



Regeneration of three-way automobile catalysts using biodegradable metal chelating agent—S, S-ethylenediamine disuccinic acid (S, S-EDDS)

B. Subramanian^a, S.Y. Christou^b, A.M. Efstathiou^b, V. Namboodiri^c, D.D. Dionysiou^{a,*}

^a Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221-0071, USA

^b Heterogeneous Catalysis Laboratory, Chemistry Department, University of Cyprus, University Campus, 1678 Nicosia, Cyprus

^c National Risk Management Research Laboratory, United States Environmental Protection Agency, Cincinnati, OH 45268, USA

ARTICLE INFO

Article history:

Received 23 July 2010

Received in revised form

20 November 2010

Accepted 23 November 2010

Available online 27 November 2010

Keywords:

Three-way catalysts

Biodegradable chelating agents

EDDS

Extraction

Catalyst regeneration

ABSTRACT

Regeneration of the activity of three-way catalytic converters (TWCs) was tested for the first time using a biodegradable metal chelating agent (S, S-ethylenediamine disuccinic acid (S, S-EDDS)). The efficiency of this novel environmentally friendly solvent in removing various contaminants such as P, Zn, Pb, Cu and S from commercial aged three-way catalysts, and improving their catalytic performance towards CO and NO pollutants removal has been investigated. Four samples of catalysts from the front and rear inlets of two different TWCs with different mileages and aged under completely different driving conditions were investigated. The catalysts were characterized using various techniques, such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area measurements (N₂ adsorption at 77 K). Quantitative ICP-MS analyses and SEM-EDS studies show the removal of Zn, P and Pb. SEM-EDS images obtained at low magnification (50 μm) showed considerable differences in the surface morphology and composition after washing with S, S-EDDS. However, XRD studies indicated neither little to no removal of major contaminant compound phases nor major structural changes due to washing. Correspondingly, little or no enhancement in BET surface area was observed between the used and washed samples. Light-off curves show that the regeneration procedure employed can effectively improve the catalytic performance towards NO pollutant.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Three-way catalysts (TWCs) have been in use in automobiles for four decades now. The installation of these catalytic converters in the exhaust pipes of gasoline-powered vehicles helps to reduce emissions and hence air pollution. The TWCs convert NO_x to N₂, CO to CO₂ and unburned hydrocarbons (HCs) to water vapor and CO₂. Due to this reason, they are referred to as three-way catalytic converters.

The active metals in the catalytic converters are mostly platinum or palladium–rhodium catalysts. These catalysts undergo deactivation with continued usage. This deactivation can be of various forms, including physical blocking of the pores, chemical fouling, and mechanical or thermal effects [1]. In all these forms of deactivation, the catalyst fails partially or completely depending on the extent of damage. The causes of deactivation of TWCs are mainly of chemical origin. Contaminants like sulfur and phosphorous arising from fuel and fuel additives are the main cause of deactivation

[2–5]. Metallic contaminants like lead (Pb), iron (Fe), nickel (Ni), and cadmium (Cd) arising from the metallic engine parts also contribute to fouling [3]. Physical mechanisms of deactivation, like thermal sintering of both metal (Pt, Pd, Rh) and support (washcoat) have also been observed in TWCs. While most of these contaminants can be completely removed, and the catalysts regenerated to a good extent, there are other forms of irreversible deactivation. One of the main reasons for studying deactivation is the possibility of reactivation/regeneration of used TWCs.

Reactivation/regeneration of TWCs has attracted the interest of scientists. The reasons for regeneration are many. Initially, the reasons were economic, while later on rising awareness was brought about by environmental concerns. Several methods of TWC regeneration have been investigated, namely high-temperature heating using hydrogen [6,7] and thermal chlorine gas treatment [7,8]. Many of these methods utilize extremely harsh conditions or are invasive involving the dismantling of the catalytic converters. This results in generation of waste as all the materials cannot be reused [9]. Such disadvantages with these methods resulted in exploring alternative options, such as solvent washing as a regeneration technique. Solvent washing has been carried out with several solvents, namely acids, such as citric acid [5], oxalic acid [5] and acetic acid [3] and can be implemented *in situ*. Metal chelating agents like

* Corresponding author. Tel.: +1 513 556 0724; fax: +1 513 556 2599.

E-mail addresses: dionysios.d.dionysiou@uc.edu, dionysdd@email.uc.edu (D.D. Dionysiou).

EDTA have also been tested [10]. These solvents have been effective in removing several contaminants present in the TWC and hence have led to varying levels of regeneration. Some of the solvents used such as oxalic acid may cause irreversible interactions with the catalyst surface causing negative effects. As a result, various mild solvents have been studied for TWC regeneration and Pt/Pd recovery. One innovative study [11] reported the use of the N,N9-dimethylperhydrodiazepine-2,3-dithionediiodine adduct in a mild, non-invasive process which helped recover over 90–99% Pd from a thermally aged TWC.

Recent environmental investigations attribute the use and disposal of catalytic converters to the increase of concentrations of low solubility PGM (platinum group metals) in the environment [12]. Specifically, it was found that mechanical attrition of TWCs leads to increased incidence of Pd and Pt in the environment. The PGM metals also tend to bioaccumulate in the food chain. Research data have shown that typical recycling of TWCs is only about 20–30%. In the 80,000 km life of TWC, 70% of Pd is released into the surroundings along with other trace metals [13]. The recovery from spent TWCs in US was less than 4% in 1999 [13]. Even when regeneration of TWCs is carried out, there is a lot of waste generated as spent acids and metal chelating agents. The disposal of this secondary waste is of great concern. Complexing agents like EDTA increase the solubility of trace metals from the converters in the soil [14], which otherwise have very low solubility in surface waters and soil.

In the present study an environmentally friendly biodegradable metal chelating agent S, S-ethylenediamine disuccinic acid (S, S-EDDS) was evaluated for the regeneration of TWCs. EDDS has been used as an alternative to EDTA. EDTA is the world's most widely used metal chelating agent. However, it is highly persistent in the environment as it cannot degrade biologically. Due to these reasons, there is also a high risk of metal release into groundwater systems. EDDS has been successfully tested for the removal of toxic heavy metals from soils as well as in the enhanced phytoremediation of soils using chelating agents [15–17]. Apart from being biodegradable and environmentally friendly, EDDS is milder than the acids that are currently being used for this process. As a result of these properties, there is lesser risk of release of metals into the soil from spent EDDS [15,16]. Vandevivere et al. [18] studied the biodegradability of metal-EDDS complexes and reported that a 1 mM concentration of Ca-, Cr(III)-, Fe(III)-, Pb-, Al-, Cd-, Mg-, Na-, or Zn-EDDS degraded easily. In most soil washing processes, the efficiency of EDDS is comparable to the benchmark EDTA [15,16]. There is no reported literature of EDDS for TWC regeneration.

It may also be worthwhile to note that the majority of TWC regeneration studies published so far focus on various catalytic activity measurements after *in situ* regeneration with established solvents, like oxalic and citric acids in various concentrations [3,5,19]. The various parameters like flow rate, temperature and extraction time in the experimental setup for regeneration are varied and their effects on catalyst activity are investigated [3,10]. This work, however, reports the efficacy of EDDS in a batch process. This is an exploratory study which could lead to further investigations required to optimize the continuous *in situ* regeneration process.

Based on our initial investigation with various solvents such as organic acids, an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate), and various other biodegradable metal chelating agents (Nitrilotriacetic acid (NTA)), EDDS was selected from these solvents tested. The other solvents tested have environmental concerns. NTA, though biodegradable, is reported to cause adverse health effects [16]. The ionic liquid, Bmim [BF₄], is extremely viscous and non volatile. This leads to problems of removal of the ionic liquid from washed samples. Recent research shows that ionic liquids also pose problems of disposal and toxic product release [20,21]. In comparison to the other solvents tested, EDDS is environ-

Table 1
Technical specifications of TWC samples.

| Mitsubishi (Cyprus) | Ford (USA) |
|--|---|
| Mitsubishi Gallant 1800-model-year 1997 | Ford Windstar – model-year 1997 |
| Mileage – 161,600 miles | Mileage – 101,359 miles |
| Pd and Rh based catalyst | Pd based catalyst |
| Base material | |
| Cordierite (2MgO·2Al ₂ O ₃ ·5SiO ₂) | Cordierite (2MgO·2Al ₂ O ₃ ·5SiO ₂) |
| Dimensions | |
| DS/PS Brick – N/A | DS/PS Brick 1: 38 in ³ [3.15 in. × 4.75 in. × 2.98 in.] |
| DS/PS Brick – N/A | DS/PS Brick 2: 46 in ³ [3.15 in. × 4.75 in. × 3.67 in.] |
| Channel density | |
| N/A | 400 cells per sq in (wall thickness = 0.0065 in.) |
| Channel shape | |
| N/A | Square |
| Washcoat details | |
| Pd-only washcoat – 0.55% by weight. Major oxides – Al ₂ O ₃ , CeO ₂ and ZrO ₂ | Pd-only washcoat – 0.55% by weight. Major oxides Al ₂ O ₃ , CeO ₂ and ZrO ₂ |

mentally benign and has been suggested as an effective substitute to the chelating agent EDTA [16].

The aim of this study was to investigate the effectiveness of S, S-EDDS for three-way catalyst regeneration in a batch washing process as the first step. The extraction efficiencies, XRD structure, contaminant distribution profile in washcoat, and surface area of the washed and used samples were compared. Extraction was performed on catalyst powders and later on pieces of TWC monolith.

2. Experimental methods and procedures

2.1. Sample selection

The aged catalytic cartridges were extracted from two gasoline automobiles – Ford (USA) model Windstar, 1998, and a Mitsubishi (Cyprus) model Galant, 1997. Catalyst powders from both samples were used. Catalyst monolith pieces were only used from the Ford cartridge. The Ford (USA) samples were graciously supplied by the Ford Catalyst Research Department, Dearborn, MI, USA. The Mitsubishi samples were extracted from an aged TWC (Mitsubishi Galant) used in Cyprus. The technical specifications of the TWC samples are listed in Table 1. A similar Ford (USA) catalyst sample with 0 miles (fresh catalyst) was used as a reference sample. Both catalytic converters contained 0.55 wt% Pd. The samples used were extracted from the front inlet of two catalyst bricks. Small pieces of dimensions (2 cm × 2 cm × 2 cm) were used in the contaminants extraction experiments. The pieces of TWC were crushed for XRD and BET surface area characterization studies.

2.2. Chelating agent

EDDS was supplied by Octel Inc., London, UK. The commercial name is Octaquest E30 and is a substitute for EDTA in various applications, namely detergents and water treatment. The S, S isomer is commonly used because it is readily biodegraded [16]. The structure of EDDS is given in Fig. 1.

2.3. Regeneration procedure

The samples (ca. 100 mg) were pretreated by heating (rate 10 K/min) in a 10% H₂/Ar flow at 773 K for 1 h [19]. This pretreatment has been reported by Galisteo et al. [19] for use with Pt-based catalysts to ascertain that the surface Pt is in metallic form and

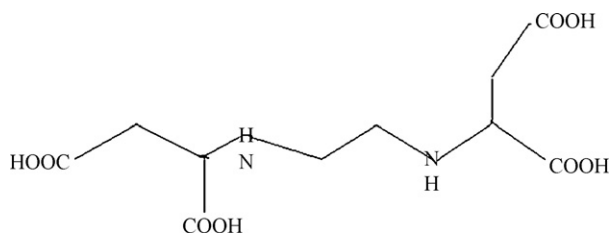


Fig. 1. The structure of EDDS [15].

would not be removed by the mild acid extraction if Pt was partially oxidized.

2.4. Extraction procedure

The EDDS was used without further dilution. A known weight of the catalyst sample was placed with a high solvent ratio (1:50 w/w sample to solvent ratio) in 120 mL Teflon lined vials. The samples were placed in a laboratory shaker for 24 h. This is because high solvent ratios give higher extraction efficiencies and also help offset the effect of pH since complexing agents like EDDS are highly pH dependant [15,17]. It has also been suggested that it may improve target metal extraction by reducing competition effects in a matrix containing other metals. After extraction the samples were washed with de-ionized water by shaking in the same manner for 12 h. Then the samples were dried in an oven at 120 °C overnight. The samples were named by adding the suffix EDDS to the name. The extracted solution was filtered with 45 μm filter and acidified before injection into inductively coupled plasma-mass spectroscopy (ICP-MS).

2.5. Quantitative chemical analysis

The amount of the metals in the liquid extractant was determined using the ICP-MS analysis. An Agilent 7500ce (Agilent Technologies, Tokyo, Japan) was used for this purpose. The samples were filtered through a 45 μm filter and diluted with water when necessary. The samples were acidified with 2 wt% HNO_3 for enhanced detection by the instrument. Analysis was performed according to the EPA method "USEPA method 6020 B" for trace metals in solution [22]. The results from the instrument were in mg/L and they were converted to mg/kg of TWC and expressed as percent removal. The concentration of the various contaminants was used as the basis for removal yield calculations. Though aluminum is a major washcoat constituent, it has been analyzed and quantified.

2.6. Scanning electron microscopy-electron dispersive spectroscopy (SEM-EDS)

SEM-EDS analyses were carried out on a Philips EDAX instrument. In the case of the monolith pieces, they were mounted on the sample holder with the washcoat surface normal to the X-ray electron beam. The elemental analysis was done on channels next to each other so that the values would be representative and there would be less deviation as suggested by Angelidis and Sklavounos [23]. Analysis of three adjacent channels was performed and the quantitative result in wt% presented here is the average of three readings. No coating of samples was done prior to analysis to avoid metal contamination from the sputter coater.

2.7. X-ray diffraction analysis (XRD)

XRD patterns of the used and washed samples were recorded using a Siemens diffractometer in the scan mode from 10 to 60 2θ (0.02/min).

2.8. Surface area and pore size distribution

BET surface area (m^2/g) and pore size distribution analyses were carried out with a Tristar ASAP 3020 (Micromeritics Inc.) with nitrogen adsorption/desorption experiments at 77 K. Degassing was carried out at 200 °C for 2 h prior to the measurements.

2.9. Catalytic activity measurements

The gas-flow system used for conducting catalytic measurements for the $\text{CO}/\text{O}_2/\text{He}$ and $\text{NO}/\text{H}_2/\text{O}_2/\text{He}$ model reactions at 1 atm total pressure consisted of a flow system, a micro-reactor, and an analysis system as previously described [24]. For the CO/O_2 reaction, the feed stream consisted of 1 vol% CO , 1 vol% O_2 and 98 vol% He as diluent. In the case of $\text{NO}/\text{H}_2/\text{O}_2/\text{He}$ reaction, the feed stream consisted of 0.2 vol% NO , 0.3 vol% H_2 , 1 vol% O_2 and 98.5 vol% He as diluent. The amount of TWC sample used was 50 mg (small pieces of 1–3 mm in length), and the total flow rate was 100 NmL min^{-1} . Prior to all measurements, samples were first calcined for 2 h at 500 °C in a 20 vol% O_2/He gas mixture, followed by reduction in H_2 (1 bar) at 300 °C for 2 h. After reduction the catalyst was brought in He flow to the reaction temperature before switching the feed to the reaction gas mixture.

3. Results and discussion

3.1. Extraction efficiencies

3.1.1. Catalyst powders

The initial tests were carried out on catalyst powders in order to test the efficiency of the solvent before testing could be done *in situ* on pieces of monolith. The tests were performed on the powders extracted from the front and rear inlets of both the Ford and the Mitsubishi TWCs.

Table 2 reports the initial amounts in mg/kg of TWC of the basic components and the various contaminants found in the aged commercial Mitsubishi and Ford automobile TWCs. As reported, the sample obtained from Ford is a Pd-only catalyst. The SEM-EDS analysis has also determined minute quantities of neodymium metal. The noble metal composition as provided by the manufacturer is about 0.55 wt% Pd based on the washcoat (Table 1). Cerium and zirconium have also been found to be present. The washcoat is considered consisting of ceria-zirconia ($\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$) mixed oxide and alumina. Since Al is a component of TWC, it cannot be considered as a contaminant. For the Mitsubishi catalyst, previous work has reported 27 wt% loading of washcoat material [3,5]. As it can be seen in Table 2, considerably high concentrations of P, S, Zn and Pb are found in the aged Mitsubishi catalyst, due to prolonged use. The contamination of TWCs has been studied extensively and various concentrations of contaminants have been reported [3,23]. Very high concentrations of contaminants

Table 2

The initial composition (mg/kg_{TWC}) of the four aged TWC samples used.

| Element (mg/kg _{TWC}) | Mitsubishi | | Ford | |
|---------------------------------|------------|---------|---------|---------|
| | FI-M | RI-M | FI-F | RI-F |
| Cu | 1229 | 339 | 878 | 592 |
| Zn | 24,620 | 5560 | 11,984 | 5520 |
| Al | 160,890 | 198,023 | 188,757 | 165,722 |
| P | 21,668 | 10,956 | 14,970 | ND |
| S | 27,421 | 617 | 712 | ND |
| Pb | 29,267 | 14,298 | 113 | 2842 |
| Pt | 75 | 2785 | ND | ND |
| Pd | 44 | 72 | 1610 | ND |
| Rh | ND | 530 | ND | ND |

FI – front inlet; RI – rear inlet; M – Mitsubishi; F – Ford. ND – not detected.

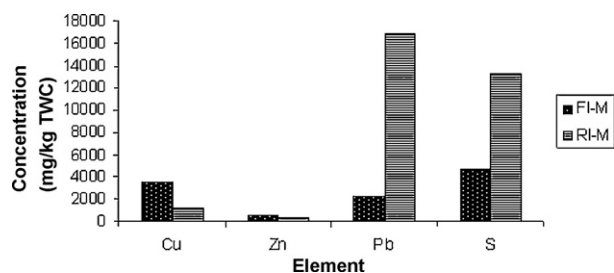


Fig. 2. Extraction of metal contaminants from the Mitsubishi TWC after washing with EDDS.

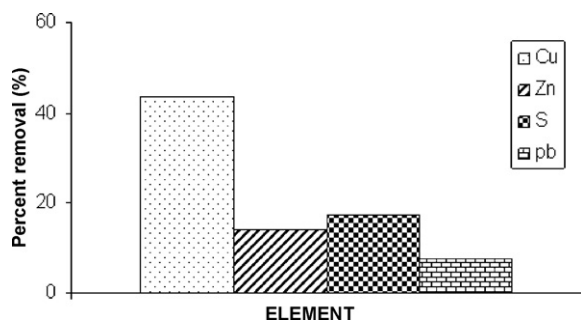


Fig. 3. Extraction efficiency (% removal) of EDDS for Front Mitsubishi.

Table 3
Regeneration of TWC pieces (Ford) by EDDS washing.

| mg/kg _{TWC} | Al | Fe(57) | Fe(66) | Pd | Pb | P | S | Zn |
|----------------------|------|--------|--------|-----|-----|------|----|------|
| Front inlet | 2513 | 1277 | 1792 | 65 | 553 | 8658 | ND | ND |
| Rear inlet | 1035 | 215 | 48 | 94 | 74 | 339 | ND | 1800 |
| Fresh | 55 | ND | ND | 118 | ND | ND | ND | ND |

ND – not detected.

have been found in a completely aged catalyst of 200,000 km [10].

Figs. 2 and 3 show the concentration (mg/kg TWC) and removal (%) of Cu, Zn, Pb and S obtained after washing the Mitsubishi catalyst with EDDS. In the case of the Ford catalyst, the contamination is almost entirely due to P and Zn (Table 2). Table 3 gives the composition of the fresh (0 miles) Ford catalyst. As seen by both SEM-EDS and ICP, there is only a negligible quantity of S present. The extraction efficiencies of EDDS for the Ford catalyst are given in Fig. 4. An important reason for reduced S concentration is the decreasing content of S in fuels due to various EPA standards in the USA since the last decade. It is well known that the source of sulfur contamination in TWCs is the fuel and its additives. The main source of Zn and P is from ZDDP (zinc dialkyl dithio phosphate) which is used as a lubricant and an anti-wear agent in the vehicle systems [25,26].

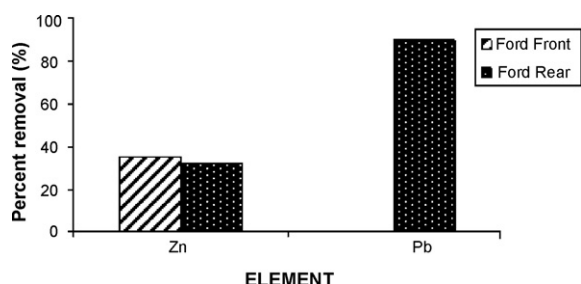


Fig. 4. Extraction efficiency (removal %) of EDDS for Zn and Pb for Ford TWC.

3.1.2. Extraction of contaminants on TWC pieces

The results of the extraction of contaminants on 2 cm × 2 cm × 2 cm cubic TWC pieces (Ford) are reported in Table 3. From these values, it can be seen that the Ford catalyst was considerably contaminated after comparing the fresh and used TWCs. Sulfur was not detected in this catalyst both by ICP-MS and SEM-EDS analyses, thus suggesting that this specific TWC can be considered to be largely contaminated by phosphorous. The characterization of P-poisoned TWCs has been studied extensively by Rokosz et al. [27]. Phosphorous was found to form an overlayer of Zn, Mg phosphates and a layer of aluminum phosphates within the pores of the washcoat. The removal of phosphorous was found to be about 8600 mg/kg from the front inlet, where the contamination by P is significantly higher than in the rear inlet (Table 3).

The removal of P by oxalic acid has been investigated and results were reported [10,28]. Oxalic acid is a relatively stronger acid than EDDS with a pKa of 1.20. Such an acid has been found to have greater dissolution efficiency towards phosphates and phosphites. EDDS, on the other hand, has a pKa value of 2.4 indicating that it is a much weaker acid [16]. Considerably high concentrations of Fe and Zn were also observed in the liquid extracts. Aluminum leaching from the used samples was significantly higher than the fresh sample. This could be explained by the fact that poison-P was in the form of some Al salts resulting in the removal by the EDDS. A similar case was observed by Galisteo et al. [19] in the washing process by citric acid of a commercial diesel catalyst. The leaching of Al was much higher than that of the fresh sample. These observations suggest that EDDS is a promising solvent for the removal of metal and P contaminants deposited on a TWC. The leaching of the active metal Pd was much higher in the fresh sample where it was in an uncombined, elemental form. The extraction of Pd was drastically reduced in the used samples and this can be explained by the multiple effects of Pd sintering at such severe TWC operation conditions as well as the reduction of PGM that takes place along with Ce present on the surface of washcoat [2,29,30]. This has been explained using various model PGM catalysts loaded on the surface of Al₂O₃/Ce–Zr mixed oxides, where hydrogen gas used for reduction was consumed to a larger extent than what required for the reduction of the active metals, thus suggesting a “hydrogen-spillover” effect.

A main parameter for the extraction of metals by chelating agents is the stability constant *K*. Stability constant values of various metals for complexation by EDDS have been determined previously [16]. The log *K* values are given as 12.7 for Pb and 22 for Fe [31,32]. Cu-EDDS (log *K* = 18.4) and Zn-EDDS (log *K* = 13.4) are stronger complexes than Pb-EDDS [32]. The stability constant (*K*) is an important parameter which determines the stability of a metal complex in the environment. The conditional log *K* values of most metal complexes in EDDS have been found to be higher than those reported in the literature for citric, oxalic, and acetic acids which have been used for the regeneration of TWCs. Formation of metal–EDDS complexes in soil has been found to be highly influenced by the presence of Ba and Ca in soils [16]. Quantitative metal analyses have shown the presence of considerable concentrations of Ba and Ca in the present TWC samples (results not presented here). In previous studies, the effect of competition on the regeneration of TWCs has not been considered. In the case of EDTA, the extraction of metals could be influenced by competition with Ba and Ca [16]. Further fundamental studies are required to establish competitive effects of other metals present in the sample on extraction efficiencies with EDDS as a solvent, to better understand the mechanisms of regeneration.

3.2. Characterization results

3.2.1. SEM-EDS analysis

Table 4 shows the wt% concentration of the chemical elements detected in the Ford TWC pieces averaged over two areas on each

Table 4
Concentrations (wt%) of various chemical elements measured by EDS analysis over Ford TWC pieces.

| Element | Fresh | Used | Washed-EDDS |
|---------|-------|------|-------------|
| Ni | 3.4 | 1.9 | – |
| Zn | 3.6 | 2.4 | – |
| Mg | 1.9 | 1.2 | 0.8 |
| Al | 52.4 | 50.4 | 34.3 |
| Si | 5.4 | 6.5 | 4.6 |
| P | 14.1 | 14.7 | 9.1 |
| S | 0.9 | 0.8 | – |
| Pd | 5.8 | 4.6 | 4.5 |
| O | – | – | 46.7 |
| Nd | 12.5 | 17.3 | – |

of the adjacent channels of the washcoat. The SEM-EDS analysis was carried out on both powders and monolith pieces of catalyst. In the case of powders, it was not possible to obtain a concentration profile of the components in the TWC. The elemental analysis of the powders was carried out before and after washing. In the case of catalyst monolith pieces, the composition of the channels in the TWC was analyzed. A variation in the elemental composition of the used and washed samples was observed. In the case of the catalyst monolith, the analysis was done on the washcoat directly. As explained in the previous section, the TWC was exposed normally to the electron beam. Al, Si and Pd are clearly detected which are components of TWC, along with Zn, P, Ni. Mg might be considered as contaminant in TWC, however, this element could also be originated from cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) which is used as support of washcoat material. Lead (Pb) which has been found in the present sample by ICP analyses, has not been detected in this analysis. It is not clear whether Pb peak is present here among the noise. Another possibility is that Pb could be present inside the depth of the washcoat [22]. The configuration used here does not detect the signals from inside the washcoat. The values reported in Table 4 are representative of the whole surface.

Figs. 5 and 6 show the composition of the same catalyst (Ford) analyzed as both monolith pieces and powder, respectively. There is a high probability that the peak marked as sulfur (Fig. 5) is noise, because the major emission lines of S were not present. This is further validated by the fact that the ICP analysis found almost no S present in the samples. One aspect that needs discussion here is that the P emission peak is significant but its values expressed in wt% show a remarkable decrease when compared to the used catalyst. There is also a reason of possible superimposition by the Zr L peak as the P K and Zr L energy lines are very close to each other at 2 KeV [2,18]. In the used sample, the peak might correspond to P due to the high concentration present. In the washed sample, the higher side of the peak must correspond to the Zr emis-

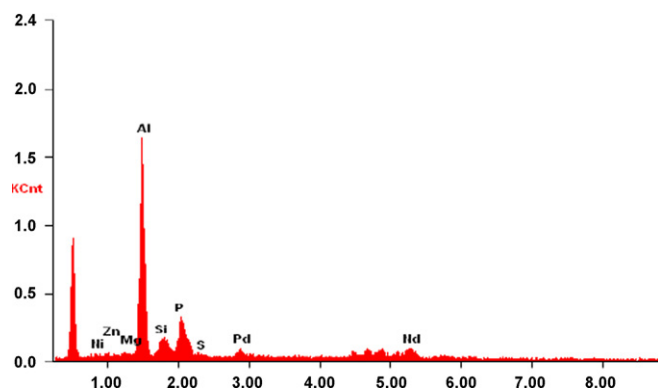


Fig. 5. EDS energy lines of catalyst pieces (used).

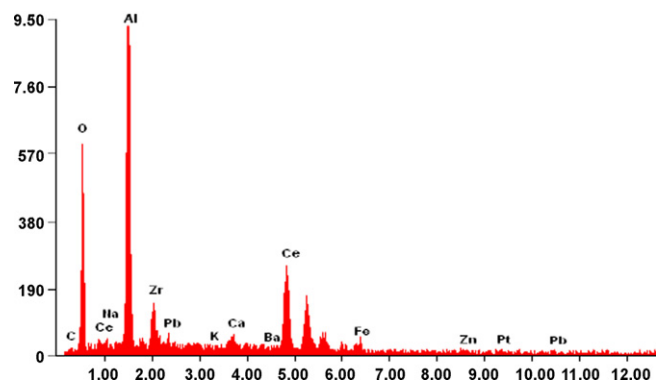
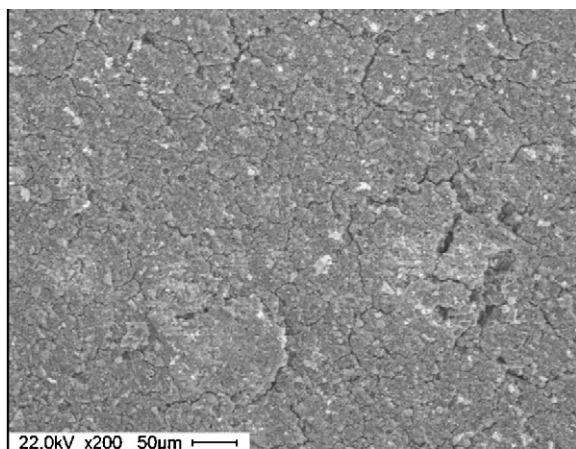


Fig. 6. EDS energy lines of catalyst powder.

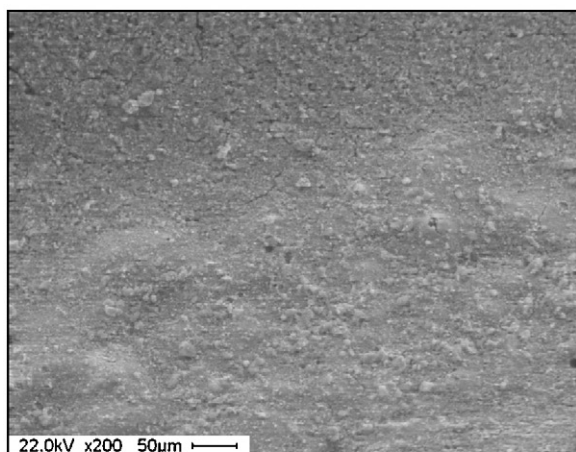
sion. This is evident from the SEM analysis of the powders wherein the Zr L peak is visible in Fig. 6 but has been covered by the P peak as shown in Fig. 5. Such characteristics have been observed in previous SEM-EDS analyses of TWCs [2]. The comparison of the SEM-EDS energy lines in Figs. 5 and 6 does not show a significant difference indicating that the composition was very similar in the case of this catalyst, analyzed in both powder and monolith piece forms. The SEM micrographs (fresh, used and washed) are compared at very low power (Fig. 7). The surface differences are very clear in the micrographs A, B and C. The surface of the fresh catalyst is very smooth, whereas the catalyst after use seems to have some visible roughness. Previous studies [23] have conducted extensive SEM-EDS analyses on TWC samples. The authors reported surface roughness due to the pore fouling of the TWC samples by the formation of inorganic phosphate salts such as calcium phosphates and other metal phosphates. This probably could be used to explain the difference in morphology of the TWC samples in the present case.

3.2.2. XRD analysis

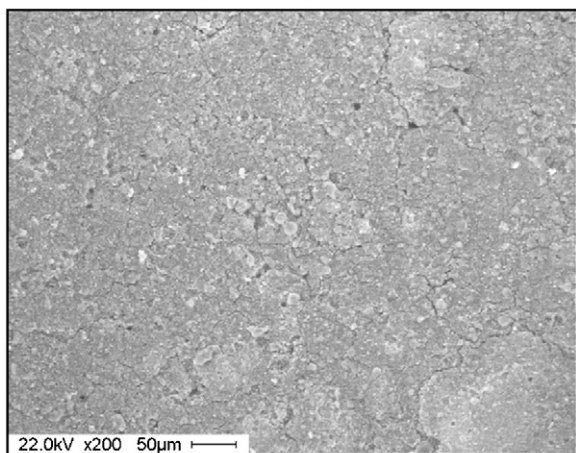
Fig. 8 shows the 2θ region from $10\text{--}60^\circ$ of the fresh, used and regenerated Ford TWC. The reflections of the cordierite are clearly visible (marked with *) because there are no interferences from other peaks. This is because this sample is uncontaminated. The peaks corresponding to $2\theta = 29.0^\circ$, 33.4° and 48.5° belong to the Ce–Zr–O mixed oxide which is a major washcoat component. At lower values of 2θ , there is considerable interference by the cordierite peaks which are most intense in this region. In the used sample, the peaks corresponding to 28.90° , 27.06° and 31.28° were assigned to CePO_4 (Cerium phosphate – JCPDS file no. 84-0247). These are the three maximum intensity peaks of this compound, which are visible even after superimposition by other peaks. The crystalline structure of cordierite is not altered after use but the mixed oxide peaks become narrower and intense due to sintering. This has also been previously explained by Larese et al. [2]. AlPO_4 (JCPDS file no. 84-0854) was also detected at $2\theta = 26.4^\circ$ (maximum intensity peak). Calcium zinc phosphate $\text{CaZn}_2(\text{PO}_4)_2$ (JCPDS file no. 84-1569) was found at $2\theta = 30.23^\circ$ though the characteristic peak at 21.54° and 29.70° and is not visible probably because of interference by cordierite. This compound along with $\text{Zn}_3(\text{PO}_4)_2$, $\text{Zn}_2\text{P}_2\text{O}_7$ and $\text{MgZn}_2(\text{PO}_4)_2$ is responsible for pore blocking by forming an impervious glassy layer on the washcoat [27]. There is a possibility of another cerium phosphate peak $\text{Ce}(\text{PO}_3)_3$ at $2\theta = 25.93^\circ$ as reported [1]. As seen from Fig. 8, there is no distinct difference in the XRD patterns of the used and washed TWC. This could also suggest that there was no removal of crystalline phases and hence no improvement in the surface area was seen (see Section 3.2.3). The intensity of some phases containing P is reduced indicating the partial removal of some crystalline phases.



A. SEM micrograph image of the used catalyst



B. SEM micrograph image of the fresh catalyst



C. SEM micrograph image of the washed catalyst (with EDDS)

Fig. 7. (A–C) SEM micrograph images of the Ford catalyst pieces at 50 μ magnification.

3.2.3. BET surface area measurements

The BET surface area and the pore size distribution of the fresh, used and washed samples were compared. The surface area of the fresh TWC (0 miles) was determined to be 22 m²/g. The surface areas of the used and washed TWCs were found to be 10.3 m²/g and 9.5 m²/g, respectively. This indicates that washing with EDDS did not cause any marked difference in the BET surface area of the catalyst. In order to confirm that this decrease in the surface area was

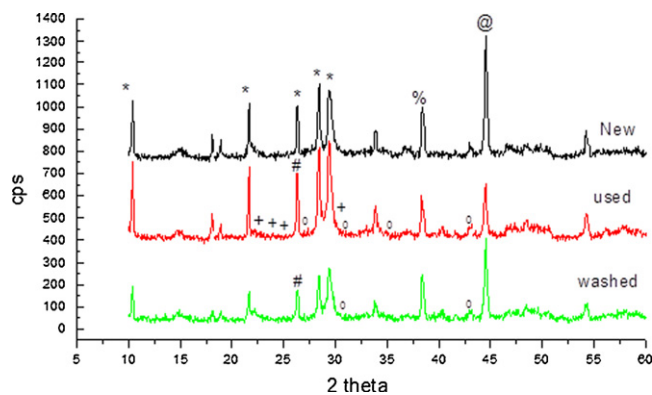


Fig. 8. XRD patterns obtained in the 10–60° 2θ range over the fresh, used and washed Ford TWC. (*) Cordierite; (%) Alumina sample holder; (@) Ce–Zr–O oxides; (#) AlPO₄; (O) CePO₄; (+) CaZn₂(PO₄)₂.

not due to deposition of solvent, the used TWC was also washed with oxalic acid in the same batch process and no enhancement in the surface area was observed. There is a considerable number of published studies that have compared the BET surface areas of TWCs before and after washing [6,10]. However, all these processes have used continuous flow systems with recirculation of solvent. The conditions of these systems have been optimized for catalytic activity. One of these previous works reports their operating conditions and emphasize on the flow rate of the system as an important parameter [10].

The conditions under which the catalyst has been aged also play an important role in the pore size distribution. With TWC aging, there is a change from the microporous structure of the Ce–Zr–O oxides to a mesoporous one [33]. Fig. 9 compares the pore size distributions of the fresh, used and washed TWC samples. It can be seen that after EDDS washing a similar pore size distribution to that of the aged catalyst was obtained. However, the specific volume of the pores decreased after washing. Other published studies report an increase in surface area after washing using acetic, citric and oxalic acids [34]. The increase in the BET surface area after washing was attributed to the uncovering of the pores and it was found that oxalic acid was more effective than citric acid [10]. The uncovering of pores results in regaining catalytic activity due to exposing more active sites that are responsible for CO and NO conversions [35,36]. It appears that the EDDS washing method fails to retrieve the large surface area and pore volume loss (around 50% loss) obtained after aging under real driving conditions and is probably the result of severe thermal sintering as reported [37]. Oxychlorination treatments applied on commercial [6–8] as well as on model TWCs [38,39] were found to reverse the effects of thermal sintering through the redispersion of sintered noble metal parti-

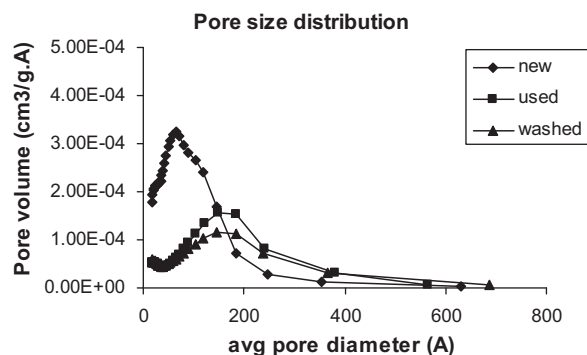


Fig. 9. Pore size distribution curves obtained for the fresh, used and washed Ford TWCs.

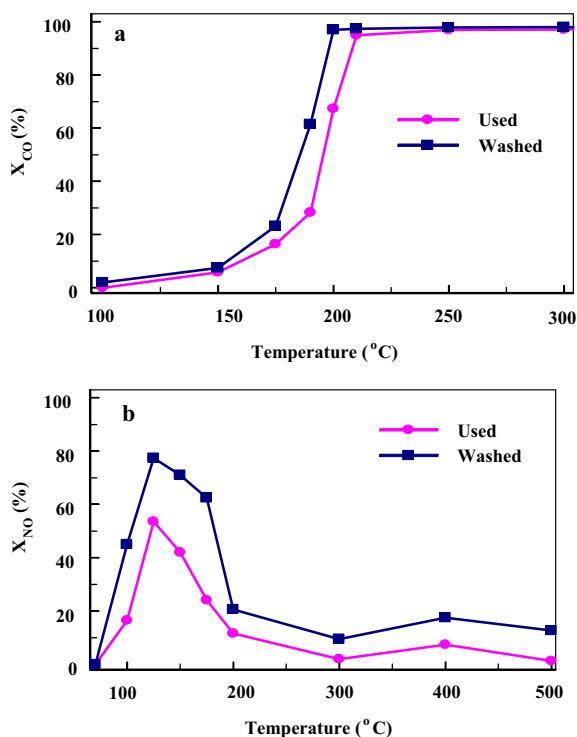


Fig. 10. Light-off profiles for (a) 1% CO/1% O₂/98% He and (b) 0.2% NO/0.3% H₂/1% O₂/98.5% He reactions obtained over the used (●) and washed (■) TWC samples (Ford, USA).

cles. The proposed EDDS regeneration method concentrates on the removal of contaminants as it is already previously discussed, thus reversing the effects of chemical poisoning.

3.2.4. Catalytic activity measurements

Fig. 10 presents the light-off profiles for (a) the 1 vol% CO/1 vol% O₂/He and (b) 0.2 vol% NO/0.3 vol% H₂/1 vol% O₂/He reactions obtained over the used and EDDS-washed TWC (Ford, USA) samples. In order to investigate the effectiveness of the regeneration method under study on regaining the catalytic activity of the aged TWC, two probe reactions, the CO oxidation and NO reduction by H₂ were examined. It should be noted that the used feed concentrations of CO, NO, H₂ and O₂ are representative average values found in the exhaust gas stream composition at the inlet of a three-way catalyst installed in a gasoline-driven car. Therefore, the present TWC sample is exposed to gas streams that simulate two important reactions promoted by the TWC. The CO conversion versus temperature profile for the washed sample is similar to that of used sample in the 100–175 °C range, where only slight improvements in the light-off behaviour for CO were observed following regeneration with EDDS (Fig. 10a). However, in the 185–200 °C range significant improvements can be seen.

Larese et al. [2] reported that the formation of CePO₄ can be invoked to explain the deteriorating catalytic properties displayed by a used TWC compared to the respective fresh one. The authors proposed that due to this the locked Ce³⁺/Ce⁴⁺ pair is unable of participating in the rapid Ce³⁺ ↔ Ce⁴⁺ redox process required for the proper functioning of TWC [2]. Since oxygen mobility is significantly restricted on the surface of the catalyst, where CePO₄ crust is formed around CeO₂, oxidation of adsorbed CO by lattice oxygen of ceria is expected to be enhanced by reaction temperature. It is noted that EDDS washing was found to remove phosphorous compounds from the TWC surface only partially (XRD results, Fig. 8).

However, a significant improvement in the whole NO conversion versus temperature profile (X_{NO}, %, Fig. 10b) was observed

after regeneration and particularly in the 100–190 °C range. The NO conversion profiles of the used and washed samples consist of typical volcano-type curves (Fig. 10b) with the NO conversion passing through a maximum around 125 °C. The reduction of NO by hydrogen in the presence of oxygen was found to result mainly in the production of H₂O and N₂. It is noted that the N₂ selectivity of NO reduction was found to be ~98%, and only up to 40 ppm of N₂O was seen. NH₃ and NO₂ were not detected. According to the results of Fig. 10b, the superiority of the regenerated sample against the used one is evident in all the reaction temperature range investigated. A maximum conversion of NO reached the value of 78% for the washed sample, while that of 53% for the used one. Furthermore, at 100 °C almost 3 times higher NO removal is attained after washing of the TWC sample with EDDS. Therefore, it might be said that the regeneration procedure employed can effectively improve the catalytic performance towards NO pollutant. The removal of Zn and Pb contaminants after using the EDDS washing medium appears to result in the uncovering of catalytic active sites for NO adsorption and reduction, the latter being most likely those at the noble metal surface.

4. Conclusions

EDDS is found to be an effective solvent for the regeneration of TWCs with respect to metal and P contaminant removal and NO emissions reduction. EDDS can help offset the present environmental limitations imposed by EDTA which can persist in water and soils due to its non-biodegradable nature. On the other hand, EDDS can be easily biodegraded. Metal complexes with EDDS are also easily broken down. This makes the handling of secondary waste simpler.

In the present study, EDDS was found to be effective towards the removal of P, Pb, Cu, Zn and Fe. Sulfur (S) was not found in the present investigated aged TWC (Ford). XRD and SEM results revealed that phosphate compounds are partially removed by EDDS washing. As a result, no significant enhancement was found in the BET surface area. Sintering of the TWC samples was also observed in the XRD analysis as seen by the narrowing of mixed metal oxide diffraction peaks. Further advanced characterization methods such as high resolution transmission electron microscopy (HRTEM) of the TWC samples are necessary to determine the extent of sintering that contributes to the catalyst fouling [40]. Since TWC regeneration appears to be very process and parameter specific, further extraction studies of a continuous mode are necessary. Future experiments should be conducted *in situ* with a continuous flow-system with recirculation. In addition, the effectiveness of this solvent with respect to catalytic activity needs to be evaluated with dynamometer tests.

This study assessed the effectiveness of EDDS in a laboratory scale TWC batch washing process. Further studies are required before *in situ* washing can be implemented. This work can be thought of as the first step towards the development of a regeneration process using EDDS.

Acknowledgements

Funding for this research was provided by Cyprus Research Promotion Foundation through the projects TEXNO/0603/09 and DIDAKTOR/DISEK/0308/33. Thanks are due to Dr. Caroline Hubbard of the Ford Catalyst Research Institute, Dearborn, MI for providing the Ford catalyst samples.

References

- [1] M. López Granados, F.C. Galisteo, P.S. Lambrou, R. Mariscal, J. Sanz, I. Sobrados, J.L.G. Fierro, A.M. Efstathiou, Role of P-containing species in phosphated CeO₂ in the deterioration of its oxygen storage and release properties, *J. Catal.* 239 (2006) 410–421.

- [2] C. Larese, F.C. Galisteo, M.L. Granados, R. Mariscal, J.L.G. Fierro, M. Furió, R.F. Ruiz, Deactivation of real three-way catalysts by CePO_4 formation, *Appl. Catal. B. Environ.* 40 (2003) 305–317.
- [3] T.N. Angelidis, V.G. Papadakis, Partial regeneration of an aged commercial automotive catalyst, *Appl. Catal. B: Environ.* 12 (1997) 193–206.
- [4] H. Birgersson, M. Boutonnet, S. Jaras, L. Eriksson, Deactivation and regeneration of spent three-way automotive exhaust gas catalysts (TWC), *Top. Catal.* 30–31 (2004) 433–438.
- [5] S.Y. Christou, H. Birgersson, J.L.G. Fierro, A.M. Efstathiou, Reactivation of an aged commercial three-way catalyst by oxalic and citric acid washing, *Environ. Sci. Technol.* 40 (2006) 2030–2036.
- [6] H. Birgersson, M. Boutonnet, F. Klingstedt, D.Y. Murzin, P. Stefanov, A. Naydenov, An investigation of a new regeneration method of commercial aged three-way catalysts, *Appl. Catal. B: Environ.* 65 (2006) 93–100.
- [7] H. Birgersson, L. Eriksson, M. Boutonnet, S.G. Järäs, Thermal gas treatment to regenerate spent automotive three-way exhaust gas catalysts (TWC), *Appl. Catal. B: Environ.* 54 (2004) 193–200.
- [8] H. Birgersson, M. Boutonnet, F. Klingstedt, D.Y. Murzin, P. Stefanov, A. Naydenov, An investigation of a new regeneration method of commercial aged three-way catalysts, *Appl. Catal. B* 65 (2006) 93–100.
- [9] R. Mariscal, M.L. Granados, J.L.G. Fierro, P. Brettes, O. Salas, Reactivation of a commercial diesel oxidation catalyst by acid washing, *Environ. Sci. Technol.* 39 (2005) 3844–3848.
- [10] S.Y. Christou, H. Birgersson, A.M. Efstathiou, Reactivation of severely aged commercial three-way catalysts by washing with weak EDTA and oxalic acid solutions, *Appl. Catal. B: Environ.* 71 (2007) 185–198.
- [11] A. Serpe, F. Bigoli, M.C. Cabras, P. Fornasiero, M. Graziani, M.L. Mercuri, Pd-Dissolution through a mild and effective one-step reaction and its application for Pd-recovery from spent catalytic converters, *Chem. Commun.* 8 (2005) 1040–1042.
- [12] D. Cicchella, B. De Vivo, A. Lima, Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: possible effects of catalytic exhausts, *Sci. Total Environ.* 308 (2003) 121–131.
- [13] K.E. Jarvis, S.J. Parry, J.M. Piper, Temporal and spatial studies of autocatalyst-derived platinum rhodium, and palladium and selected vehicle-derived trace elements in the environment, *Environ. Sci. Technol.* 35 (2001) 1031–1036.
- [14] S. Lustig, S. Zang, B. Michalke, P. Schramel, W. Beck, Transformation behaviour of different platinum compounds in a clay-like humic soil: speciation investigations, *Sci. Total Environ.* 188 (1996) 195–204.
- [15] S. Tandy, R. Schulin, B. Nowack, The influence of EDDS on the uptake of heavy metals in hydroponically grown sunflowers, *Chemosphere* 62 (2006) 1454–1463.
- [16] S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack, Extraction of heavy metals from soils using biodegradable chelating agents, *Environ. Sci. Technol.* 38 (2004) 937–944.
- [17] E. Meers, A. Ruttens, M.J. Hopgood, D. Samson, F.M.G. Tack, Comparison of EDTA and EDDS as potential soil amendments for enhanced phytoextraction of heavy metals, *Chemosphere* 58 (2005) 1011–1022.
- [18] P.C. Vandevivere, H. Saveyn, W. Verstraete, T.C.J. Feijtel, D.R. Schowanek, Biodegradation of metal-[S,S]-EDDS complexes, *Environ. Sci. Technol.* 35 (2001) 1765–1770.
- [19] F.C. Galisteo, R. Mariscal, M.L. Granados, J.L.G. Fierro, P. Brettes, O. Salas, Reactivation of a commercial diesel oxidation catalyst by acid washing, *Environ. Sci. Technol.* 39 (2005) 3844–3848.
- [20] B. Jastorff, K. Mölter, P. Behrend, U. Bottin-Weber, J. Filser, A. Heimers, B. Ondruschka, J. Ranke, M. Schaefer, H. Schröder, A. Stark, P. Stepnowski, F. Stock, R. Störmann, S. Stolte, U. Welz-Biermann, S. Ziegert, J. Thöming, Progress in evaluation of risk potential of ionic liquids-basis for an eco-design of sustainable products, *Green Chem.* 7 (2005) 362–372.
- [21] B. Jastorff, R. Störmann, J. Ranke, K. Mölter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nüchter, B. Ondruschka, J. Filser, How hazardous are ionic liquids; structure-activity relationships and biological testing as important elements for sustainability evaluation, *Green Chem.* 5 (2003) 136–142.
- [22] U.S. Environmental Protection Agency, Test methods for evaluating solid wastes SW-846 EPA Method 6020 B: Inorganic Elements by ICP-MS, in: *Test Methods for Evaluating Solid Waste*, 3rd edition, 3rd update: Washington, DC, 1996, pp. 1–8.
- [23] T.N. Angelidis, S.A. Sklavounos, A SEM-EDS study of new and used automotive catalysts, *Appl. Catal. A: Gen.* 133 (1995) 121–132.
- [24] C.N. Costa, T. Anastasiadou, A.M. Efstathiou, The selective catalytic reduction of nitric oxide with methane over $\text{La}_2\text{O}_3\text{-CaO}$ systems: synergistic effects and surface reactivity studies of NO, CH_4 , O_2 , and CO_2 by transient techniques, *J. Catal.* 194 (2000) 250–265.
- [25] W.B. Williamson, H.S. Gandhi, M.E. Hegde, G.A. Zawacki, Deactivation of three-way catalysts by fuel contaminants – lead phosphorous and sulfur, *SAE Preprints* 790942 (1979).
- [26] S.A. Sklavounos, A SEM-EDS study of new and used automotive catalysts, *Appl. Catal. A: Gen.* 133 (1995) 121–132.
- [27] M.J. Rokosz, A.E. Chen, C.K. Lowe-Ma, A.V. Kucherov, D. Benson, M.C. Paputa Peck, R.W. McCabe, Characterization of phosphorus-poisoned automotive exhaust catalysts, *Appl. Catal. B* 33 (2001) 205–215.
- [28] A. Martínez-Arias, M. Fernández-García, A.B. Hungria, A. Iglesias-Juez, K. Duncan, R. Smith, J.A. Anderson, J.C. Conesa, J. Soria, Effect of thermal sintering on light-off performance of $\text{Pd}/(\text{Ce,Zr})\text{O}_x/\text{Al}_2\text{O}_3$ three-way catalysts model gas and engine tests, *J. Catal.* 204 (2001) 238–248.
- [29] C. Larese, F. Cabello Galisteo, M. Loípez Granados, R. Mariscal Loípez, J.L.G. Fierro, P.S. Lambrou, A.M. Efstathiou, Effects of calcination temperature on the stability of CePO_4 detected in vehicle-aged commercial three-way catalysts, *Appl. Catal. B: Environ.* 48 (2004) 113–123.
- [30] S. Bernal, J.J. Calvino, M.A. Cauqui, J.M. Gatica, C. Larese, J.A. Pérez Omil, et al., Some recent results on metal/support interaction effects in NM/CeO_2 (NM: noble metal) catalysts, *Catal. Today* 50 (1999) 175–206.
- [31] B. Kos, D. Leštan, Induced phytoextraction/soil washing of lead using biodegradable chelate and permeable barriers, *Environ. Sci. Technol.* 37 (2003) 624–629.
- [32] A.E. Martell, R.M. Smith, R.J. Moetikitis (Eds.), *NIST Critically Selected Stability Constants Of Metal Complexes*, version 6. 0, NIST, Gaithersburg, MD, 2001.
- [33] P. Fornasiero, G. Balducci, R. Di Monte, J. Kašpar, V. Sergio, G. Gubitosa, A. Ferrero, M. Graziani, Modification of the redox behaviour of CeO_2 induced by structural doping with ZrO_2 , *J. Catal.* 164 (1996) 173–183.
- [34] C. Larese, M.L. Granados, F.C. Galisteo, R. Mariscal, J.L.G. Fierro, TWC deactivation by lead A study of the Rh/CeO_2 system, *Appl. Catal. B: Environ.* 62 (2006) 132–143.
- [35] S.Y. Christou, A.M. Efstathiou, Efficient in-situ regeneration method of the catalytic activity of aged TWC, *Top. Catal.* 42–43 (2007) 415–420.
- [36] S.Y. Christou, J. Gásste, H.L. Karlsson, J.L.G. Fierro, A.M. Efstathiou, Regeneration of aged commercial three-way catalytic converters, *Top. Catal.* 52 (2009) 2029–2034.
- [37] H.-W. Jen, G.W. Graham, W. Chun, R.W. McCabe, J.-P. Cuif, S.E. Deutsch, O. Touret, Characterization of model automotive exhaust catalysts Pd on ceria and ceria-zirconia supports, *Catal. Today* 50 (1999) 309–328.
- [38] R.A. Daley, S.Y. Christou, A.M. Efstathiou, J.A. Anderson, Influence of oxychlorination treatments on the redox and oxygen storage and release properties of thermally aged $\text{Pd-Rh}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{Al}_2\text{O}_3$ model three-way catalysts, *Appl. Catal. B: Environ.* 60 (2005) 117–127.
- [39] J.A. Anderson, R.A. Daley, S.Y. Christou, A.M. Efstathiou, Regeneration of thermally aged $\text{Pt-Rh}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2\text{-Al}_2\text{O}_3$ model three-way catalysts by oxychlorination treatments, *Appl. Catal. B: Environ.* 64 (2006) 189–200.
- [40] S. Bernal, J.J. Calvino, M.A. Cauqui, J.M. Gatica, C. López Cartes, J.A. Pérez Omil, Characterization of three-way automotive after treatment catalysts and related model systems, *Top. Catal.* 28 (2004) 31–44.