

Efficient In-Situ Regeneration Method of the Catalytic Activity of Aged TWC

Stavroula Y. Christou and Angelos M. Efstathiou*

Chemistry Department, Heterogeneous Catalysis Laboratory, University of Cyprus, P.O. Box 20537, CY 1678 Nicosia, Cyprus

The expansion of durability of deactivated “three-way” catalysts (TWCs) used in gasoline-driven cars by applying efficient, economically viable and environmentally friendly methods for the *in situ* regeneration of their performance to acceptable levels was investigated. New experimental results on the use of a *weak oxalic acid washing solution* as a means of an efficient regeneration method of a severely aged (83,000 km mileage) commercial TWC are presented. Oxalic acid is shown to be the most efficient extracting agent of phosphorus, a severe poison of TWCs, among acetic acid, citric acid, NTA and EDTA investigated. X-ray diffraction studies provided strong evidence that washing of the aged TWC results in the removal of CePO_4 , AlPO_4 and $(\text{Mg,Ca,Zn})_3(\text{PO}_4)_2$ type phosphates leading to a significant increase of BET area and pore volume, as well as of CO and NO conversions (catalytic activity tests). The latter is strongly related with the increase in the number of active catalytic sites, as illustrated by *in situ* DRIFTS studies, after opening closed pores and uncovering additional catalyst surface.

KEY WORDS: TWC regeneration; oxalic acid washing; TWC deactivation; phosphorus contamination.

1. Introduction

A “three-way” catalyst (TWC) installed in the exhaust system of gasoline-driven car for controlling CO, NO_x and C_xH_y emissions comprise nowadays an essential part of car’s engine design system. This emissions after-treatment technology must guarantee a conversion level higher than 95%. The minimum life expectancy of a TWC is about 80,000 km [1]. Once a TWC fails to meet the required emissions standards, it is replaced by a new one, whereas the spent TWC is completely destructed and treated as potential resource of platinum group metals (PGM) [2,3]. Hydrometallurgical procedures employed for recovering PGM use highly aggressive and corrosive reagents for complete dissolution of TWC which produce large quantities of liquid and solid wastes. Technical challenges encountered in these processes also involve the presence of various contaminants accumulated on the TWC upon usage, such as P, Ca, Zn, Mg, Pb and S, typical oil- and fuel-derived contaminants, and Fe, Cu, Ni and Cr originating from the engine and exhaust system construction materials [2,4–7]. Chemical poisoning and high-temperature aging comprise the main causes of TWC deactivation [4–10].

There is no yet a method applied for the *in situ* regeneration of aged commercial TWCs. The interest in finding suitable *in situ* regeneration methods of commercial TWCs has recently grown. The use of liquid solvents, such as weak organic acids (e.g., acetic, oxalic and citric acids) for extraction of contaminants has been reported [11,12], as well as the application of various

thermo-chemical treatments using O_2 , H_2 and Cl-containing gas mixtures [13,14] or other Cl-containing reagents (e.g., 1,2-dichloropropane) [15] for the redispersion of large noble metal particles.

The present work has investigated for the first time the effects of the oxalic acid-washing procedure on the physical and structural properties of a severely aged commercial TWC (83,000 km mileage), leading to the improvement of its catalytic activity. The removal of large amounts of P-containing compounds from the aged TWC, known to severely deteriorate the catalytic and oxygen storage and release properties of TWC [5,9], after applying the oxalic acid washing procedure is shown to significantly improve the activity of the aged TWC towards CO and NO conversions. Results on the efficiency of nitrilotriacetic (NTA) and EDTA weak organic acid solutions on the removal of P from the same aged TWC are also presented.

2. Experimental

2.1. Sample Selection

TWC samples were extracted from the catalytic converter of a car (model Mazda 323) driven for 83,000 km in Cyprus. The samples studied were taken from the center of the first 2 cm in length (inlet) of the ceramic monolith of TWC in cubic shapes ($2 \times 2 \times 2 \text{ cm}^3$).

2.2. Regeneration of Aged Commercial TWC Samples

The oxalic acid solution regeneration method was applied on the cubic monolith fragments extracted from the aged TWC using a lab-constructed apparatus [11]. The TWC samples were treated with the oxalic acid

* To whom correspondence should be addressed.
E-mail: efstath@ucy.ac.cy

solution (0.1 M) for 1 h, where the latter was then replaced by a fresh one used for an additional 1 h. The flow rate of the acid solution recirculated was 600 mL/min, whereas its temperature was kept constant at 50°C [11]. After acid washing, each catalyst specimen was washed thoroughly with de-ionized water for 30 min followed by drying at 120°C overnight and at 200°C for further 2 h for complete removal of acid residues.

2.3. ICP-AES Chemical Analysis of Aged and Acid-Washed TWC Samples

Prior to ICP-AES analyses, 100 mg of the TWC sample were gently crashed into powder and dissolved in a liquid mixture of aqua regia ($\text{HNO}_3:\text{HCl} = 3:1$ v/v) at 80°C. All chemical species were entered in the acid solution except Si, which was wept out by filtration. The solution was then diluted in de-ionized water and the concentrations of the basic components of TWC (e.g., Pd, Pt, Rh, Ce, Zr, Al and Ba) and contaminant species (e.g., P, Pb, Zn, Mn, Ca, Fe, Cu, Cr and Ni) in the aged and acid-washed TWC samples were measured by ICP-AES (ICPS-7500 Plasma Emission Spectrometer, Shimadzu). Sample concentrations (mg/L) were then converted into g/kg of TWC (dry weight basis).

2.4. X-ray Diffraction Studies

Powder X-ray diffraction (XRD) patterns of the aged and acid-treated TWC samples were recorded in the 15–35° 2θ range (scan mode = 0.02°/s) using a Shimadzu 600 Series System after employing $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Å).

2.5. BET Surface Area and Pore Size Distribution Measurements

BET surface area, and pore size distribution of the used and acid-washed samples were determined by nitrogen adsorption-desorption isotherms at 77 K (Micromeritics Gemini Surface Area and Pore Size Analyser, BJH method). Prior to any measurements, the samples were outgassed at 200°C for 2 h.

2.6. In Situ DRIFTS Studies of CO and NO Chemisorption

DRIFTS spectra were recorded using a Perkin Elmer Spectrum GX II FTIR spectrometer at a resolution of 2 cm^{-1} coupled with a high-pressure temperature controllable DRIFTS cell (Spectra Tech) equipped with ZnSe IR windows. Catalyst sample in finely powder form (~30 mg) was placed firmly into the ceramic cup of the DRIFTS cell. Gas mixtures of 0.1vol%NO/He and 1vol%CO/He were used for the NO and CO chemisorption experiments, respectively. Before any measurements were taken, the samples were calcined in a 20% O_2 /Ar gas mixture at 700°C for 2 h followed by H_2 reduction (1 atm) at 300°C for 2 h. DRIFTS spectra

were collected in the 2500–800 cm^{-1} range and analysed by the instruments Spectrum for Windows software.

2.7. Catalytic Activity Measurements

The flow system used for conducting catalytic measurements for the CO/O_2 (1vol%CO/1vol% O_2 /He) and $\text{NO}/\text{H}_2/\text{O}_2$ (0.1vol%NO/0.3vol% H_2 /1vol% O_2 /He) reactions at 1 atm total pressure was previously described [16]. The amount of TWC sample used was 50 mg (small pieces of 1–3 mm in length), and the total flow rate was 100 $\text{NmL}\cdot\text{min}^{-1}$. Samples were first calcined in a 20 vol% O_2 /He gas mixture at 700°C for 2 h, followed by H_2 reduction (1 atm) at 300°C for 2 h.

3. Results and Discussion

3.1. ICP-AES Analyses

The investigation of a number of complexing agents for extracting various metal and inorganic contaminants accumulated in aged TWCs showed that oxalic acid was the most efficient in removing P-containing species (~85% removal) among acetic acid, citric acid, EDTA and nitrilotriacetic acid (NTA) (Fig. 1). This is likely due to the fact that oxalic acid is the strongest acid among the others investigated, having, therefore, larger dissolution efficiency towards phosphates. On the other hand, citric acid, EDTA and NTA appeared to be more efficient than oxalic acid in removing Pb, Zn, Ca, Mn, Ni, Cr and Fe metal contaminants. No removal of precious metals Pd, Pt, and Rh (16:1:1) was observed. However, little Ce and Ba removal (~10%) and no Zr removal were observed. According to Battistoni et al. [17], after extended operation of TWC the surface concentration of Ba in the form of BaO increased substantially due to its segregation from the bulk of washcoat towards the surface. Surface enrichment in ceria has been also observed upon annealing [18]. Thus, it is reasonable to state that surface enrichment in Ce- and Ba-species would favor their removal through dissolution in the acid solution. In addition, CePO_4 was

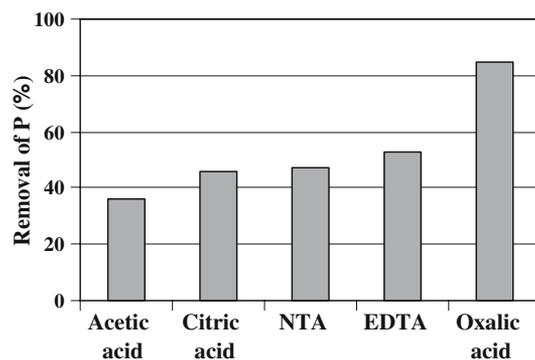


Figure 1. Removal of P (%) after washing of aged TWC with acetic acid, citric acid, NTA, EDTA, and oxalic acid solutions (0.1 M).

found to predominate in the form of a crust at the surface/subsurface of CeO_2 and $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid crystals [9]. Thus, it could be said that cerium removal would probably correspond to a large extent to that present in CePO_4 (XRD results).

Based on XPS results [11], Ce and Zr surface concentrations were found to significantly increase only after oxalic acid washing. These results imply that the latter procedure largely uncovers the TWC washcoat surface through the removal of most of P-containing overlayer which was reported to be constituted of Zn, Ca, Mg, Ce and Al phosphates [4–6,9].

3.2. X-ray Diffraction Studies

Figure 2 compares the XRD patterns of the aged and regenerated samples in the $2\theta = 15\text{--}35^\circ$ range. The diffractograms present intense reflections which are assigned to cordierite (\bullet) and $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution (\blacktriangledown) [9]. Several weak but clearly visible diffraction peaks are also seen in the XRD pattern of the aged sample. The reflections at 20.2 and 22.2° are assigned to a mixture of $\text{MgZn}_2(\text{PO}_4)_2$ (\square) and $\text{CaZn}_2(\text{PO}_4)_2$ (\circ) [4]. The broad peak centered at 22.2° provides also indication for the presence of orthorhombic $\text{Zn}_2\text{P}_2\text{O}_7$ and tridymite-type AlPO_4 [4,5]. Reflections at 25.6 , 27.0 , 29.8 , 31.0 and 34.3° are due to the presence of CePO_4 (σ) [6,9].

3.3. BET Surface Area and Pore Size Distribution Measurements

The BET area of the aged TWC was found to be $16.7 \text{ m}^2/\text{g}$, whereas that of oxalic acid-washed sample $22.5 \text{ m}^2/\text{g}$, where an increase by 35% is noted. Figure 3 presents BJH pore size distribution plots obtained for the aged and acid-treated TWC samples. After washing with oxalic acid, the specific pore volume (cm^3/g) corresponding to a given average pore's diameter was increased significantly. The increase in the number of small pores that become larger due to the applied acid washing could be excluded considering the fact that

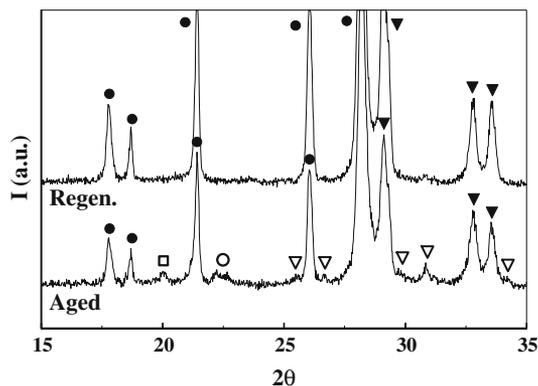


Figure 2. XRD patterns obtained for the aged and oxalic acid regenerated TWC samples.

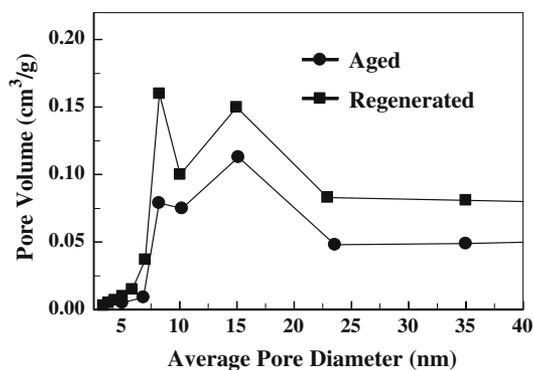


Figure 3. BJH pore size distributions obtained over the aged and oxalic acid regenerated TWC samples.

formation of larger pores would generally lead to lower surface area. The view that the main quantities of contaminants accumulated on the washcoat surface, whereas accumulation inside the pores of washcoat was considerably lower, and, therefore, fouling (closing of pores) was the main deactivation mechanism, is widely accepted [4–9]. CePO_4 and AlPO_4 were also reported to be formed around the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and $\gamma\text{-Al}_2\text{O}_3$ particles as a crust (washcoat-pores blocking) [5,6].

XRD studies (Fig. 2) revealed that after oxalic acid washing, phosphates of the $(\text{Mg,Ca,Zn})_3(\text{PO}_4)_2$ type as well as Ce and Al phosphates disappeared from the aged TWC. These results imply that the increase of pore volume in the acid-treated sample (Fig. 3) can be ascribed to the unclogging of pores by the removal of large quantities of P-containing compounds.

3.4. In Situ DRIFTS Studies of CO and NO Chemisorption

Figure 4 presents in situ DRIFTS spectra obtained after adsorption of CO (Fig. 4a) and NO (Fig. 4b) on the aged and regenerated TWC samples. In Fig. 4a, the IR bands at 2175 and 2120 cm^{-1} correspond to linearly adsorbed CO on Pd, positively charged and neutral, respectively. The bands at 2000 and 1830 cm^{-1} correspond to multi-bridged CO on Pd, whereas the bands in the $1650\text{--}1200 \text{ cm}^{-1}$ range correspond to carbonates on Pd and/or the washcoat [19]. In Fig. 4b, the IR bands at 1920 and 1845 cm^{-1} correspond to linearly adsorbed NO on Rh, positively charged and neutral, respectively. The band at 1695 cm^{-1} corresponds to linear NO on Pd, whereas the bands at 1540 and 1340 cm^{-1} correspond to nitrates on Pd and/or the washcoat [19]. As seen in Figs. 4a and 4b, the concentration of adsorbed CO and NO species, respectively, increased significantly in the regenerated TWC sample. These results confirm the removal of large amounts of contaminants after washing of the catalyst with oxalic acid, which increased significantly the number of active Rh and Pd free adsorption and catalytic sites.

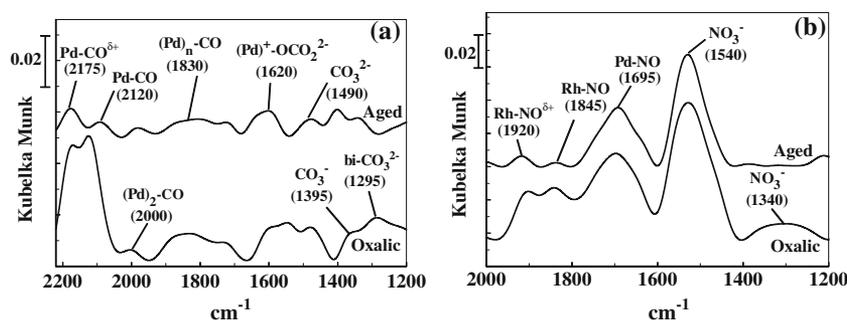


Figure 4. In situ DRIFTS spectra obtained after adsorption of CO (a) and NO (b) on the aged and regenerated (oxalic acid-washed) TWC samples.

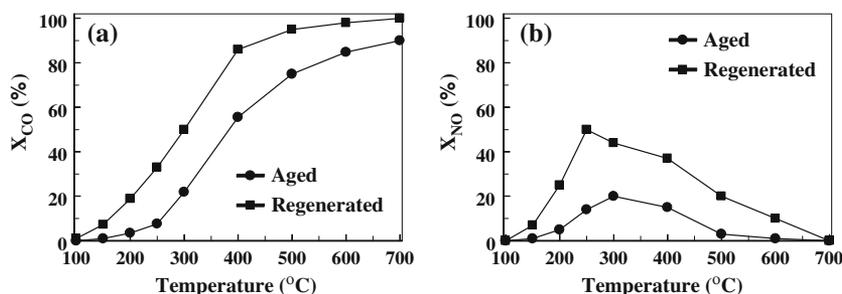


Figure 5. Light-off curves for the 1%CO/1%O₂/He (a) and 0.1%NO/0.3%H₂/1%O₂/He (b) reactions obtained over the aged and oxalic acid regenerated TWC samples.

3.5. Catalytic Activity Measurements

Figure 5a presents light-off curves for the CO/O₂ reaction over the aged and regenerated TWC samples. The light-off curve of the regenerated sample is considerably above that of the aged TWC, thus higher temperatures are needed to reach the same level of conversion for the aged TWC compared with the acid-treated one ($T_{50}^{\text{aged}} = 390^{\circ}\text{C}$ vs. $T_{50}^{\text{regen.}} = 300^{\circ}\text{C}$). Furthermore, an increase in X_{CO} by more than five and two times, respectively, compared with the aged TWC was obtained at 200 and 300°C. Significant improvements were also observed in the NO conversion (Fig. 5b). Similar results were also observed for X_{CO} and X_{NO} under *real exhaust-gas conditions* (*dynamometer tests*) [11]. Less improvements in the catalytic behaviour were observed after washing with acetic acid, citric acid, EDTA and NTA solutions compared with the oxalic acid [11,12]. Based on the results of the present work and those recently reported [11], improved catalytic performance and OSC [11] after oxalic acid washing were obviously accomplished due to the removal of large amounts of contaminants, mainly P-containing compounds, resulting in the exposure of a larger number of active catalytic sites.

It might be appropriate to state that removal of small amounts of Ce and Ba as previously mentioned does not seem to have a strong negative effect on the conversion of CO and NO since significant improvement of these parameters was observed after regeneration (Fig. 5).

4. Conclusions

The results reported in the present work provide further evidence [11] that washing of aged commercial TWCs with weak oxalic acid solutions can result in a significant recovery of their catalytic performance due mainly to the removal of large amounts of Ce, Al, Mg, Ca, and Zn phosphates, resulting in the opening of closed pores, thus exposing active catalytic sites associated with the CO and NO conversion, and reducing mass transport resistances. The present regeneration method aiming at expanding the durability of gasoline-driven aged commercial TWCs appears to be the most promising among similar ones reported (use of other weak organic acid washing solutions) [12].

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