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Causes of deactivation and an effort to regenerate a commercial spent three-way catalyst

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1. ABSTRACT

The main aim of the present paper is to summarize the research work of our group with respect to the deactivation and regeneration of the three-way automotive catalysts (T.W.C.). Measurements describing the effect of the thermal deactivation and contaminants accumulation on the structure and the efficiency of an aged T.W.C. are presented. A variety of techniques, such as SEM-EDS, XRD, CTEM, ICP-AES, ICP-MS and AAS, were applied in this effort. Since, thermal deactivation is more or less irreversible, special attention was given to the nature and the distribution of the contaminants accumulated on the T.W.C. active surface. Based on these observations, a leaching procedure with acetic acid was tested and optimized in laboratory scale for the removal of the contaminants. The leached samples of the T.W.C. were examined with respect to their catalytic activity (CO and C<sub>2</sub>H<sub>4</sub> oxidation, NO reduction and N<sub>2</sub> production). The leaching procedure seems to improve considerably the catalytic activity of the aged catalyst.

2. INTRODUCTION

During operation the three-way automotive catalysts (T.W.C.) display a general loss of their catalytic activity. Deactivation of the T.W.C. can result from many processes. The processes fall into four general categories: chemical, thermal, fouling and mechanical [1]. During vehicle operation, any or all of the categories can contribute to catalyst deactivation. With current catalyst package technology in combination with properly-tuned engine operation and emission control, deactivation resulting from carbonaceous deposits fouling and mechanical categories is minimal. Thus, catalyst deactivation during normal vehicle operation typically results from mechanisms in the chemical and/or thermal categories. Thermal deactivation includes the

following mechanisms [2]: noble metals sintering, noble metals alloying, support changes, noble metal-base metal interactions, metal/metal oxide-support interactions, oxidation (alloy segregation), noble metal surface orientation changes and metal volatilization.

The methods to study thermal deactivation mechanisms are direct or indirect. The direct methods include microscopic studies by various techniques of the constituents of the catalyst's washcoat (active metals, promoters, stabilizers, contaminants and support constituents) and macroscopic physical characteristics (total and active surface, pore size and volume) [3-8]. Indirect methods include comparison of the catalytic activity between fresh and aged catalyst [2,7,9]. The catalyst is usually aged in laboratory scale by simple heating in a controlled atmosphere furnace at high temperatures (800°C-1000°C), which induce thermal deactivation mechanisms. Extrapolation of results obtained from laboratory reactor experiments to the actual exhaust environment should be done with caution [4]. The aim of the present research was to examine in what extent XRD (X-Rays Diffraction) and CTEM (Conventional Transmission Electron Microscopy) may give information on the thermal deactivation mechanisms (mainly precious metals sintering and support changes) of a commercial T.W.C. aged under vehicle operating conditions. This is important, since during laboratory aging normally the conditions are selected to induce only a specific deactivation mechanism, while under vehicle operation conditions the situation is more complex, due to the simultaneous presence of all deactivation mechanisms.

Chemical deactivation is the result of contaminants accumulation on the active surface of the T.W.C. and their action as poisons. There are three types of poisoning mechanisms [10]:

- chemical poisoning (the poisons interact chemically with the substrate or the active metals)
- physical poisoning (the poisons interact mainly as foulants by clogging the pores of the substrate)
- inhibition (instantaneous and active for the time period while the poison is present in the exhaust gas flow).

The most detrimental contaminants are those originating from fuel and engine oil [11-12]. Most lubricating oils for engine use contain additives designed to improve such properties as lubricity, detergency, oxidation resistance and viscosity. The common lubricating additive ZDP (zinc dialkyldithiophosphate) [13-15] 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, the presence of small quantities is unavailable. So the fuel is a potential contributor of such contaminants. Another possible fuel originating contaminant is Mn, from the fuel additive MMT (methylcyclopentadienyl manganese tricarbonyl added to unleaded gasoline in order to improve the performance of the engine [16-17]. The engine and exhaust system construction material can also contribute by 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. Chemical quantitative analysis by ICP-AES (Inductively-Coupled Plasma/Atomic Emission Spectrometry) and ICP-MS (Inductively-Coupled Plasma/Mass Spectrometry) were applied to determine the contaminants accumulation and longitudinal distribution and estimate precious metals losses on the aged T.W.C..

The main compounds formed by the contaminants at the T.W.C. operational conditions are phosphates, sulphates, aluminates and oxides [12-13,17]. The contaminants are selectively

accumulated on the external surface of the washcoat [18]. Most of these compounds are readily dissolved in acidic environment. Thus, an acid-leaching procedure is expected to remove substantial quantities of the contaminants from the catalyst surface. The use of strong acids is not recommended since, they will possibly attack the useful constituents of the substrate and weak organic acids (acetic or oxalic) are preferred. Oxalic acid has been applied for the regeneration tests of a hydrodesulphurization catalyst [19] and acetic acid for a Pt/NiO industrial catalyst [20]. Acetic acid ( $pK_a=4.72$ ) is preferred since, is a weaker acid than oxalic acid ( $pK_{a1}=1.21$ ). Preliminary leaching tests using acetic acid combined with SEM photos and EDS surface analysis shown a substantial removal of contaminants from the surface of the catalyst [18]. A summary of our comprehensive work [21] on regeneration of T.W.C. by acetic acid leaching, in an effort to optimize the leaching conditions and to check the catalytic activity of the leached material is cited in this presentation.

### 3. STUDIES OF THERMAL DEACTIVATION

#### 3.1. Experimental

A fresh and an aged commercial monolithic catalytic converter of the same origin were used for the XRD and CTEM studies. The aged catalyst was derived from an automobile with 60000km mainly under urban conditions. The main characteristics of the examined catalysts were:

- shape: oval
- dimensions: length 15.2 cm, max major axis 14.5cm, minor major axis 6.7cm
- channels density: 62.2 channels/cm<sup>2</sup>
- wall thickness: 0.16mm
- hydraulic diameter: 1.1mm

The same fresh and aged T.W.C. were used in all experiments included in this presentation.

Qualitative Energy Dispersion (EDS) analysis, performed by a JEOL 840 (LINK AN10S, ZAF 4) scanning electron microscope, show that the external surface of the new and the aged T.W.C. mainly consists of Al (Al<sub>2</sub>O<sub>3</sub>) and Ce (CeO<sub>2</sub>) as support, Zr (ZrO<sub>2</sub> as promoter), Ba (BaO or BaSO<sub>4</sub> as stabilizer). Calcium and phosphorous detected in the aged catalyst are contaminants originating from the lubricants and the fuel.

Material derived by scraping of the wash coat of the fresh and the aged T.W.C. was ground down to fine powder before XRD (SIEMENS D-500 X-ray generator with a CuK $\alpha$  X-ray source) and CTEM (JEOL 120CX operating at 120kV) analysis. For the CTEM analysis, ethanol was added in a few finely ground grains of the catalyst washcoat and the resultant suspension was treated in an ultrasonic bath before deposition of a few drops on a 200mesh copper grid coated with a holey carbon film.

#### 3.2. Results and discussion

Preliminary XRD studies were carried out in the range of 30°<2 $\theta$ <50° for the fresh and the aged catalyst samples in the range of 30°<2 $\theta$ <50° in order to include the main Pt [111] and [200] reflections at  $d=2.265\text{\AA}$  ( $l/l_0=100$ ) and  $1.962\text{\AA}$  ( $l/l_0=53$ ) respectively. The XRD pattern of the fresh catalyst show pronounced reflection peaks representative of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub> and cordierite (small quantities scraped during the washcoat separation procedure). A reflection

peak at  $d=2.2733\text{\AA}$  was a possible indication of Pt[111], but was confused with the  $\gamma\text{-Al}_2\text{O}_3$ [222] reflection peak at  $d=2.28\text{\AA}$ . The reflection peak of Rh was not expected to have measurable intensity, since Rh is in the atomic state or in the form of very small particles [11]. The XRD pattern of the aged catalyst show significant changes. New high temperature  $\text{Al}_2\text{O}_3$  phases ( $\delta$  and  $\theta\text{-Al}_2\text{O}_3$ ) are present [4]. The Pt[111] reflection peak is again confused with the  $\gamma\text{-Al}_2\text{O}_3$ [222] and the  $\delta\text{-Al}_2\text{O}_3$  at  $d=2.28\text{\AA}$  reflection peaks. The position where the Pt/Rh alloy exists [6] is covered by the pronounced alumina and cerium oxide reflection peaks. The characteristic reflection peaks of the compound  $\text{CeAlO}_3$  observed by Hubert et al.[6] at temperatures higher than  $950^\circ$ , were not derived during this study, since, possibly under the specific vehicle conditions, temperatures in this range were not achieved.

In the wash-coat of fresh catalyst the existing phases were recognized by Selected Area Diffraction (SAD) using  $1\ \mu\text{m}$  aperture. Two discrete cases can be distinguished as shown on the Fig.1(a) and (b). In the first one, the characteristic polycrystalline material rings are identified, corresponding to the intense reflections of  $\text{ZrO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$ , with an accuracy of 1%, respected to the X-rays diffraction data. They are shown with big and small arrows respectively on the Fig.1(a) and (b). The second case presents a mixture of  $\text{CeO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$ . The rings that corresponds to the  $\text{CeO}_2$  diffraction intensity are shown by big arrows and the small arrows indicates the positions of the  $\gamma\text{-Al}_2\text{O}_3$  rings. The electron diffraction patterns from the aged catalyst samples are shown on Fig.2(a) and (b) that correspond to the above mentioned cases. From the spots size on Fig.2(a) it is clear that the size of the  $\text{ZrO}_2$  particles of the aged material does not change sensibly. On the other hand the spot size on the Fig.2(b) directly reveals the change of  $\text{CeO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  particles into larger ones. Another interesting result is the presence of very weak extra spots, indicated by double arrows on Fig.2. These spots are invisible on E.D. patterns from the samples of the fresh catalyst and they are rarely present on E.D. patterns from the aged material. The presence of the extra spots on the E.D. patterns of the aged material on the position that exactly corresponds to that of the strongest Pt[111] reflection suggest the origin of these spots to be the sintered Pt particles. Although the vicinity of the Pt [111] spot to that of  $\text{CeO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  rings does not allow the direct imaging of the Pt particles by using Dark Field (D.F.) mode, due to the high contrast support ( $\text{Al}_2\text{O}_3$ ). The average particle size was estimated to be less than 10 nm.

The use of CTEM enables particle size to be measured and in several cases make possible the distinguish between their nature, using dark field imaging mode. As already mentioned the existence of Pt particles is suggested from ED patterns but the diffraction conditions restrict the direct imaging. The  $\text{CeO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  particles were directly presented on D.F. images. On E.D. patterns on Fig.1 and Fig.2 the small circles indicate characteristic positions of the objective aperture for the selective D.F. imaging of the several phases. The corresponding images are presenting in Fig.3 and in Fig.4 for fresh (a) and aged catalyst (b) respectively. On Fig.3 the D.F. micrographs imaging  $\text{ZrO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  crystallites are shown. The objective apertures DF11 (on Fig.1(a)) and DF21 (on Fig.2(a)) were used, corresponding to [111] ring of  $\text{ZrO}_2$ . In the same way the micrographs on Figs.3 represent the particles of  $\gamma\text{-Al}_2\text{O}_3$  and Fig.4 the  $\text{CeO}_2$  crystallites. The size of  $\text{ZrO}_2$  crystallites was found to be from 4 to 9 nm for the fresh catalyst and from 6 to 12 nm for the aged material. The size for  $\text{CeO}_2$  crystallites was from 5 to 15 nm and 10 to 45 nm respectively. In the case of  $\gamma\text{-Al}_2\text{O}_3$  particles from 10 to 17 nm and from 20 to 45 nm were measured, although large crystallites of  $\gamma\text{-Al}_2\text{O}_3$  with size up to 250 nm were detected. It is obvious that the size of  $\text{CeO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  particles is nearly

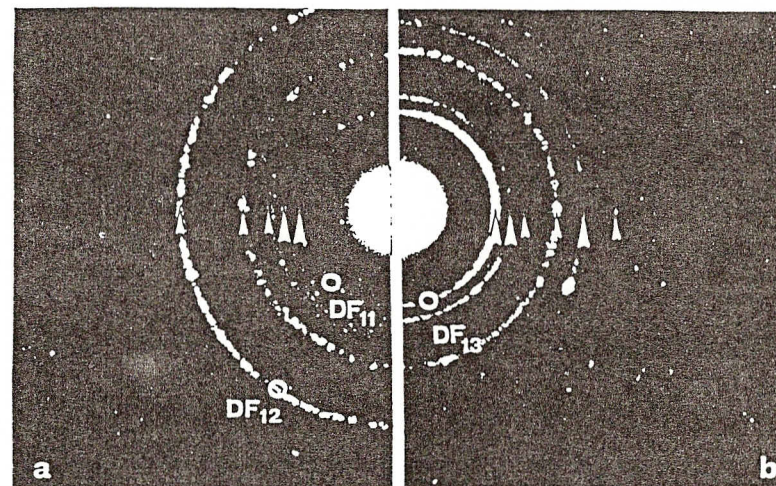


FIGURE 1. E.D. patterns from the washcoat of the fresh T.W.C.. The small circles indicates the positions of the objective aperture used for D.F. imaging. The small arrows show the diffraction rings due to  $\gamma\text{-Al}_2\text{O}_3$  and big arrows the position of  $\text{ZrO}_2$  and  $\text{CeO}_2$  rings.

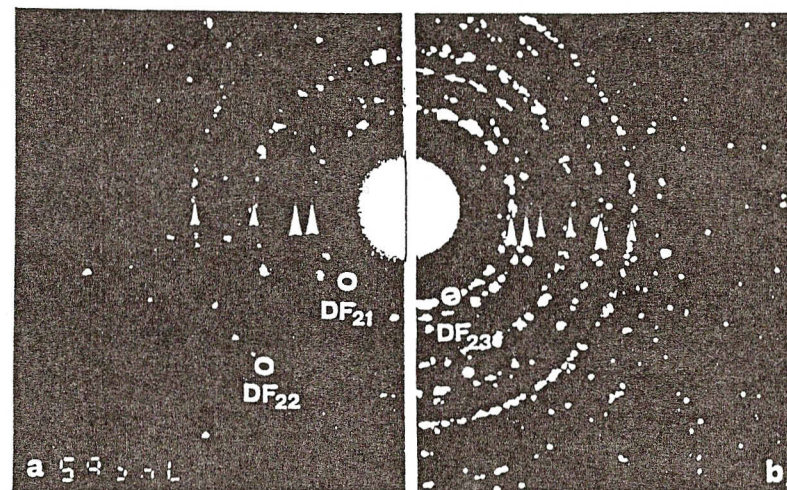


FIGURE 2. E.D. patterns from the washcoat of the aged T.W.C.. The small circles indicates the positions of the objective aperture used for D.F. imaging. The small arrows show the diffraction rings due to  $\gamma\text{-Al}_2\text{O}_3$  and big arrows the position of  $\text{ZrO}_2$  and  $\text{CeO}_2$  rings.

duplicated as the main result of the sintering effect, while the  $ZrO_2$  particles remain almost unchanged.

Although XRD and CTEM permits the study of thermal deactivation due to the crystalline changes of the major washcoat constituents (in our case  $\gamma-Al_2O_3$ ,  $CeO_2$  and  $ZrO_2$ ), poor indications were obtained with respect to precious metals thermal changes (mainly sintering and alloying). The main cause was the low content of the precious metals and the interference from the major washcoat constituents. Further investigation is in progress with respect to the selective dissolution of alumina from the washcoat samples by acids, in order to prevent interference during the XRD and CTEM studies.

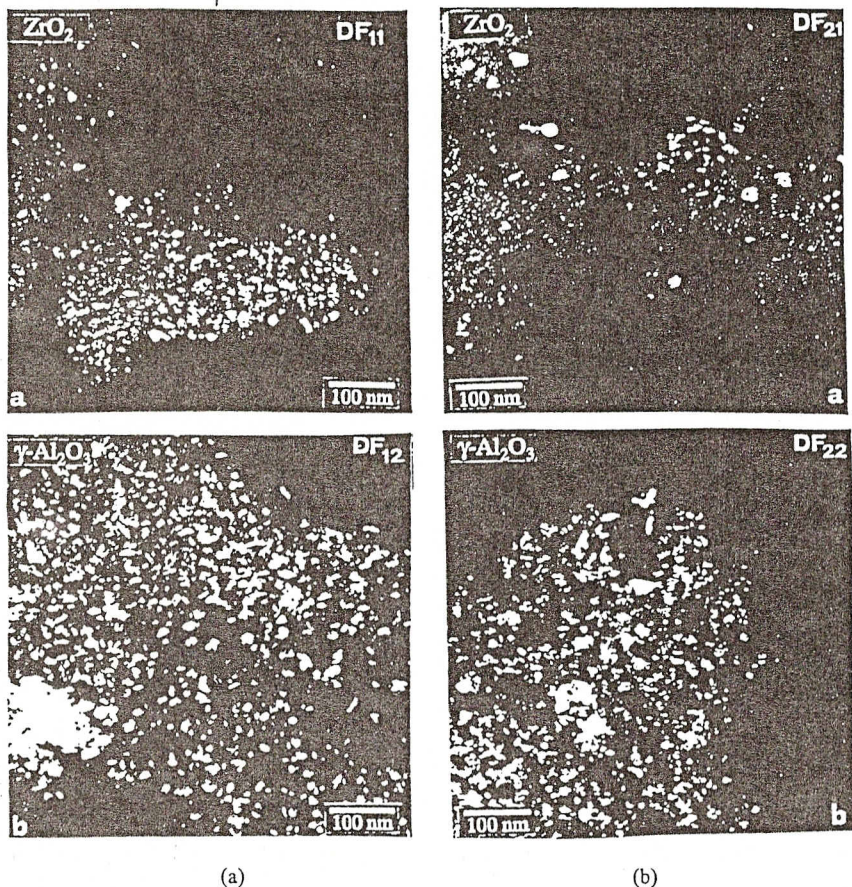


Figure 3. Selective D.F. imaging of  $ZrO_2$  and  $\gamma-Al_2O_3$  particles from the fresh (a) and the aged (b) T.W.C.. The objectives apertures used for the D.F. imaging are indicated in Figs. 1&2

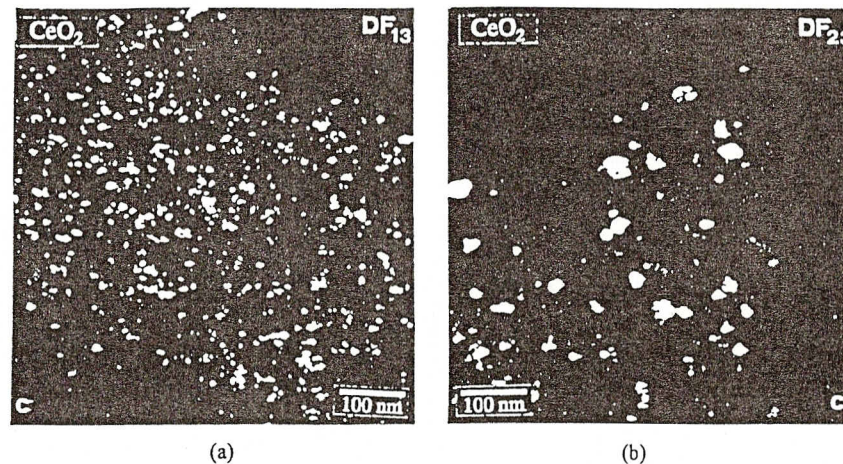


Figure 4. Selective D.F. imaging of  $CeO_2$  particles from the fresh (a) and the aged (b) T.W.C.. The objectives apertures used for the D.F. imaging are indicated in Figs. 1&2

#### 4. CONTAMINANTS ACCUMULATION AND DISTRIBUTION

##### 4.1. Experimental

Selected samples from the center of the fresh T.W.C. and the inlet, center and outlet of the aged T.W.C. were ground down to fine powder and mixed thoroughly to be homogenized. The homogenized samples were heated at  $550^\circ C$  for 6h to remove any volatile carbonaceous material. Then they were digested under pressure for five hours at  $180^\circ$  in PTFE containers (200mg of material with 3ml  $HNO_3$  65%+1ml  $HCl$  37%+0.5ml  $HF$  40%). All chemicals used were at least of analytical grade. Twenty two elements were quantitatively detected. Zn, Ba, Mn, Fe, V, Ti, Sr, Ca, Na, K, P and S were measured by ICP-AES (Perkin Elmer 400), with the cross flow nebulizer and scandium as internal standard. Cr, Co, Ni, Cu, Zr, Nb, Rh, Hf, Pt and Pb were measured by ICP-MS (Perkin Elmer ELAN 6000), with cross flow nebulizer and indium as internal standard. The presented results are the mean of four separate measurements for samples of the same origin.

##### 4.2. Results and discussion

Some of the measured elements (Ti, Zr and Ba) are mainly components of the T.W.C. acting as catalytic activity promoters or washcoat stabilizers and their content does not change considerably between the fresh and the aged T.W.C.. The same happens with another group of elements (Co, Nb, Hf, V, Sr, K and Na), which seems to be rather impurities of the raw materials used in the construction of the T.W.C. than contaminants. Sulphur was detected in both aged and fresh catalyst almost in stoichiometry with  $BaSO_4$ , which is the possible form of Ba used as washcoat stabilizer, and it was difficult to separate the quantity of sulphur accumulated as contaminant. The rest of the elements (Cr, Ni, Cu, Zn, Mn, Fe, Pb, P and Ca)

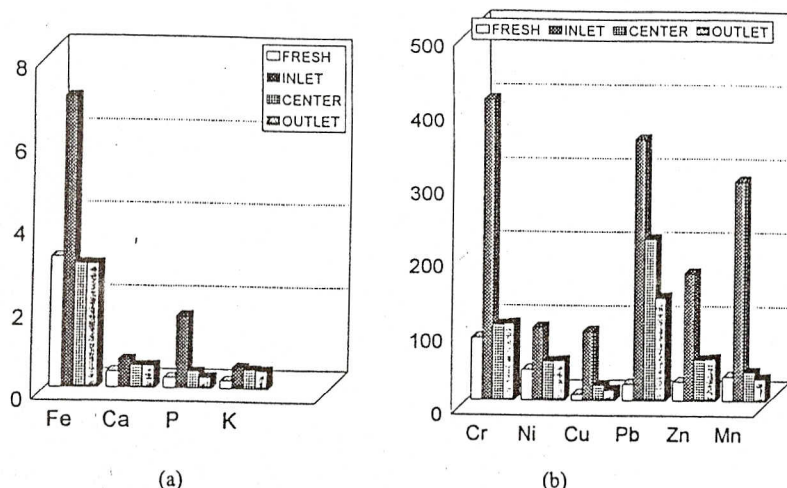


Figure 5. Comparison between the longitudinal contaminants distribution and the content of the respective elements in the fresh T.W.C. ((a) in g/kg and (b) in mg/kg).

as well as the active metals show a significant difference between the contents in the samples of the fresh and the aged catalyst. The longitudinal distribution of the content of the contaminants is shown in Fig.5 and for the precious metals in Table 1. For all contaminants the near exhaust gas inlet content is considerably higher than the respective contents of the fresh and the other parts of the aged T.W.C.. The same results were obtained by SEM-EDS analysis [18]. The content of the active metals seems to be considerably lower in the aged than in the fresh T.W.C., especially at the gas inlet section. Although a part of these differences may be attributed to weight changes (due to contaminants accumulation and crystalline changes of the washcoat), losses of active metals for mechanical reasons is possible.

Table 1. Precious metals content in the fresh and longitudinal distribution in the aged one (mg/kg).

Metal	Fresh	Inlet	Center	Outlet
Pt	4100	3400	3600	3600
Rh	794	680	700	710

## 5. REGENERATION PROCEDURE

Cylindrical specimen (length 2.2cm, diameter 1.6cm) derived from the inlet of the aged catalyst, where the main quantity of contaminants was detected, were used for the leaching

tests. The leaching tests were accomplished in a glass column, while the leaching solution was continually pumped upstream through the specimen channels and recycled. After leaching the specimen were thoroughly washed by deionized water to remove remaining traces of acetic acid. Before and after each leaching test, part of the specimen was treated with *aqua regia* by heating at atmospheric pressure in order to dissolve the major part of the washcoat and the contaminants accumulated on the washcoat surface (the extremely refractory cordierite substrate is not affected by these dissolution conditions). The products of this dissolution procedure were analyzed for selected contaminants (P, Zn, Fe and Pb) to determine the main contaminants removal yield of the process. Zn, Fe and Pb were analyzed by AAS (Perkin Elmer 2380) and P by UV spectroscopy (Hitachi U-2000), applying the ammonium molybdate method. As series of experiments at various acetic acid concentrations, temperatures and leaching solution rates was accomplished in order to determine the optimum leaching conditions. The as above determined optimum conditions were: 5% w/w solution of acetic acid, feed rate 18ml sec<sup>-1</sup> (space velocity based on the open front area of the T.W.C. specimen 21600h<sup>-1</sup>) and temperature 40°C. The contaminants removal yields achieved at the optimum conditions were: 78.6% for P, 85.1% for Zn, 64.5% for Fe and 69.5% for Pb.

A number of specimen leached at the optimum leaching conditions, were used in the catalytic activity tests. The tests were accomplished in a laboratory scale apparatus. A gas mixture, which simulates the stoichiometric composition of common car emissions (0.8%CO, 0.1%C<sub>2</sub>H<sub>4</sub>, 0.2%NO and 0.6%O<sub>2</sub> with He as inert gas) was fed to the catalytic reactor. The total flow rate was kept at 1000 ml min<sup>-1</sup>. The analysis of the reactants and products was carried out by means of gas chromatography (Shimadzu GC-14B with two parallel columns, Poropak Q and Molecular Sieve 13X) combined with vacuum chemiluminescence spectrometry for NO<sub>x</sub> analysis (Teledyne Anal. Instrument-NO<sub>x</sub> stack gas emissions analyzer, model 911/912). The conversion yield of pollutants and nitrogen production yield measured at

Table 2. Light-off temperatures for CO and C<sub>2</sub>H<sub>4</sub>, NO reduction and N<sub>2</sub> production (°C). Leached means that these specimen have been washed with the acetic solution at the optimum conditions.

Reaction	Fresh Leached	Fresh	Aged Leached (1)	Aged Leached (2)	Aged
CO	198	200	229	232	258
C <sub>2</sub> H <sub>4</sub>	239	233	237	252	265
NO	234	226	232	243	257
N <sub>2</sub>	256	264	261	265	279

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various temperatures were used for the light-off temperature determination. The results obtained are summarized in Table 2, where the light-off temperatures for fresh, acetic acid leached and aged T.W.C. specimen are compared.

The results show a significant improvement of the catalytic activity for the studied substances. After verification by long term activity tests and real size experiments, may be applicable in practice. The procedure is simple and does not require the removal of the T.W.C. from the exhaust system. The acetic acid solution could be pumped through the exhaust system using the dismantled gas inlet and outlet. The highly corrosive resistant construction of the exhaust system (chromium steel) is not expected to be attacked by the weak acetic acid.

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## Pb Poisoning on Pd-only TWC Catalysts

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**Abstract:** The Pd-only catalyst has made a strong comeback in both TLEV and LEV applications. However, it has been found that Pd-only catalysts are susceptible to Pb poisoning, despite the high Pd loading thereon. Several commercially available Pd-only catalysts were evaluated in this study. After aging with leaded fuel, lead deposition was discovered on these catalysts. The lead appears to be front-loaded and concentrated on the surface of washcoat coatings. It can also penetrate into the washcoat. The impact on catalyst performance is mainly on NOx conversion reduction. TEM elemental mapping and XPS results suggest that Pb preferentially associates with Pd. The hypothesis is proposed that Pb deposition onto Pd occurs because the Pd is competing with Pb for sulfur. Rh-containing catalysts may prove to be strong candidates in compensating for the compromised NOx performance observed in Pd-only catalysts aged with leaded fuel.

## 1. INTRODUCTION

Advances made in TWC catalyst development have made the use of the Pd-only catalysts [1] possible in TLEV and LEV applications, replacing the traditional Pt/Rh catalysts. While Pd-only TWC catalysts had encountered some difficulties with regard to their use in NOx conversion in the past, recent developments have suggested that the NOx emission reduction engendered by the Pd-only catalyst is as noteworthy as that of the Pt/Rh catalyst, while HC and CO conversions are generally better than those obtained using Pt/Rh catalysts [2], despite that the Pd-only catalysts were aged with sulfur-containing fuel [3]. The superior performance of the Pd-only catalyst can, however, be undermined by Pb-poisoning. This paper will cover the Pb poisoning effect on different Pd-only TWC catalysts, Pb association with Pd particles, and the alternative Pb-resistant TWC catalysts.

## 2. EXPERIMENTAL

### 2.1 Catalyst Preparation

Two kinds of Pd-only TWC catalysts were made. One catalyst contains oxygen storage compound (OSC); the other does not. Precious metal and substrate sizes are as follows: