Reactivation of an Aged Commercial Three-Way Catalyst by Oxalic and Citric Acid Washing

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The efficiency of dilute oxalic and citric acid solutions on improving the oxygen storage capacity (OSC) and catalytic activity of a severely aged (83 000 km) commercial three-way catalyst (TWC) has been investigated. Washing procedures applied after optimization of experimental parameters, namely, temperature, flow-rate, and concentration of acid solution, led to significant improvements of OSC and catalytic activity (based on dynamometer test measurements) of the aged TWC. The latter was made possible due to the removal of significant amounts of various contaminants accumulated on the catalyst surface (e.g., P, S, Pb, Ca, Zn, Si, Fe, Cu, and Ni) during driving conditions, as revealed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and X-ray Photoelectron Spectroscopy (XPS) analyses. For the first time, it is demonstrated that dilute oxalic acid solution significantly improves the catalytic activity of an aged commercial TWC toward CO, C_xH_y, and NO_x conversions under real exhaust gas conditions (dynamometer tests) by two to eight times in the 250−450 °C range and the OSC quantity by up to 50%. Oxalic acid appears to be more efficient than citric acid in removing specifically P- and S-containing compounds from the catalyst surface, whereas citric acid in removing Pb- and Zn-containing compounds, thus uncovering surface active catalytic sites.

Introduction

Regardless of the advanced gasoline-fueled internal combustion engine designs developed nowadays with more robust combustion and reduction in engine out emissions, the latter still need to be further reduced due to more and more stringent environmental regulations imposed. For this reason, the use of a three-way catalytic converter (TWC) has proven to be the most effective and indispensable system for controlling carbon monoxide, unburned and other hydrocarbons, and nitrogen oxides (NO, NO_2) gas emissions.

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Three-way catalytic converters tend to lose their catalytic activity and selectivity over time and become almost inactive after about 150 000 km mileage (*1*, *2*). Understanding catalyst deactivation is of crucial importance in TWC technology since significant enhancement in the durability of TWC would be expected and that suitable regeneration technology of TWC could also be developed. The deactivation of TWC is the result of a number of chemical and physical changes which occur in the structure and surface chemical state of the active catalyst composition and of other components of the washcoat material used, leading to the loss of active catalytic sites (*3*). The causes of TWC deactivation are classically divided into three categories: thermal, chemical, and mechanical (*1−5*). They may occur separately or in combination with each other, where the net effect is always the loss of active catalytic sites. Mechanical deactivation is known to be irreversible and involves physical breakage or attrition of the monolith (*4*). Sintering of precious metals and washcoat solid material crystallites due to either their exposure at high operational temperatures (greater than 900 °C) or thermal shocks is part of thermal deactivation (*3*).

Chemical causes of TWC deactivation comprise poisoning of the catalyst surface by the interaction of impurities (compounds present in the exhaust gas) with the catalyst active sites. The impurities originate from fuel additives (e.g., Pb and S) (*6*, *7*), lubricant oil additives (e.g., P, Zn, and Ca) (*5*, *8*), and the construction materials of the engine and exhaust pipe systems (e.g., Fe, Ni, Cu, and Cr) (*9*, *10*). The impurities can irreversibly be adsorbed or react with the catalyst surface causing induced reconstruction of the catalyst surface and physical/chemical blockage of the support pore structure (*4*). Metal contaminants appear in TWCs either in the form of an overlayer constituting Zn, Ca, and Mg phosphates or as aluminum and cerium phosphates formed after the reaction of washcoat components with phosphorus compounds (*2*, *5*). Other metal compounds formed in the presence of SO_2 in the exhaust gas were reported to include sulfates, sulfonates, and sulfides (*4*, *6*, *7*).

Despite the extended use of three-way catalysts in automotive industry for so many years, only a few attempts have yet been made aiming at expanding the durability of gasoline-driven aged commercial TWCs and in situ regenerating their catalytic performance after applying economically attractive and environmentally friendly techniques. These attempts include extraction of contaminants by the use of liquid solvents such as weak organic acids (e.g., acetic, oxalic, and citric acids) (*10−12*) and employment of different combinations of thermal and chemical treatments by oxygen, hydrogen, and chlorine-containing gas mixtures (*13*, *14*) or other chlorine-containing reagents such as carbon tetrachloride, hydrochloric acid, and 1,2-dichloropropane (*15*, *16*). Chlorine treatments tend to reverse the effects of thermal aging on noble metal particle size (decrease of noble metal dispersion) by redispersing the large particles of these metals (increase of metal dispersion). Removal of contaminants accumulated on the active surface of TWC by the use of weak organic acid solutions is accomplished through dissolution of their respective compounds and complexation of the metal and other ions formed in solution. Weak organic acids are preferred to prevent destruction of the washcoat material.
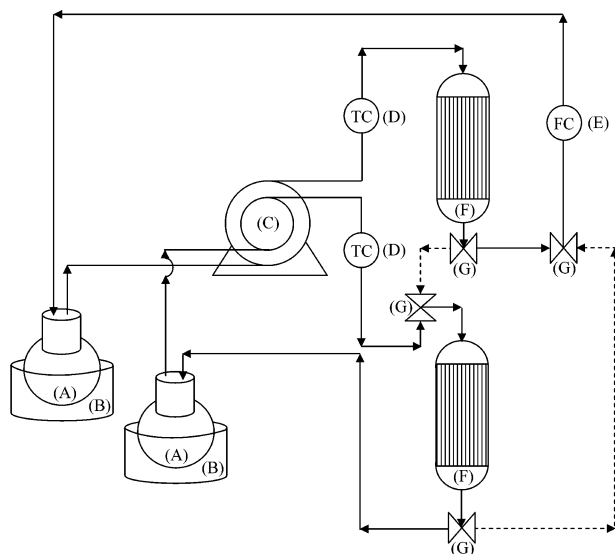
The present study was undertaken to investigate for the first time the effects of the use of dilute oxalic and citric acid solutions on the improvement of catalytic activity under real driving conditions and of the oxygen storage capacity of a severely aged commercial three-way catalyst (83 000 km

FIGURE 1. Flow diagram of the lab-constructed apparatus for studying reactivation by acid washing of aged commercial three-way catalysts. A: spherical flask; B: heating-stirring mantle; C: peristaltic pump; D: temperature controller; E: rotameter; F: reactor-columns; and G: three-way valves.

mileage). The removal of various contaminants (e.g., P, S, Pb, Ca, Zn, Si, Fe, Cu, and Ni) accumulated on the catalyst surface under real driving conditions after applying the present acid washing procedures was correlated with the catalytic and oxygen storage/release properties of TWC. The weak oxalic acid washing solution is shown to significantly improve the catalytic activity of the aged three-way catalyst toward CO, NO_x, and HC conversions under real exhaust gas conditions, very likely due to the removal of large amounts of phosphorus- and sulfur-containing compounds from the aged TWC. It is demonstrated that oxalic acid better recovers the catalytic activity and oxygen storage capacity of the aged TWC compared with the citric acid washing solution.

Experimental Section

Sample Selection. Three-way catalytic samples were extracted from the converter of a gasoline-driven automobile (model Mazda 323, 83 000 km) in Cyprus provided by STELCO Ltd. Company based in Cyprus. The aged TWC dismantled from the Mazda car constituted one cartridge having an ellipsoid shape with length $L = 14.4$ cm and diameters $d_1 = 14.8$ and $d_2 = 7.7$ cm. The samples studied were taken from the center of the first 2 cm in length (inlet) of ceramic monolith of the TWC in practically cubic shapes ($2 \times 2 \times 2$ cm³). Determination of the basic components of the aged TWC and its contaminants was performed by ICP-AES analyses.

Regeneration of Aged Commercial TWC Samples. The regeneration procedures investigated for significant improvement of TWC activity and its oxygen storage and release properties were applied on small monolith fragments (cubic shape, $2 \times 2 \times 2$ cm³) using a lab-constructed apparatus (Figure 1). The latter consists of a metering peristaltic pump for recirculation of the weak organic acid washing solution through the TWC sample, two reactor-columns operating in series or parallel, where the TWC sample was placed in, a rotameter for an optical observation of liquid flow, a temperature controller for continuous control and monitoring of solution temperature, and spherical flasks placed on heating-stirring mantles for homogeneous heating and stirring of the washing weak acid solution.

The solid samples extracted from the aged TWC after being placed in the reactor-column were treated with the oxalic or citric acid solution the concentration of which was set to 0.1

M. About 80 mL of liquid acid solution was continuously pumped upstream through the sample channels for 1 h. The solution in the flask (1 L) was then replaced by a fresh one which was used for an additional 1 h. The volumetric flow rate of the acid solution recirculated was set to 600 mL/min, whereas the temperature of solution was kept constant at 50 °C. It is noted that under the experimental conditions applied the surface of the washcoat adhered on the ceramic monolith was in full contact with the washing solution.

After washing, each catalyst specimen was thoroughly washed in the reactor-column by continuous recirculation of deionized water for 30 min at the same conditions employed for the washing procedure. The samples were then dried at 120 °C overnight and at 200 °C for 2 h for complete removal of water and organic acid residues. It should be noted that the acid concentration in solution, the temperature, and the flow-rate of acid solution used were optimized with respect to their removal efficiency of contaminants and not of any important catalytic components.

Quantitative Chemical Analysis of Aged and Acid-Washed TWC Samples by ICP-AES. Prior to ICP-AES analysis, 100 mg of TWC sample was gently crashed into powder and dissolved in a liquid mixture of aqua regia (HNO_3:HCl = 3:1 v/v) and HF at 80 °C. All chemical species were entered in the latter acid solution except Si, which was swept out by filtration. The solution was then diluted in deionized water, and the concentrations of contaminant species in the aged and acid-washed TWC sample solutions were measured by ICP-AES analyses. The model instrument used for the ICP-AES analyses was an ICPS-7500 plasma emission spectrometer (Shimadzu).

All aged and regenerated samples were analyzed for Pb, Zn, Mn, Ca, Fe, Cu, Cr, Ni, Pd, Pt, Rh, Ce, Zr, Ba, and P using appropriate ICP-AES calibration standards. Solutions of HNO_3 (without sample) were used as reagent blanks, where detection levels of all species were below the detection limits of the instrument. The quantitative analysis (mg/L) of samples and standard solutions was based on the average value of three experimental readings. Sample concentrations (mg/L) were then converted in g/kg of TWC (dry-weight basis).

X-ray Photoelectron Spectroscopy (XPS) Studies. XPS studies were performed with a VG Escalab 200 R spectrometer equipped with a hemispherical electron analyzer and an Mg Kα (1253.6 eV) X-ray source. The sample was mounted on a sample-rod in the pretreatment chamber of the spectrometer and degassed at room temperature for 1 h before being transferred to the analysis chamber. A certain region of the X-ray photoelectron (XP) spectrum was then scanned a number of times in order to obtain a good signal-to-noise ratio. The binding energies (BE) were referenced to the spurious C1s peak (284.6 eV) used as an internal standard. Data processing was performed with the *XPS peak* program. The spectra were decomposed with the least-squares fitting routine provided by the software and using Gaussian/Lorentzian (90/10) product function after subtracting a Shirley background. Atom percent surface composition was calculated using peak areas normalized on the basis of published sensitivity factors (*17*).

Oxygen Storage Capacity (OSC) Measurements. The Oxygen Storage Capacity of the aged and regenerated TWC samples (50 mg) was measured using the pulse injection method (*18*). The "Oxygen Storage Capacity Complete, *OSCC*" of the TWC is defined as the amount of reducible oxygen species (μmol-O/g) that reacts with consecutive pulses of CO or H_2 titrating molecules. The amount of the most reactive (labile) oxygen species of the catalyst is called "Oxygen Storage Capacity, *OSC*" and is defined as the amount of oxygen that reacts during the first CO or H_2 pulse. The apparatus and experimental procedure applied for OSC measurements have been reported in detail elsewhere (*1*).

TABLE 1. Concentrations of Various Basic Components and Contaminants Measured by ICP-AES Analyses at the Inlet (First 2 cm) and Central Region of an Aged Commercial TWC (83 000 km)

TWC Basic Components (g/kg of TWC)						
Pd	Pt	Rh	Ce	Zr	Al	Ba
2.510	0.142	0.153	18.517	38.426	255.024	10.238

TWC Contaminants (g/kg of TWC)						
Pb	S	P	Zn	Ca	Fe	Cu	Ni
10.746	2.617	15.406	3.155	11.125	1.408	1.447	0.131

Catalytic Activity Measurements (Dynamometer Tests). Activity tests were carried out in a quartz tube reactor with an internal diameter of 22 mm and using the apparatus previously described (*14*). Real exhaust gas was provided by a spark ignition engine and was directed into the reactor after passing through a heating coil with GHSV in the 100 000–140 000 h^{-1} range. The gas was further preheated to 120 °C prior to entering the reactor, and the final temperature was set to 550 °C. Exhaust gas from a vehicle running at a constant speed (50 km/h) in idling mode with a lambda (λ) value of 1.0 was utilized in all activity measurements. The exhaust gas contained 15 000 ppm CO_2, 6500 ppm CO, 3000 ppm NO_x, and 300 ppm C_xH_y (average values with variation of about ±5%). Activity measurements were performed both prior to and after the regeneration treatment of the same TWC sample. CO, C_xH_y, and NO_x conversions were calculated based on appropriate mass balances and the experimental gas concentrations measured.

Results and Discussion

Chemical Characterization of Aged and Acid-Washed TWC Samples. Table 1 reports the initial amounts (g/kg of TWC) of basic components and contaminant elements found in the aged commercial three-way catalyst (83 000 km mileage). As reported in Table 1, the TWC investigated contains a combination of Pd, Pt, and Rh noble metals in about 16:1:1 ratio. These metals are well-known to have been used in former three-way catalysts in a similar ratio for the appropriate control of exhaust gas emissions (*19*), whereas the current TWCs contain only Pd and Rh. The noble metal loading based on the data reported in Table 1 was estimated to be about 1 wt % based on the washcoat (27 wt % of TWC), which is within the range of the amount usually reported for commercial TWCs. Cerium and zirconium are present in the three-way catalyst composition in the form of CeO_2, ZrO_2, or $Ce_xZr_{1-x}O_2$ solid solution. Based on the Ce and Zr amounts measured, a chemical composition of $Ce_{0.32}Zr_{0.68}O_2$ was calculated (assuming that all Ce and Zr are contained within this solid solution phase). On the other hand, if it is assumed that all Ce and Zr are present in the washcoat as CeO_2 and ZrO_2, respectively, a composition of 27 wt % of washcoat material is calculated. Here, the washcoat is considered consisting of CeO_2, ZrO_2, and Al_2O_3 phases. The loading of 27 wt % for the washcoat is an upper value since Al is present in the ceramic support monolith. Barium oxide is known to be added at ∼5–10 wt % as a surface area stabilizer of alumina (*19*). Therefore, the fact that 5.7 wt % of this oxide is found in the present TWC is reasonable. Remarkably high concentrations of P, Ca, and Pb compared with other contaminants were measured in the aged catalyst (Table 1) as a result of severe chemical deactivation derived from gasoline- and lubricant oil-additives. Amounts of Pb between 15 and 25 g/kg$_{TWC}$ were reported by Angelidis et al. (*9*) over various aged commercial TWCs (40 000–200 000 km) which are even higher than that measured in the present study (Table 1).
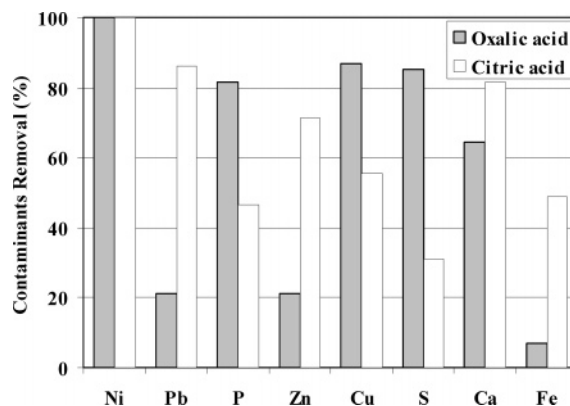
FIGURE 2. Percent removal of Ni, Pb, P, Zn, Cu, S, Ca, and Fe obtained by using oxalic and citric acid washing procedures over aged TWC samples.

Figure 2 shows the percentage removal of Ni, Pb, P, Zn, Cu, S, Ca, and Fe obtained after using oxalic or citric acid washing solutions for the regeneration (increase of catalytic activity) of the present aged commercial TWC. It is worth noting that Ni metal contaminant was not detected in the acid-washed samples compared with the aged TWC sample (Table 1), implying that the applied regeneration methods led to complete removal of Ni present at a relatively low amount in the aged catalyst (Table 1).

The highest percentage of Pb-removal is obtained with citric acid (86%), whereas the lowest one is obtained with oxalic acid (21%). This is probably due to the fact that removal of Pb^{2+} through complexation with citric acid anions is enhanced due to the higher negative charge of the latter ions compared with the oxalic acid derived ones (*20*). This is also likely the reason for obtaining higher amounts of Zn, Ca, and Fe metal contaminants percent removal, when citric acid instead of oxalic acid is used (Figure 2). High values of Zn-removal (68–90%) were also obtained with the use of citric acid solution in a previous work from our laboratory (*1*) on two different in origin and mileage commercial TWCs. In the present work, 71% of initial Zn is removed from the aged TWC. Zn was found to accumulate as a glassy and amorphous overlayer consisting of $Zn_3(PO_4)_2$, $CaZn_2(PO_4)_2$, $MgZn_2(PO_4)_2$, and $Zn_2P_2O_7$ (*2*, *5*). BET surface area (m^2/g) measurements performed on the aged and acid-treated TWC samples revealed that an increase of 28 and 35% was obtained for the citric and oxalic acid treatments, respectively. These results strongly support also the removal of such solid overlayers which potentially block pore mouths of the macropores of washcoat material.

The percentage removal of phosphorus (P) after using the oxalic and citric acid treatments is also presented in Figure 2. Maximum removal of P is obtained with oxalic acid treatment (81%), whereas only 46% removal of initial P is obtained with citric acid. This is likely due to the fact that oxalic acid is a stronger acid (pK_{a1} = 1.20) compared with citric acid (pK_{a1} = 3.06), having therefore a greater dissolution efficiency compared with citric acid toward phosphates, phosphites and other P-containing species (*20*) present in aged automotive TWCs.

Oxalic acid is found to better dissolve sulfates, sulfonates, and/or sulfites (S-containing species) compared with citric acid (Figure 2). This result coincides with the fact that Cu is more efficiently removed from the aged TWC after using oxalic than citric acid, suggesting that Cu is likely linked to $CuSO_4$ and/or Cu_2S which are more easily dissolved by the stronger oxalic acid.

The combined use of a mixture of citric and oxalic acids (0.1 M each) resulted in the removal of a larger number of contaminants than by any of the individual acid washing.
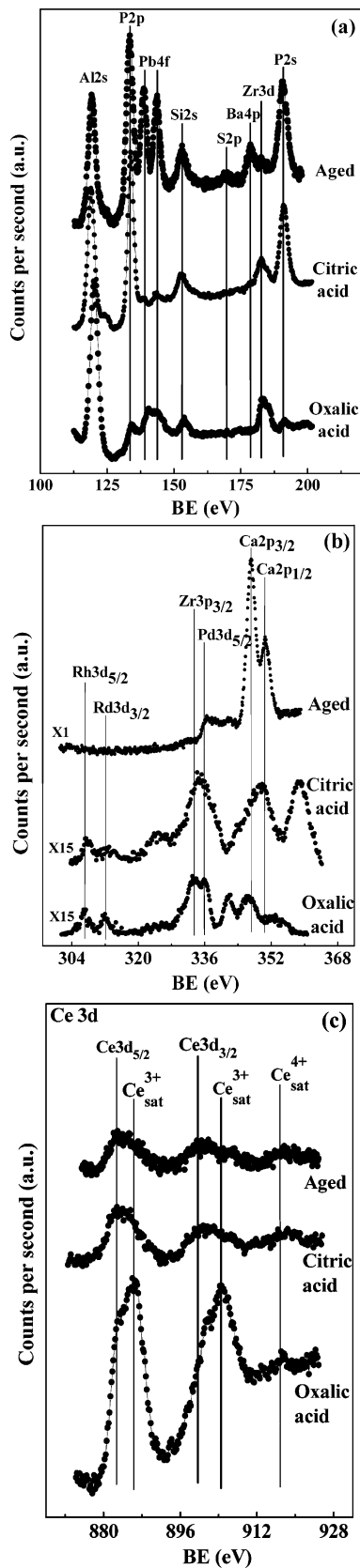
FIGURE 3. X-ray photoelectron spectra of (a) Al 2s, P 2p, Pb 4f, Si 2s, S 2p, Ba 4p, Zr 3d, and P 2s; (b) Rh 3d, Pd 3d, Zr 3p, and Ca 2p; and (c) Ce 3d obtained on the aged and washed with oxalic and citric acid TWC samples.

However, the % removal obtained was not higher than that reported in Figure 2.

TABLE 2. Surface Atom Ratios of Aged and Acid-Washed TWC Samples Based on XPS Analyses

surface atom ratio	aged TWC	oxalic acid-washed TWC	citric acid-washed TWC
Pd/Al	0.018	0.016	0.014
Rh/Al	a	0.003	0.002
Ba/Al	0.124	0.021	0.017
Zr/Al	0.012	0.025	0.016
Ce/Al	0.018	0.041	0.018
P/Al	0.846	0.112	0.475
Pb/Al	0.048	0.018	0.005
Ca/Al	0.326	0.045	a
Zn/Al	0.017	0.046	0.004
Fe/Al	0.018	a	a
Cu/Al	0.010	a	0.005

^{a} Not detected.

X-ray Photoelectron Spectroscopy Studies. Figure 3a presents X-ray photoelectron spectra in the $100-210$ eV range obtained on the aged and washed with oxalic and citric acid TWC samples. In this energy region, Al 2s, P 2p, Pb 4f, Si 2s, S 2p, Ba 4p, Zr 3d, and P 2s X-ray photoelectron peaks appear. As seen in Figure 3a, intense peaks of P 2p at 133.8 eV (± 0.2) and P 2s at 191.2 eV appear in the aged catalyst. The P 2p peak is attributed to phosphates (PO_4^{3-} or HPO_4^{2-}), whereas no XP peak at 127.6 eV associated with P in phosphides (*21*) appears. Table 2 shows the estimated surface atom ratios of the elements detected in the used and washed TWC samples relative to Al species. Based on the P/Al ratio for the aged TWC sample (0.846, Table 2), it can be stated that a high concentration of P-containing species is accumulated on the catalyst surface. Oxalic acid treatment seems to largely reduce phosphorus concentration (87% removal, Table 2), whereas treatment with citric acid leads to a removal of only 44% of initial P (Table 2). Looking at the most intense emission peak of phosphorus (P 2p, Figure 3a), it becomes clear that phosphorus almost disappears after washing with oxalic acid, whereas a smaller reduction is seen after citric acid washing. These results are in excellent agreement with those obtained from ICP-AES analyses (Figure 2), indicating that oxalic acid is a much better washing solution for extracting P compared with citric acid. X-ray diffraction (XRD) studies also revealed that after oxalic acid washing $CePO_4$ and $AlPO_4$ phases detected in the aged TWC had disappeared, whereas small in intensity diffraction peaks of these phases were observed in the case of citric acid washed sample. These results are in harmony with the XPS results previously described.

The S 2p feature (Figure 3a) was only observed in the aged catalyst at a binding energy of 169.0 eV, which is in the BE range normally associated with sulfate compounds (e.g., $Al_2(SO_4)_3$) (*12*). SO_2 adsorption studies on ceria led to the observation of two doublets occurring at this energy region (*22*). The first doublet at the high BE was assigned to surface SO_4^{2-} species, whereas the one at the low BE to surface SO_3^{2-} species. In the present work, the observation of only one doublet (S $2p_{3/2}$–S $2p_{1/2}$) with BE of the most intense S $2p_{3/2}$ component at 169.0 eV indicates that only sulfate species are present in the aged catalyst. What is of great importance here is that the S 2p peak disappears in the XP spectra of the acid-washed samples, indicating that surface sulfate species are all removed from the catalyst surface but not all of those found in the subsurface region of the solid (Figure 2).

The Pb 4f energy region (Figure 3a) displays the characteristic Pb $4f_{7/2}$–Pb $4f_{5/2}$ doublet whose BE (139.1 eV) of the most intense Pb$4f_{7/2}$ component fits with the reported value for PbO species (*23*). Table 2 and Figure 3a show that Pb is better removed from the catalyst surface after using the citric acid washing solution.

The value of ca. 153.0 eV for Si 2s (Figure 3a) agrees with those reported in the literature for SiO$_2$ (24). As shown also by other authors (12), the intensity of Si 2p peak increased substantially from the fresh to the aged catalyst, confirming that silicon can be consider as a chemical contaminant. However, the authors (12) did not extract silicon after washing with citric acid. In the present study, the intensity of the Si 2s peak decreased after washing and is less prominent in the oxalic acid-washed sample (Figure 3a). Therefore, it can be stated that washing with weak oxalic acid leads to partial removal of silicon contaminant from the catalyst surface.

In Figure 3a the peak at 182.2 eV is attributed to Zr $3d_{5/2}$ photoemission, which coincides with the value reported for ZrO$_2$ (24). The intensity of Zr 3d peak increases after washing, and in particular when oxalic acid was used. It has been reported that the BE value of the Ba $3d_{5/2}$ peak in BaO lies in the 779.1−779.9 eV range (24), whereas that of barium sulfate shifts to higher values (780−781 eV) (25). According to Table 2, Ba detected at 780.5 eV is suggested to largely concentrate on the surface of washcoat in the form of BaSO$_4$, where the latter is removed completely after acid washing since no sulfur (S 2p) and significantly less barium (Ba $4p_{3/2}$) were measured on the surface of the regenerated samples (Figure 3a). Ba $4p_{3/2}$ is the most intense peak of the Ba $4p_{3/2}$-$4p_{1/2}$ doublet. The less intense peak (Ba $4p_{1/2}$) falls out of the energy region shown in Figure 3a.

Copper (Cu) and iron (Fe) contaminants were not detected in the oxalic acid-washed sample, whereas Fe was not detected also in the citric acid-washed sample (Table 2). It should be noted that differences observed in the results obtained from XPS and ICP-AES analyses are assigned to some small variations in radial distribution of these contaminants in the aged three-way catalyst monolith (8).

Figure 3b presents X-ray photoelectron spectra of Ca 2p, Rh 3d, and Pd 3d core electrons. XP peak at 346.3 eV is assigned to Ca^{2+} contaminant (26), and it is seen to be almost completely removed from the surface of the aged catalyst after citric and oxalic acid treatments (note the difference in the scaling factor in Figure 3b). In particular, the value of surface atom ratio of Ca in the aged sample is found to be 0.326, whereas after citric acid treatment it becomes practically zero (Table 2). These results are in harmony with the ICP-AES results (Figure 2). On the other hand, Rh concentration on the catalyst surface is not affected by either citric or oxalic acid washing (Figure 3b). Surface rhodium (Rh) was not detected in the aged catalyst but only in the acid-washed samples (Figure 3b, Table 2). The Rh $3d_{5/2}$ peak (308.2±0.2 eV) is evident of Rh$^+$ since this BE corresponds to oxidation states between fully oxidized Rh^{3+} (308.8 eV) and metallic Rh^0 (306.8 eV) (27). This result suggests that rhodium clusters become oxidized to Rh$^+$ by −OH groups, the latter present in the weak acid washing solutions used. Weng-Sieh et al. (25) reported a BE of 308.1 eV for hexagonal Rh$_2$O$_3$ and a value in the 308.0−308.6 eV range for RhOOH.

Pd $3d_{5/2}$ XP peak appeared at 336.1 and 335.6 ± 0.2 eV in the aged and regenerated samples, respectively (Figure 3b). The latter value corresponds to Pd^0 (metallic state). A Pd 3d binding energy reported at about 336.7 eV is ascribed to Pd^{2+} or to the Pd atom in an oxygen environment (28). A small variation of the Pd/Al atom ratio between the aged and regenerated samples (Table 2) is due to the slightly different radial location examined and to overlapping with the Zr $3p_{3/2}$ XP peak (Figure 3b). These results are consistent with the ICP-AES analyses that show no removal of Pd.

No X-ray photoelectron peak for Pt was recorded for any of the three samples due to overlapping and the low intensity of this peak. This was also observed by Galisteo et al. (12) who only detected Pt in fresh diesel oxidation catalysts. The present ICP-AES analyses (Table 1) showed that Pt is one of the noble metals present in the investigated TWC.
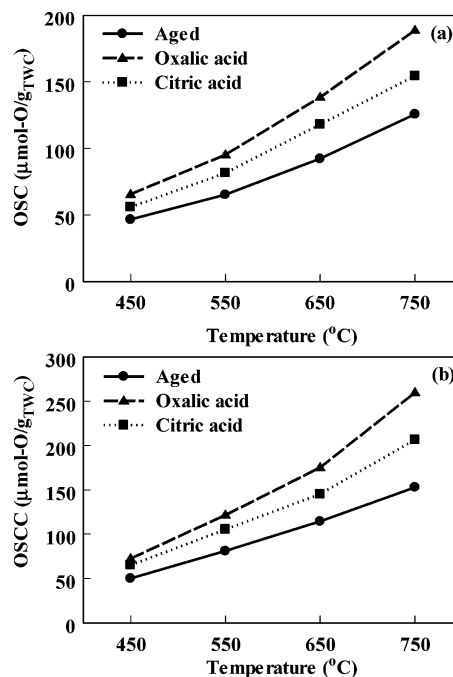
FIGURE 4. OSC (a) and OSCC (b) quantities (μmol-O/g) measured by H$_2$ pulsed-feed experiments in the 450−750 °C range over the aged (●), oxalic acid (▲), and citric acid (■) washed TWC samples.

The Ce 3d core-level spectra of the aged and washed TWC samples are displayed in Figure 3c. The sample washed with oxalic acid displays a Ce 3d spectrum dominated by two strong satellite lines of Ce^{3+} (at 885.8 and 904.6 eV) and a very small satellite of Ce^{4+} at about 917.0 eV. However, the aged and citric acid-washed samples show small satellites of Ce^{3+} and a major one at 917.0 eV, which is conclusive that Ce^{4+} species are dominant. The literature values for Ce $3d_{5/2}$ are in the 881.8−882.4 eV range (24, 28), whereas in the present work a difference by about 0.5 eV is observed (882.8 eV). This difference likely arises from the overlapping of the principal Ce $3d_{5/2}$ component and one of the Ce^{3+} satellites placed around 885.8 eV. According to Table 2, washing of TWC with the oxalic acid solution led to a significant increase of the Ce/Al ratio, whereas no change was observed when citric acid was used. Based on the ICP-AES and XPS results, oxalic acid appears to be the most efficient extracting agent of a large amount of P-containing compounds (Figures 2 and 3a). It can be said that washing with weak oxalic acid solution largely uncovers the TWC washcoat surface through removal of the P-contaminant overlayer, as seen also for the Rh, Ce, and Zr surface concentration increase after oxalic acid washing (Table 2).

Oxygen Storage Capacity Measurements. Figure 4 presents OSC (Figure 4a) and OSCC (Figure 4b) measurements of TWC after using H$_2$ pulses in the 450−750 °C range over the aged, oxalic, and citric acid-washed TWC samples. It is obvious that the applied regeneration procedures result in a significant improvement of OSC and OSCC quantities of the aged TWC. As previously shown (Figures 2 and 3), washing of TWC with weak oxalic and citric acid solutions results in the removal of significant amounts of contaminants, which are considered to suppress the rates of oxygen storage and release. Many works support the view that large quantities of contaminants accumulate on the washcoat surface, whereas accumulation inside the pores of washcoat is considerably lower, and, therefore, fouling is the main deactivation mechanism (4, 9). Lower OSC values measured in the aged TWC sample compared with the regenerated ones might also be explained as due to diffusional resistances caused by pore-blocking of fine pores due to accumulation

of contaminants.

The most significant improvement in the measured OSC quantity of aged TWC is observed after using the oxalic acid washing solution (Figure 4). According to Figures 2 and 3 and Table 2, phosphorus- and sulfur-containing contaminant compounds found in the present aged TWC were more effectively removed by oxalic compared with citric acid solution. It was previously shown (12) that P, S, and Si were preferentially deposited on the top of washcoat in an aged diesel oxidation catalyst. These results strongly support the view that removal of large amounts of P, S, and Si contaminants from the washcoat surface after regeneration of aged TWC with oxalic acid results in the uncovering of active catalytic surface (as concluded from XPS measurements), thus partly restoring the oxygen storage and release properties of CeO_2 and $Ce_xZr_{1-x}O_2$ solids. According to recent works (29−31), formation of cerium phosphate in aged TWCs is responsible for locking the Ce^{3+}/Ce^{4+} redox couple and significantly deteriorating the oxygen storage and release properties of TWC. $CePO_4$ and $AlPO_4$ were found around the CeO_2 and γ-Al_2O_3 particles (29−31), within the macropores of washcoat, in the form of a crust, thus causing "physical" deactivation (washcoat pore blocking). It seems that this crust along with the contaminants overlayer are removed from the catalyst surface, thus opening closed pores and exposing active catalytic sites associated with the OSC phenomenon (e.g., noble metals, $Ce_xZr_{1-x}O_2$) to the reactant gases.

As seen in Figure 4a,b, the use of citric acid washing solution led to a lower extent of increase of OSC and OSCC quantities of the aged TWC compared with oxalic acid, likely due to the fact that only half of the initial amount of P present in the aged catalyst was removed. Unlike oxalic acid, citric acid was found to lead to significantly higher amounts of Pb, Zn, and Fe removal (Figure 2). It is interesting to note that recent results from our laboratory (32) have shown that Fe (0.1−0.3 wt %) deliberately deposited onto a 1 wt % Pd/ 20%CeO_2−Al_2O_3 model "three-way" catalyst does not influence in a negative way the OSC quantity. In contrary, Fe acts as a promoter of the oxygen storage capacity and catalytic activity, especially with increasing reaction temperature (32). These results suggest that higher OSC quantities should be expected to be measured on a catalyst containing Fe metal. This agrees with the present case of oxalic acid-washed sample, where only 7% of initial Fe in the aged sample was removed.

Catalytic Activity Measurements (Dynamometer Tests). Figure 5 presents the light-off curves of CO (a), C_xH_y (b), and NO_x (c) conversions obtained over the aged and washed with oxalic and citric acids TWC samples under real exhaust-gas conditions (dynamometer tests). The CO (Figure 5a), C_xH_y (Figure 5b), and NO_x (Figure 5c) conversions of the washed TWC samples are significantly higher in the 300−450 °C range compared with the ones of aged TWC. In particular, the use of oxalic acid results in the highest improvement in light-off behavior of all three major pollutants present in the exhaust gas. The aged TWC presents significantly higher values of T_{50} (the temperature at which 50% conversion of a given pollutant is achieved) for CO conversion compared with the acid-washed samples. For the aged TWC, a T_{50} greater than 450 °C is obtained, whereas for the citric and oxalic acid-washed samples, T_{50} values of 395 and 370 °C, respectively, are obtained. In addition, after washing with oxalic acid an increase in X_{CO} by more than eight and two times with respect to the aged TWC is obtained at 350 and 450 °C, respectively. This is indeed an impressive result. Similar results are observed for the hydrocarbon conversion behavior. Improvements in the NO conversion (Figure 5c) are also observed after applying the given acid washing procedure. However, the latter appear to be smaller than those seen for the CO and C_xH_y conversions. As noted in Figure 5c,
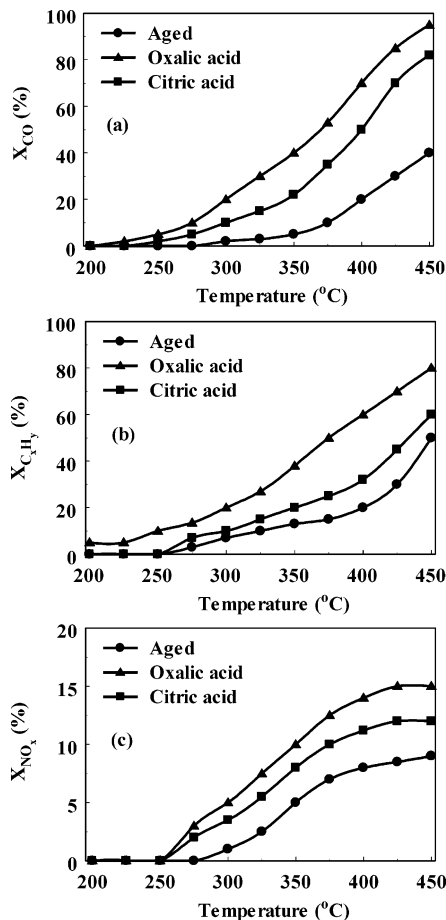
FIGURE 5. Conversion profiles of CO (a), C_xH_y (b), and NO_x (c) obtained over the aged (●), oxalic acid (▲), and citric acid (■) washed TWC samples under real exhaust gas conditions (dynamometer tests).

significantly higher temperatures are needed to reach the same conversion for the aged sample compared with the acid-washed ones. Based on the results reported in Figures 2, 3, and 5, improved catalytic performance after acid washing is obvious that is accomplished due to the removal of large amounts of contaminants resulting in the exposure of a larger number of active catalytic sites to exhaust gases.

Angelidis et al. (10) examined the use of acetic acid washing solution for the regeneration of an aged commercial automotive catalyst. They showed an increase in the catalytic performance of the aged commercial TWC using simulated exhaust gas compositions. However, as shown in a previous study (11), the use of acetic acid washing solution was the least efficient method for the removal of TWC contaminants and the recovery of OSC compared with oxalic and citric acid washing solutions. Galisteo et al. (12) also proposed the use of dilute citric acid washing solution in a commercial diesel oxidation catalyst. They showed the beneficial effect of such a treatment on the improvement of catalytic activity of an aged TWC for CO and C_3H_6 oxidation reactions.

The experimental results reported in the present work provide for the first time evidence that washing of a severely aged commercial TWC with oxalic acid results in a significant recovery of OSC and catalytic activity. Other dilute weak organic acids such as acetic and citric acids provide less improvement in the catalytic behavior. This pioneer study aiming at expanding the durability of a gasoline-driven aged commercial TWC and in situ regenerating its catalytic performance by applying effective, economically viable and environmentally friendly (waste reduction, preserving of raw materials) techniques seems to be one of the most promising

procedures among others that utilize weak organic acid washing solutions ever reported in the literature.

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