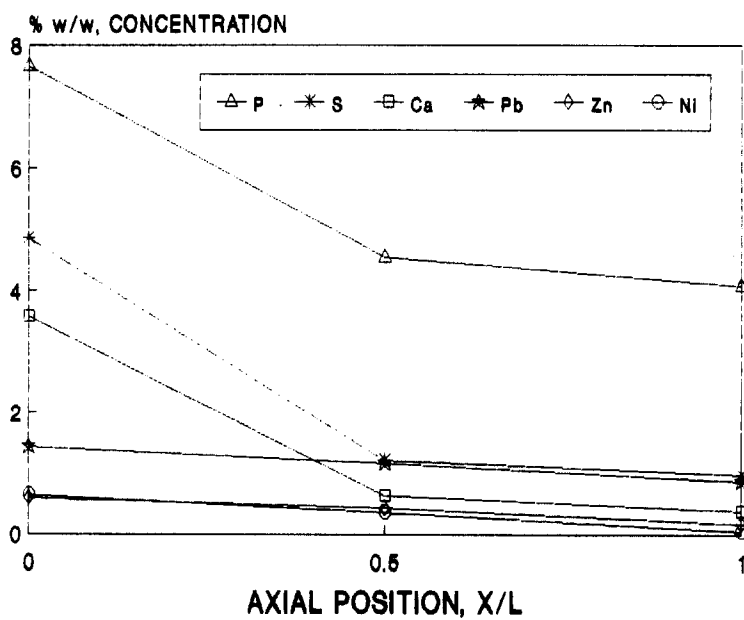


Fig. 2. Axial distribution of contaminants on monolithic catalyst (Nissan 40 000 km).

Two series of samples were used, the first for images and qualitative analysis and the second for quantitative analysis. For the first series the following procedure was followed:

- Small particles of the catalyst were covered with conductive carbon film by evaporation under vacuum.
- The particles were placed on the instrument holder using conductive glue.

For the second series the procedure was:

- The samples were mounted in epoxy resin;
- were ground and polished with diamond paste;
- were covered with conductive carbon;
- were analyzed quantitatively using the instrument's ZAF 4 programme.

3. Results and discussion

3.1. New and used catalyst comparison

Washcoat composition

In Fig. 3 a comparison is made between the washcoat surface composition of a new and a used catalyst of the same origin. The difference between the two is focused on the expected contaminants namely, phosphorus, calcium, sulphur, zinc, lead, iron and nickel. Small quantities of copper and chromium determined by chemical analysis beyond the EDS sensitivity. Magnesium and silicon concentra-

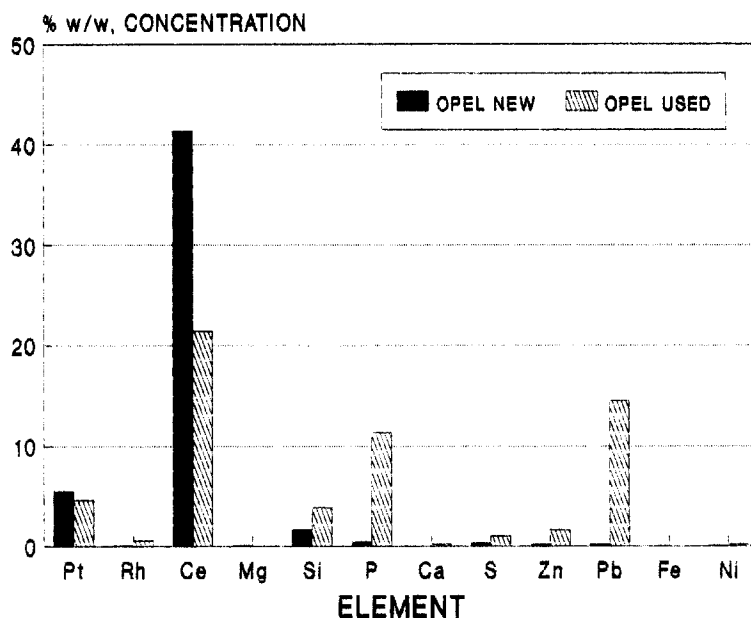


Fig. 3. Comparison of the washcoat composition of fresh and used monolithic catalyst of the same origin (Opel).

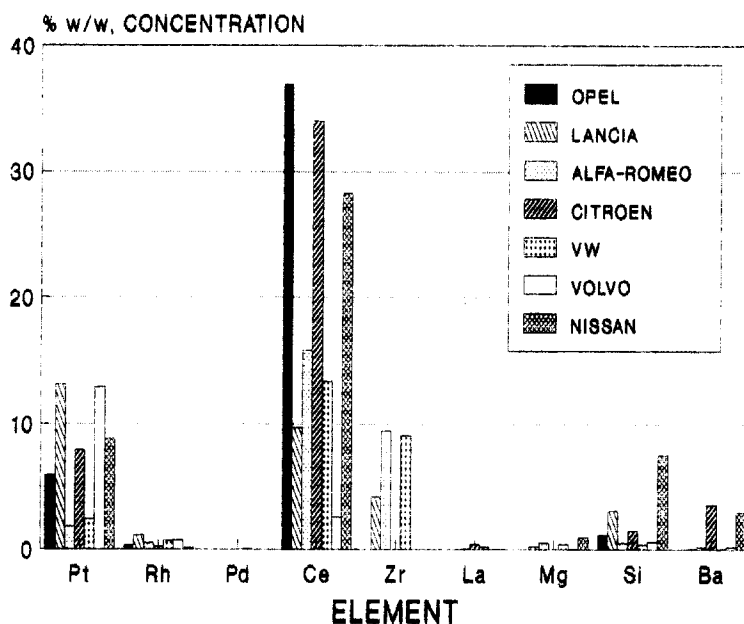


Fig. 4. Various catalyst washcoat compositions.

tions are originating either in the cordierite substrate or may be considered in part as contaminants [10].

In Fig. 4 a comparison is made between the various catalysts concerning the washcoat surface composition (aluminium common in all washcoats as the main constructive material is not included). In all catalysts platinum and rhodium were

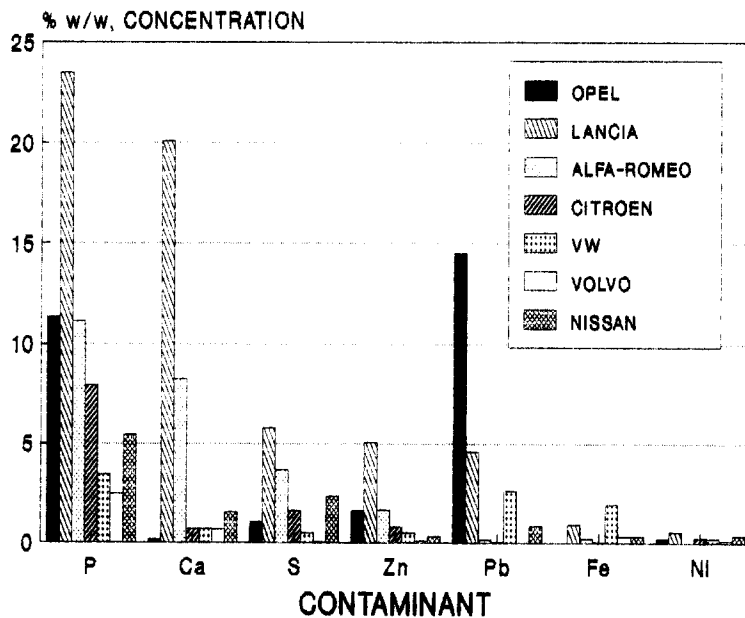


Fig. 5. Comparison of accumulation of contaminants on the washcoat surface for various monolithic catalysts.

Table 2
Comparison of washcoat external (A) and internal (B) relative contaminant concentrations

| Element | P | | Ca | | S | | Zn | | Pb | |
|------------|------|-----|------|-----|-----|-----|-----|-----|------|-----|
| | A | B | A | B | A | B | A | B | A | B |
| Opel | 11.3 | 0.2 | 0.2 | 0.1 | 1.0 | 0.3 | 1.6 | 0.0 | 14.5 | 0.3 |
| Lancia | 23.5 | 6.0 | 20.1 | 0.4 | 5.8 | 0.4 | 5.1 | 0.2 | 4.6 | 0.8 |
| Alfa Romeo | 11.1 | 0.4 | 8.2 | 1.8 | 3.7 | 2.0 | 1.6 | 0.9 | 0.2 | 0.2 |
| Citroen | 7.9 | 1.5 | 0.7 | 0.1 | 1.6 | 2.0 | 0.8 | 0.5 | 0.1 | 0.0 |
| Volkswagen | 3.4 | 1.3 | 0.7 | 0.1 | 0.5 | 0.4 | 0.5 | 0.2 | 2.6 | 0.0 |
| Volvo | 2.5 | 1.6 | 0.7 | 0.9 | 0.1 | 0.3 | 0.1 | 0.2 | 0.0 | 0.0 |
| Nissan | 5.4 | 1.3 | 1.5 | 0.1 | 2.4 | 0.4 | 0.3 | 0.2 | 0.9 | 0.0 |

detected as the active metals. Small quantities of palladium detected in some catalysts may be rather a platinum admixture, since the use of palladium has been replaced by rhodium especially in catalysts produced in Europe [7,11]. From the other elements cerium was present in all catalysts while lanthanum, zirconium and barium were detected in some of them. All of these are additives to stabilize the γ -alumina washcoat and the active metals and to improve the catalytic activity. Cerium stabilizes alumina and acts as an oxygen storage, helping oxidative catalytic activity under oxygen pure operating conditions, zirconium improves rhodium catalytic activity and barium stabilizes alumina [12–14].

Contaminants and their distribution in the washcoat

In Fig. 5 and Table 2 the washcoat surface distribution of the main contaminants is shown. The influence of the vehicle active life is obvious since the surface concentrations increase considerably with time showing a cumulative effect. The

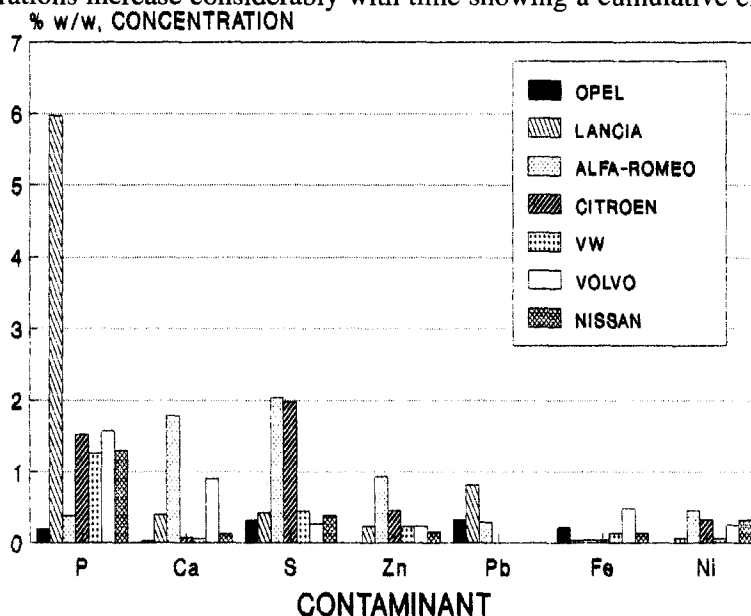


Fig. 6. Comparison of accumulation of contaminants inside the washcoat for various monolithic catalysts.

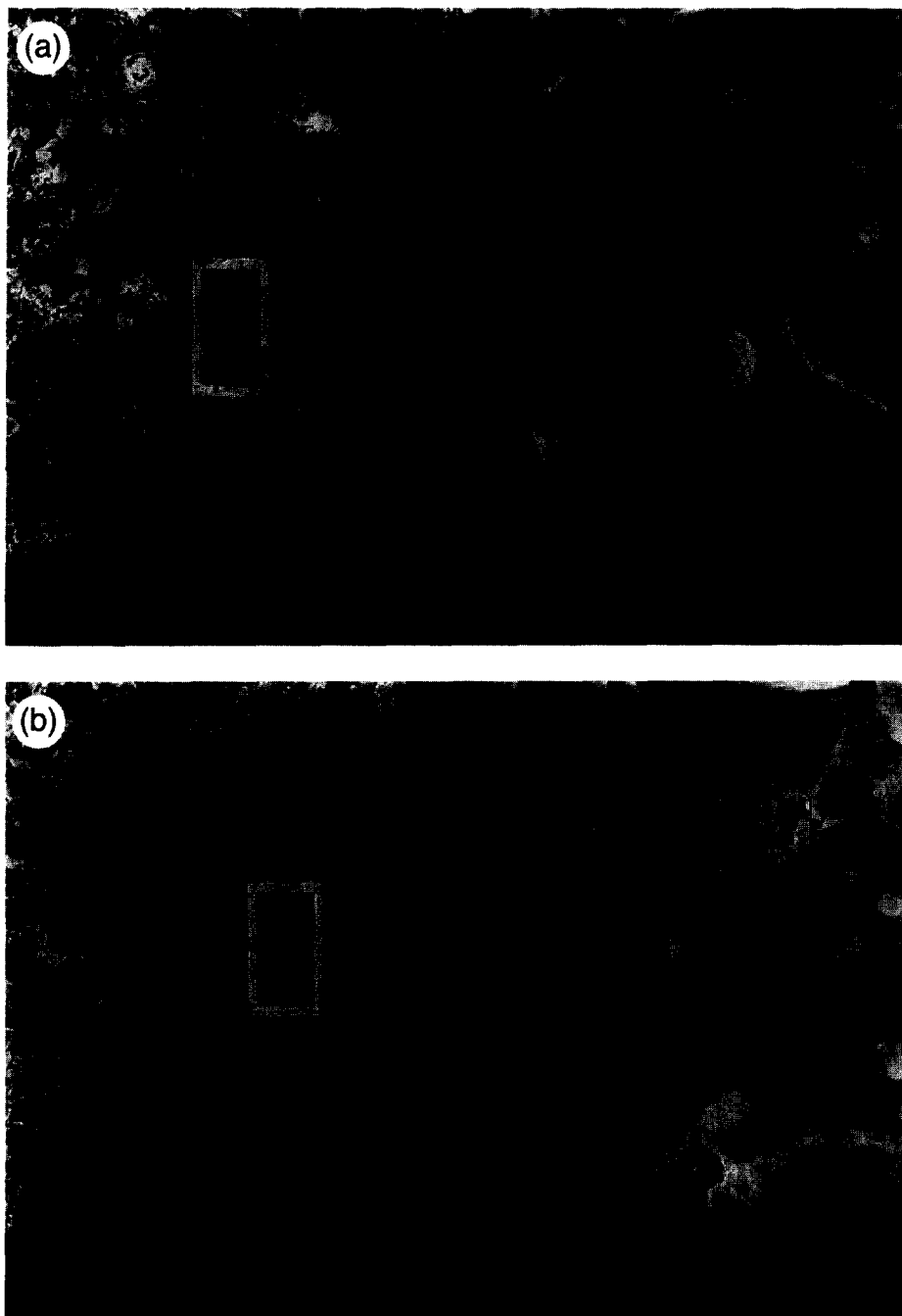


Fig. 7. Surface images of a new (a) and a used (b) monolithic catalyst (Volkswagen).

main contaminant is phosphorus originating from engine oil, followed by the other conventional oil additives, calcium and zinc. The main fuel-originating contaminants, sulphur and lead, vary considerably, due to the various qualities of fuels used

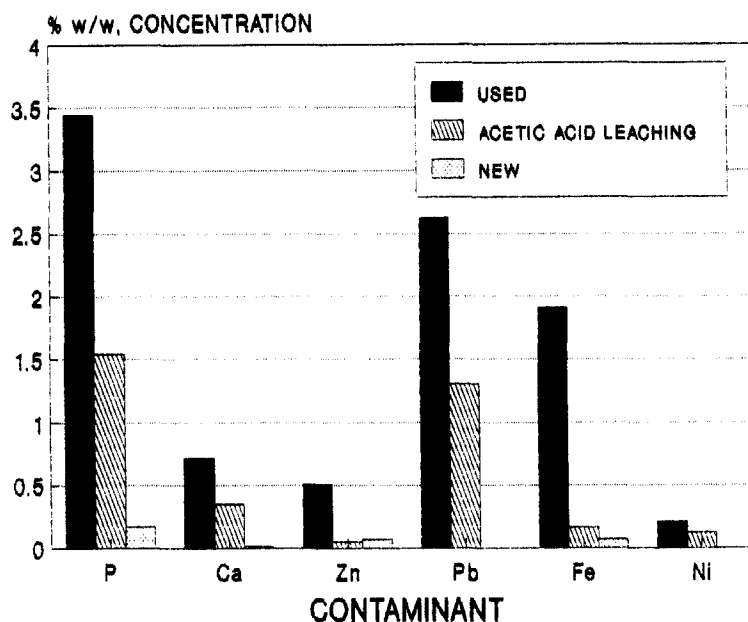


Fig. 8. Comparison of the surface accumulation of contaminants of a new, used and acetic acid leached monolithic catalyst (Volkswagen).

in the vehicles. Lead content, however, is considerably lower than the reported values from catalysts used with leaded gasoline in USA at 70's and 80's (up to 10% w/w of lead has been reported) [1]. In Fig. 6 and Table 2 a comparison is also made between the surface contaminants concentration on the washcoat surface and in the washcoat pores. For all catalysts the surface concentrations were considerably higher than those in the pores showing that the main part of the contaminants is accumulated on the washcoat surface. In Fig. 7 images of the surface of a new and a used catalyst are shown. The used catalyst surface configuration is influenced by foreign particles originating in contaminants. This surface contaminants accumulation acting by a fouling (pore-mouth poisoning) mechanism influences the catalytic activity by clogging the surface pores. Phosphorus, as stated in many previous studies [5,15,16], has no direct interaction with active metals but it acts by a cumulative fouling mechanism. The possible chemical forms of accumulated phosphorus are various phosphates such as calcium phosphate (as shown in Fig. 5 there is a correlation between phosphorus and calcium surface concentration for most of the used catalysts) and other metal phosphates. At higher temperatures ($> 900^{\circ}\text{C}$) the formation of aluminium phosphate is also possible [16]. From the other contaminants, sulphur [17,18] and lead [19] are significant, since they may cause direct deactivation of the active metals. The main quantity of lead is leaving the catalyst with the exhaust gases, the remaining forms stable compounds such as lead sulphate [5]. Since acetate is a good leaching lixiviant, both for phosphates and lead sulphate, an acetic acid [20] leaching test was selected to test the possibility of removing these basic contaminants.

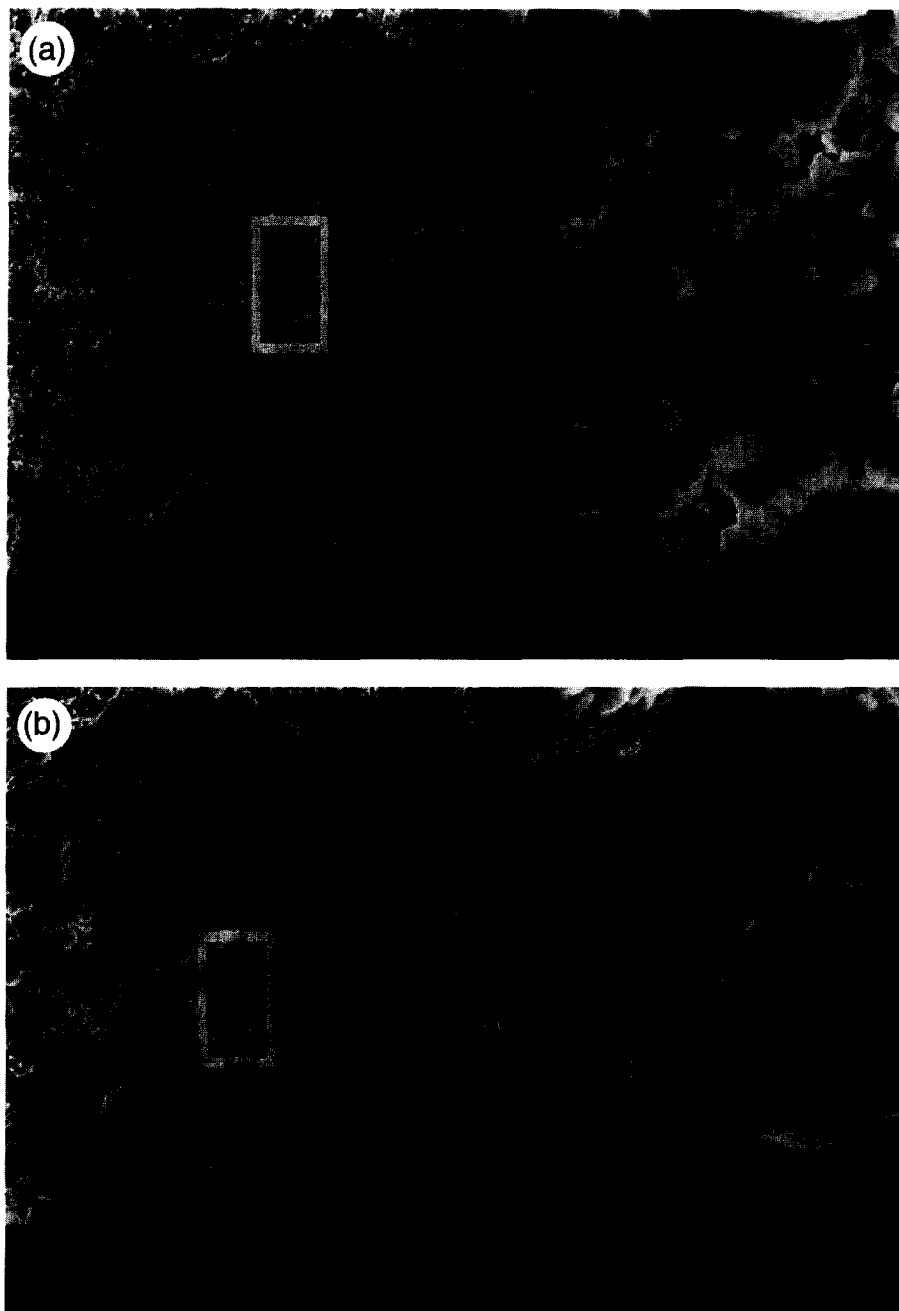


Fig. 9. Surface images of used (a) and acetic acid leached (b) monolithic catalyst (Volkswagen).

3.2. Acetic acid leaching test

To demonstrate the above suspected deactivation mechanism, a preliminary acetic acid leaching test was done. Acetate was used as a rejuvenation procedure

Table 3
Acetic acid leaching results

| Element | Catalyst type and composition (% w/w) | | | |
|------------|---------------------------------------|------|---------|-------------------------|
| | New | Used | Leached | Contaminant removal (%) |
| Phosphorus | 0.17 | 3.44 | 1.54 | 55.2 |
| Calcium | 0.01 | 0.71 | 0.35 | 50.7 |
| Zinc | 0.05 | 0.51 | 0.07 | 86.6 |
| Lead | 0.00 | 2.62 | 1.31 | 50.2 |
| Iron | 0.07 | 1.91 | 0.17 | 91.2 |
| Nickel | 0.00 | 0.21 | 0.12 | 42.0 |

for catalysts contaminated by large amounts of lead at the times when leaded gasoline was used [6]. Acetic acid is a proposed lixiviant for calcium phosphate dissolution [20]. The leaching test was carried out by treating catalyst samples with 8% acetic acid solution at 40°C for two hours in an agitated water bath. The results of this test are presented in the form of SEM images (Fig. 8) and EDS surface analysis (Fig. 9). In Fig. 8 a comparison is made between the surface image of a used and a leached catalyst. It is obvious that after leaching a large amount of the clogged pores is liberated. This effect is followed by a significant removal of contaminants from the surface as shown in Fig. 9 and Table 3. The above test strengthens the argument that fouling is the main deactivation process in used catalysts and a rejuvenation procedure is possible.

4. Conclusion

SEM-EDS analyses were used to examine used commercial automotive catalysts of various types and active life.

Phosphorus, lead, calcium, sulphur, iron and zinc were found to be the main inorganic contaminants accumulated on the catalyst washcoat surface.

Engine oil seems to be the main contributor of contaminants.

The accumulation of contaminants decreases longitudinally (upstream to downstream).

The main quantity of contaminants is accumulated on the washcoat surface, while accumulation inside the washcoat pores is considerably lower.

Fouling (possibly through pore-mouth poisoning) is possibly the main deactivation mechanism.

The main contaminants are easily removed by acetic acid leaching and a rejuvenation procedure is possible.

Further work is in progress to establish a rejuvenation procedure.

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