

Partial regeneration of an aged commercial automotive catalyst

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Abstract

An aged commercial three-way automotive catalyst was examined with respect to regeneration procedures. Catalyst samples were leached with acetic acid to remove contaminants accumulated on the catalyst surface during operation. The optimum leaching conditions concerning acetic acid concentration, solution feed rate and temperature were investigated. The leached samples were examined for their catalytic activity (CO and C₂H₄ oxidation, NO reduction and N₂ production) in comparison with samples of fresh and aged catalysts. The leaching procedure improves considerably the catalytic activity, where in the case of C₂H₄ oxidation, NO reduction reaches the activity of the fresh catalyst.

Keywords: Automotive; Three-way; Regeneration; Rejuvenation; Acetic acid; Leaching

1. Introduction

The three-way automotive catalysts tend to lose their activity during operation. The causes of this aging procedure are primarily thermal deactivation and poisoning [1].

The operation temperature varies in the range of 20–850°C. Under these conditions, both the substrate and the active metals (Pt and Rh) are affected. Crystallographic changes of the substrate constituents, interactions between

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substrate and active metals, alloying, sintering and other thermal induced changes cause a decrease in the number of catalyst active sites and reduction of its activity [2–6]. Thermal changes, connected with particle size, promote mechanical material losses through the exhaust gas flow. Thermal deactivation is normally irreversible, although redispersion of the sintered metal surface is possible [1].

Poisoning is the result of the action of Pb, Zn, Ca, P, S, Si and other metal compounds and carbonaceous material [5]. With respect to the active mechanism, there are three types of poisoning [1]:

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

The first two types of poisoning are responsible for the accumulation of poisons on the catalyst surface during operation. From the main poisons, Pb and S originate mainly from the fuel, P, Zn and Ca from the lubricants, and metallic compounds (Fe, Ni, Cu and Cr) from the metallic parts of the engine and the exhaust gas system [5].

The various poisons have a large affinity to the catalyst constituents. Accumulation of poisons on the catalyst surface depends on temperature, and is promoted by operation at low temperatures. Studies of the micro- and macrodistribution of poisons have shown that the main quantity is accumulated on the external surface of the substrate, while axial distribution studies have shown higher accumulation at the inlet of the exhaust gases [7,8]. In addition, it was found that radial distribution is uniform [7,8].

The degree of the main contaminants retention on the catalyst was $P > Pb > Zn > Ca \gg S$ [7]. The contaminants originating from the lubricants predominate, since Pb and S concentration in fuel is being continuously reduced over the last decades. The main compounds formed are phosphates, sulphates, sulfides, aluminates and oxides [7,9–13]. Most of these compounds are readily dissolved in acidic environment. Thus, an acid-leaching procedure is expected to remove the poisons from the catalyst surface. The use of strong acids (e.g., HCl, HNO₃ or H₂SO₄) is not recommended since they will attack the substrate. Weak organic acids (acetic or oxalic) are preferred, since they do not considerably affect the substrate. Oxalic acid has been used for regeneration tests of hydrodesulfurization catalysts [14] and acetic acid for Pt based industrial catalyst [15]. Acetic acid is preferred because:

- it is weaker acid ($pK_a = 4.72$) than oxalic acid ($pK_{a1} = 1.2$) [16];
- it will attack the substrate of the catalyst less severely;
- it is the recommended solute for phosphates and lead compounds [17].

Acetate has been tested for lead removal in early automotive catalysts (with

high lead accumulation) giving a temporary increase of catalyst activity, since lead was the only contaminant removed from the surface and the internal lead was redistributed after operation [5]. In modern catalysts, lead accumulation is less severe and the above disadvantage may be inverted. Preliminary leaching tests using acetic acid and SEM–EDS surface analysis have shown a considerable removal of poisons from the catalyst surface and a surface beneficiation effect by removing clogging material [8].

The aim of the present work was to study in a more systematic manner the conditions under which the optimum results may be obtained. The optimum leaching conditions were determined and the catalytic activity of the leached samples was tested on laboratory scale using feed gas mixtures representative of the automotive exhaust gases.

2. Experimental

A fresh and an aged commercial monolithic catalytic converter of the same origin (CITROEN ZX) were used for the leaching and activity tests. The aged catalyst was derived from an automobile with 60,000 km under urban conditions, which promote accumulation of poisons (low temperature operation). The cordierite base (CORNING) had the following characteristics:

- shape: oval;
- dimensions: length 15.2 cm, maximum major axis 14.5 cm, minor major axis 6.7 cm;
- channels density: 62.2 channels/cm²;
- channel shape: square;
- wall thickness: 0.16 mm;
- hydraulic diameter: 1.1 mm;
- open frontal area: 76% which after the washcoat addition is approximately 68%.

A slice of the aged catalyst from the exhaust gas inlet, where the higher contaminants accumulation is observed, was used for analysis and leaching tests. Cylindrical specimens (length 2.2 cm, diameter 1.6 cm) were derived from the above slice. The rest material was used for chemical analysis and preliminary leaching tests. Chemical analysis results of the slice are shown in Table 1. Noble

Table 1
Analysis of noble metals and main poisons in various catalysts (wt.-%)

Catalyst	Pt	Rh	P	Pb	Fe	Zn	Ni
Fresh	0.403	0.79	0.005	0.002	0.06	0.003	0.002
Error %	1.7	2.5	2.5	2.5	1.5	2.3	2.0
Aged	0.361	0.72	0.189	0.040	0.08	0.018	0.003
Error %	1.5	2.4	1.3	2.3	1.2	1.6	1.8

metals analysis was performed after complete dissolution of the catalyst in autoclave (200 mg of sample with 3 ml HNO₃ 65% + 1 ml HCl 37% + 0.5 ml HF 40%, 5 h at 180°C). Analysis results showed 10% Pt and 8.9% Rh losses during operation. Poisons analysis was carried out after dissolution with aqua regia in an open vessel in order to prevent cordierite dissolution and Si interference on P measurements [18]. This procedure is not expected to affect the measurements of poisons, since the major part is accumulated on the substrate. The noble metals, Pb, Fe, Zn and Ni were analyzed by AAS (Perkin Elmer 2380), and P by UV spectroscopy (Hitachi U-2000) using the ammonium molybdate method [18]. The concentration of poisons for the aged catalyst were used as the basis of removal yield calculations.

Analytical grade acetic acid (glacial 99.5%) and FeSO₄ were used for the preparation of the leaching solutions.

Small pieces (1–2 cm) derived from the above catalytic slice were applied to the preliminary leaching tests. The cylindrical specimens derived from the fresh and aged monoliths were used for the column leaching tests. The leaching solution was continuously pumped upstream through the sample channels. Under these conditions, the whole active surface of the catalyst is in contact with the leaching solution. After leaching, each catalyst specimen was washed thoroughly in the column by continuous flow of deionized water (18 ml/min) for 1 h and then dried for 2 h at 150°C (boiling point of pure acetic acid 118.1°C [17]). The above cleaning procedure was followed in order to remove remaining traces of acetic acid, which may cause problems during the catalytic activity tests. Finally, each catalyst specimen was analyzed for phosphorus, lead, iron and nickel, following the same procedure as the one applied for the initial analyses.

Optical and near surface concentration studies by SEM–EDS were carried out in selected samples. The parameters studied were acetic acid concentration, rate of acetic acid feed, and temperature.

The catalytic activity of these specimens was measured in an appropriate apparatus. The monolithic specimen was placed in the middle of a quartz tube surrounded by a tubular furnace. Prior to activity tests, the specimen was reduced in an H₂ flow of 200 ml/min at 400°C for 2 h, and was then purged by He flow. Then, the reactor was fed with a gas mixture, which simulates the stoichiometric composition of common car emissions (0.8% CO, 0.1% C₂H₄, 0.2% NO and 0.6% O₂, with He as inert gas). The total flow rate was kept constant at 1000 ml/min. The analysis of the reactants and products was carried out by means of gas chromatography (Shimadzu GC-14B with two parallel columns, Poropak Q and Molecular Sieve 13X) combined with vacuum chemiluminescence spectrometry for NO_x analysis (Teledyne, NO_x stack gas emissions analyser, model 911/912). The conversion of each pollutant and N₂ production yield (defined as $Y_{N_2} = 2[N_2]/[NO]_{inlet}$) were measured at different temperatures. As a measure of the characteristic activity, the light-off tempera-

ture (T_{50} , the temperature of the inlet gas at which the conversion of the reactant is 50%) was used.

3. Results and discussion

3.1. Preliminary leaching tests

Preliminary leaching tests were carried out in an agitating water bath using small catalyst pieces (about 3 g each) to determine the optimum acetic acid concentration for contaminant removal. The results of these experiments are shown in Fig. 1 and Table 2. In all cases, a maximum removal yield is achieved at an acetic acid concentration of 5 wt.-%. At higher concentrations, the removal yield remains almost constant. This behaviour is possibly connected with the acidity produced by a weak acid as the one used. In Fig. 2 the predicted pH values ($pK_a = 4.72$) and the P and Pb removal yields are plotted as a function of acetic acid concentration. The comparison of the removal yields and the predicted pH values show that both of them reach an almost constant value at acetic acid concentrations higher than 5 wt.-%. The solution produced during the 5 wt.-% acetic acid leaching was used for other substrate constituents analysis. Aluminum, barium, lanthanum, titanium and zirconium were determined by AAS (nitrous oxide–acetylene flame), and cerium by the titrimetric hydroquinone method [18]. Only aluminum was found in detectable quantities by the applied analytical techniques (the respective dissolved aluminum represents 2% of the total aluminum solubilized during the poisons determination analytical

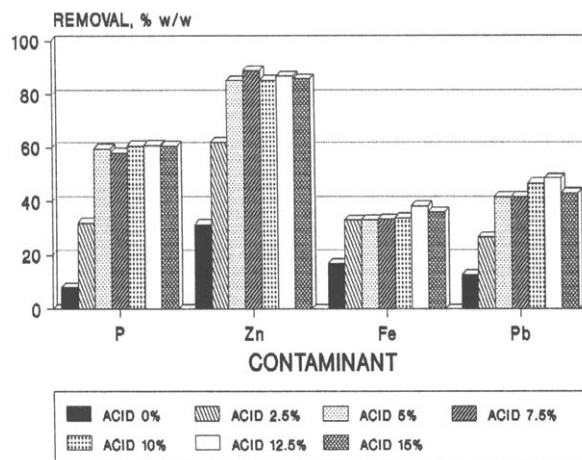
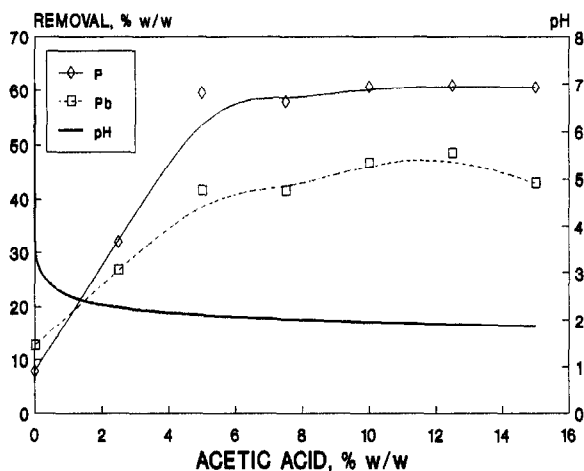


Fig. 1. Preliminary test for determining optimum acetic acid concentration (agitating bath, temperature 40°C, leaching solution volume 50 ml).

Table 2

Removal yields (%) of various contaminants obtained during preliminary and column leaching tests

Parameter	% Removal			
	P	Zn	Fe	Pb
Concentration (wt.-%) ^a				
0.0	7.9	31.4	16.8	12.6
2.5	32.0	62.0	33.0	26.7
5.0	59.6	85.2	33.1	41.6
7.5	58.0	89.0	33.3	41.6
10.0	60.7	85.4	33.8	46.7
12.5	60.9	87.0	38.2	48.5
15.0	60.6	85.9	36.0	43.0
Feed rate (ml/s) ^b				
5.5	26.1	9.5	2.2	15.9
11.4	32.9	44.5	22.5	29.9
14.1	64.1	82.7	38.9	64.3
18.0	78.6	85.1	64.3	69.5
22.0	65.7	86.4	61.1	65.6
24.4	77.4	84.9	68.7	76.0
Temperature (°C) ^c				
23	64.4	45.0	56.7	11.3
40	78.6	85.1	64.3	69.5
60	82.2	86.4	61.3	70.0

^a Agitated water bath, 40°C, volume 50 ml, 3 g sample.^b Column leaching, cylindrical samples, 40°C, 5 wt.-% acetic acid solution.^c Column leaching, feed rate 18 ml/min, 5 wt.-% acetic acid solution.Fig. 2. Phosphorus and lead removal yields (%) and predicted initial pH of the leaching solution ($pK_a = 4.72$) as a function of acetic acid concentration.

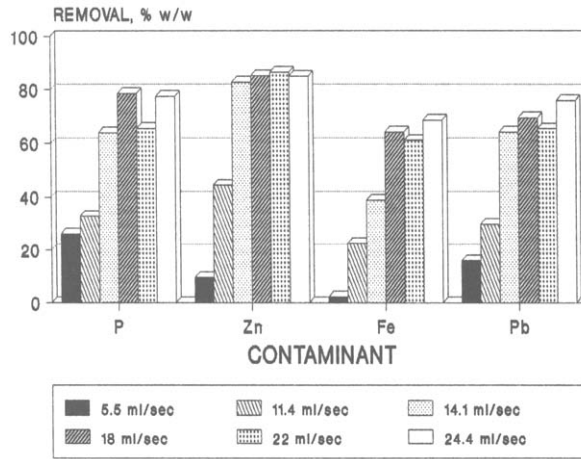


Fig. 3. Effect of the leaching solution feed rate on contaminants removal (column, acetic acid concentration 5 wt.-%, temperature 40°C).

procedure). The results above were as expected, since TiO_2 , ZrO_2 , L_2O_3 , CeO_2 and BaSO_4 (the chemical form of the above elements present in the substrate) are extremely refractory materials [19–21].

3.2. Column leaching tests

A series of experiments were carried out using cylindrical samples derived from the catalytic monolith. Acetic acid solution was pumped continuously through the channels of the catalyst, so the system could be considered as a

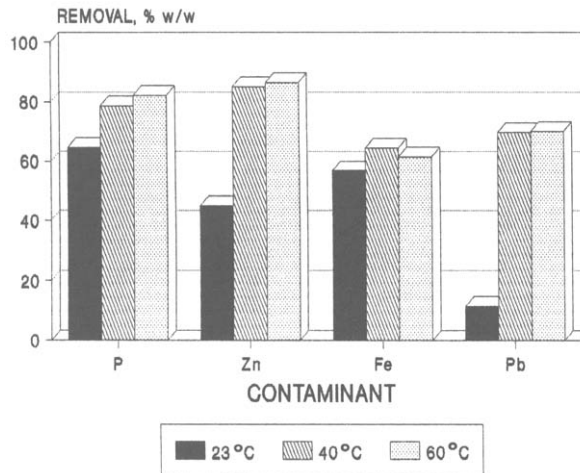


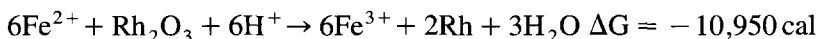
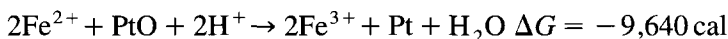
Fig. 4. Effect of the leaching solution temperature on contaminants removal (column, feed rate 18 ml/s, acetic acid concentration 5 wt.-%).

simulation of a real system in future. The parameters studied were the solution pumping rate and the temperature. The results are shown in Figs. 3 and 4 and Table 2. The removal yield seems to be constant for solution flow rates higher than 14.1 ml/s, and for temperatures higher than 40°C for all contaminants. Both results indicate that dissolution had taken place through pore diffusion control, and therefore the yield is not expected to increase considerably at higher concentrations and temperatures. According to the above experimental results, the following optimum leaching conditions were selected:

(a) acetic acid concentration 5 wt.-%; (b) leaching solution feed rate 18 ml/s (space velocity 21,600 h⁻¹, calculation based on 68% open front area) and (c) the temperature 40°C.

Analysis of the leached samples showed a slight increase in noble metal concentration (0.362 wt.-% Pt, 0.724 wt.-% Rh) suggesting that substrate losses during leaching are negligible, and the increase of noble metals concentration may be attributed to changes of the catalyst sample mass due to removal of poisons.

Two cylindrical samples were leached at the above mentioned conditions and a third one was leached by adding FeSO₄ (at a concentration of 0.1 M) in the leaching solution. FeSO₄ was added in an effort to reduce platinum or rhodium oxides possibly formed during the catalyst operation, since the reduction reactions are thermodynamically possible, e.g. (thermodynamic data from [22]):



The leached samples were studied by SEM–EDS to check the surface condition and the near surface contaminants concentration. The results obtained

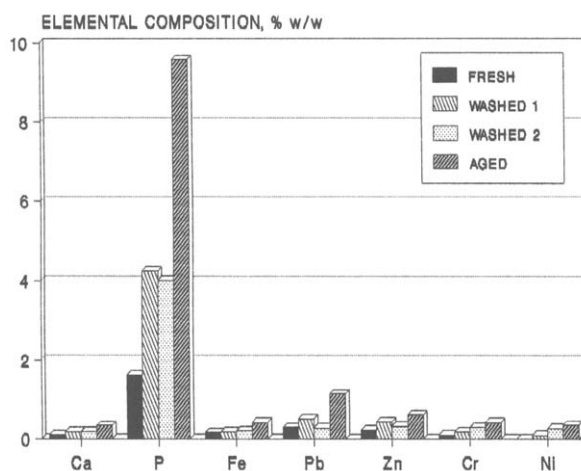


Fig. 5. Elemental contaminant's composition for treated, fresh and aged catalyst samples derived by EDS.

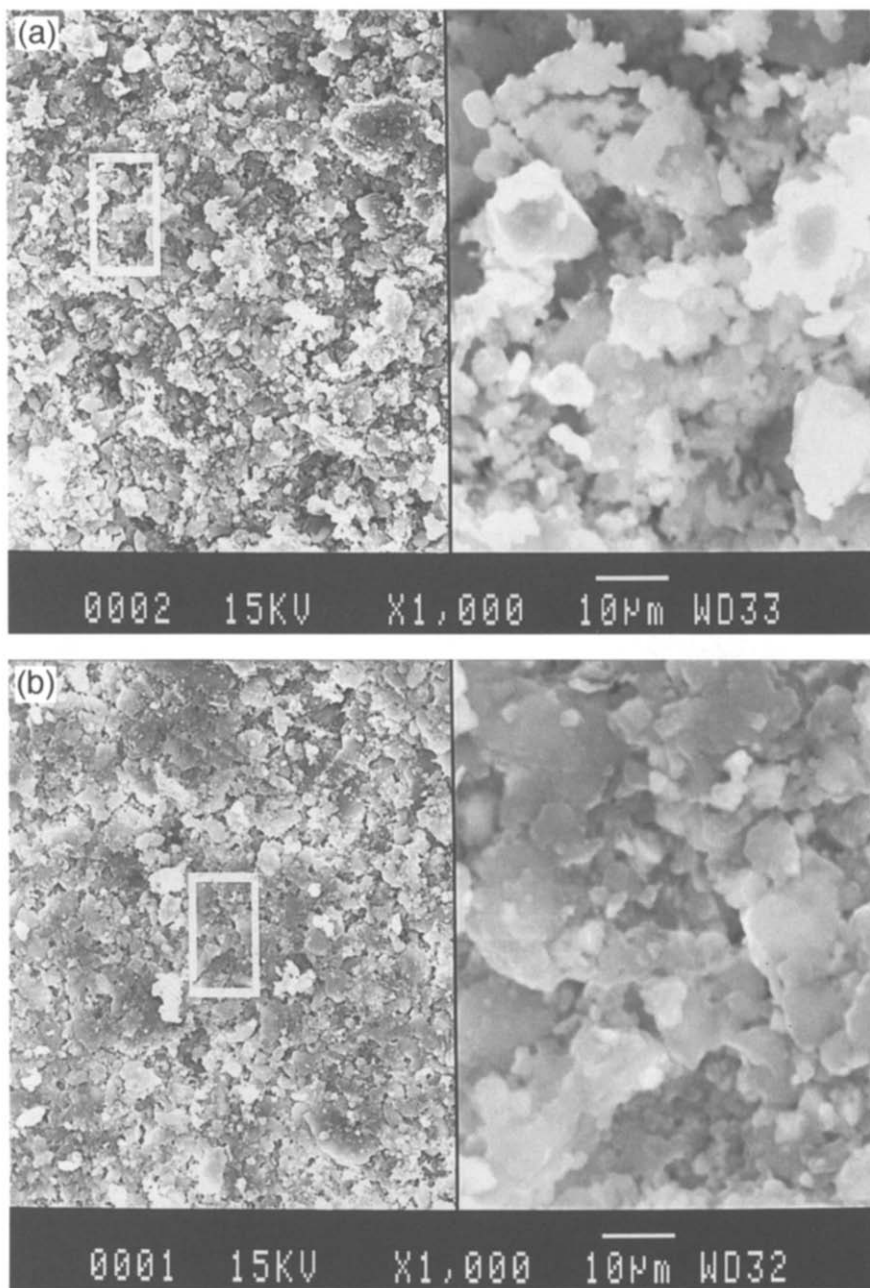


Fig. 6. Comparison of washed (a) and aged (b) catalyst surface (photos obtained by SEM).

with samples of aged and fresh catalysts are shown in Figs. 5 and 6. Contaminant concentrations were obviously reduced, while the substrate pores seem to be clean of the initial present foulants.

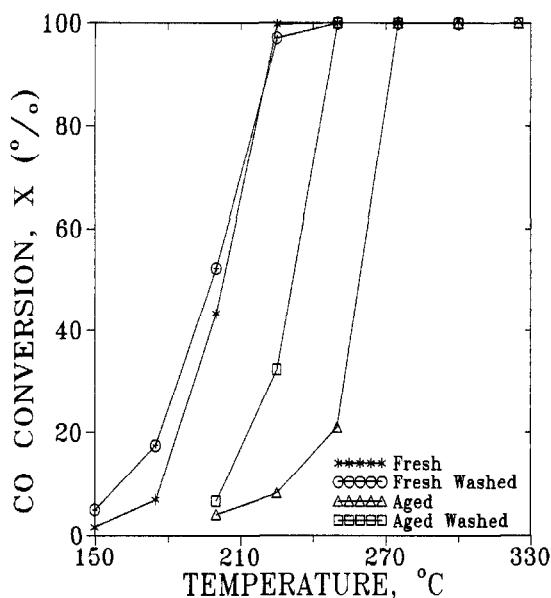


Fig. 7. Comparison of CO conversion as a function of temperature for fresh, fresh acetic acid washed, aged and aged acetic acid washed catalyst samples.

3.3. Catalytic activity tests

Catalytic activity tests were carried out using the following samples from (a) a fresh catalyst, (b) an aged catalyst, (c) one sample of fresh catalyst leached at the above determined optimum conditions, (d) two samples of aged catalyst leached at the above determined optimum conditions, (e) one sample leached by the addition of FeSO_4 in the leaching solution.

The activity test results for the above catalyst samples are shown in Figs. 7–10 in the form of % conversion of CO, C_2H_4 and NO, and % yield of NO to N_2 as a function of the inlet temperature of the reactor (for fresh catalyst,

Table 3

Light-off temperatures (T_{50}) as a function of catalyst performance history (fresh washed: sample washed at the determined optimum condition; aged (1) and aged (2): samples of aged catalyst washed at the defined optimum conditions; aged (3): sample washed at the determined optimum condition with the addition of FeSO_4)

Gas	Fresh washed	Fresh	Aged (1)	Aged (2)	Aged (3)	Aged
CO	198	200	229	232	235	258
C_2H_4	239	233	237	252	256	265
NO	234	226	232	243	234	257
N_2	256	264	261	265	275	279

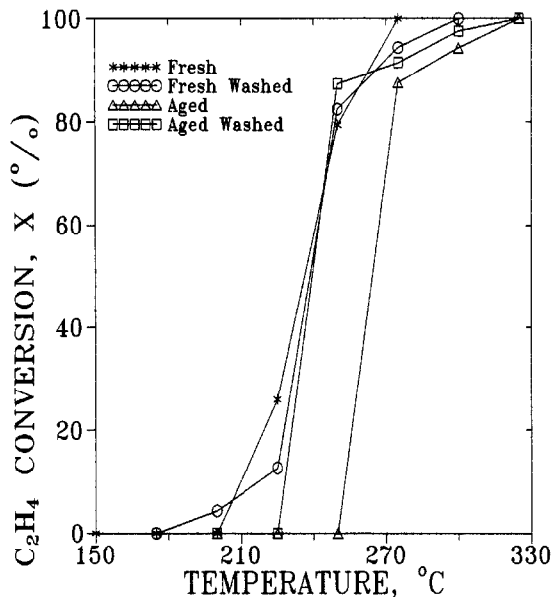


Fig. 8. Comparison of C₂H₄ conversion as a function of temperature for fresh, fresh acetic acid washed, aged and aged acetic acid washed catalyst samples.

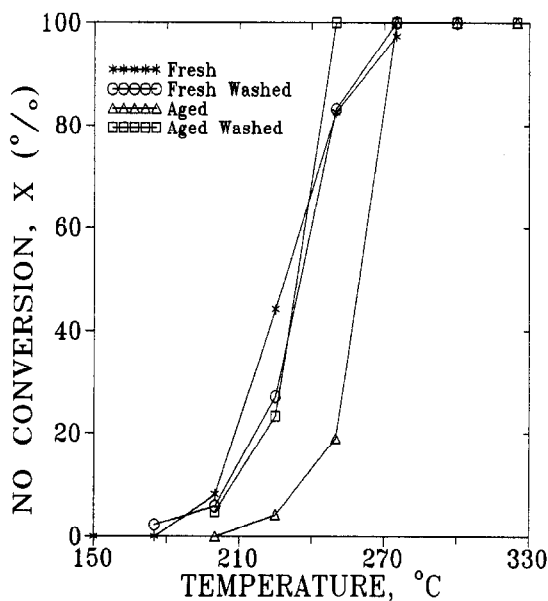


Fig. 9. Comparison of NO conversion as a function of temperature for fresh, fresh acetic acid washed, aged and aged acetic acid washed catalyst samples.

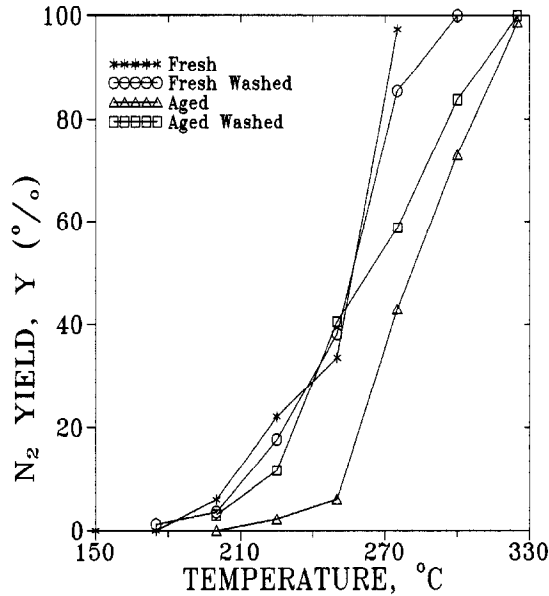


Fig. 10. Comparison of NO conversion as a function of temperature for fresh, fresh acetic acid washed, aged and aged acetic acid washed catalyst samples.

washed fresh catalyst, the first specimen of the washed aged catalyst and the aged catalyst). The light-off temperatures for each catalyst specimen and reaction are summarized in Table 3 and Fig. 11. As shown in Figs. 7–10 and Figs. 11, the washed catalysts present a clear improvement on the catalytic behaviour for all typical catalytic reactions taking place in the automotive

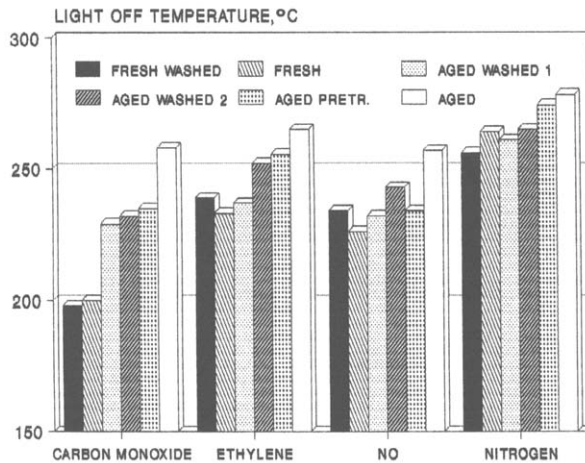


Fig. 11. Comparative results of the light-off temperatures derived from the activity tests for all the examined catalyst samples (aged pretr. is the catalyst sample leached by acetic acid 5 wt.-% and 0.1 M FeSO₄ solution).

catalytic converter. The improvement was more significant in the case of C_2H_4 oxidation, NO reduction and N_2 production (Figs. 8–11) and the respective yields are approaching the ones achieved by the fresh catalyst. Because of the fact that Rh is the noble metal which promotes reduction of NO, it is possible that the operative deactivation mechanism of Rh is simply fouling. On the contrary, Pt promotes CO oxidation which seems less improved (Figs. 7 and 11) (possibly due to the Pt sensitivity to sintering, a thermal transformation which is not reversible under the applied regeneration procedure) [23]. The addition of $FeSO_4$ in the leaching solution does not further improve the catalytic activity. This result suggests the absence of noble metal oxides. The remaining difference of catalytic activity between the fresh and aged catalysts is possibly connected with the active metal losses, which were proved by chemical analysis. The comparison of light-off temperatures for the two specimen treated at the same leaching condition show that the procedure is almost reproducible (washed catalyst (1) and (2)).

4. Conclusions

An acetic acid leaching procedure was applied to regenerate an aged three-way automotive catalyst. Catalytic activity tests have shown a remarkable increase of the performance of aged catalyst especially for the C_2H_4 oxidation, the reduction of NO and production of N_2 . The leaching conditions were optimized. The results after verification by long term activity tests and real size experiments are promising for practical application. The procedure is simple and does not require the removal of the catalyst from the exhaust system. Acetic acid could be pumped through the exhaust system using the dismantled gas inlet and outlet, an operation easily accomplished in every car service station. The highly corrosive resistant construction of the exhaust system (chromium steel) is not expected to be attacked by the weak acetic acid.

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