Valorization of Recycled Honeycombs from Exhausted TWCs by Means of Their Use as a Support of MnO\(_x\) Catalysts for Acetone Combustion

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Abstract: Exhausted TWCs subjected to chemical/thermal treatments were used as a support of MnO\(_x\) catalysts for the total combustion of acetone. The so-prepared new devices were characterized by using adherence tests, elemental and thermal analyses, XRD, \(\text{N}_2\) physisorption, and SEM-EDS. Incorporation of only 2.6 wt.% of the active phase (Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\)) to the recycled honeycomb considerably improved the catalytic response, achieving at 250 °C a 60% increase in acetone conversion with respect to the spent autocatalyst. The following procedure is proposed as a simple way to provide the TWC devoid of noble metals a second life in the VOCs’ oxidation field.

Keywords: acetone; manganese; recycling; spent TWC; VOCs’ oxidation

1. Introduction

Since three-way catalysts (TWCs) burst onto the scene in the mid-1970s as a brilliant technological solution to reduce air pollution caused by cars, they have probably become the most popular application of heterogeneous catalysis worldwide [1]. Although their chemical formulation has been continuously improved to comply with the increasingly restrictive environmental regulations, they keep being typically built from either a cordierite or metallic honeycomb-shaped substrate which is coated with a high surface area solid, such as alumina, to which active species (Pt, Pd, Rh), ceria–zirconia as oxygen buffer material, and metal oxides promoters (La, Ba, Si, among others) are added [2,3]. However, like all catalysts [4], TWCs also become less and less active with use (in general, after 100,000 km) as a consequence of the very severe conditions under which they operate. Causes of deactivation may be very diverse, ranging from the poisoning of the surface owing to the presence of C, P, Zn, Ca, Fe, and S, among other elements [5] to many different thermal mechanisms which include noble metal sintering, noble metal alloying, support changes, noble metal–base metal interactions, metal/metal oxide–support interactions, oxidation (alloy segregation), noble metal surface orientation changes, and even metal volatilization [6].

Unfortunately, there is still no industry throughout the world devoted to the regeneration of this type of catalyst to reuse it in the automotive industry, as the original performance of the fresh catalyst is never fully recovered [7]. Consequently, the exhausted catalyst becomes a waste that is nowadays considered hazardous [8]. The residue is often subject to either pyrometallurgical or hydrometallurgical procedures to extract the most precious components, the noble metals [9–13]. The former has some problems, such as large energy consumption and the production of many harmful gases as well as metallurgical slag [14]. The latter usually employs very aggressive and corrosive agents, producing a huge amount of liquid and solid waste [15]. An alternative to prevent the accumulation of these types of wastes could be their recycling for a second chance, either in the same [16] or
in a different process with environmental interest [17–19], such as the abatement of VOCs emitted by many industries. In this sense, there have already been studies in which the authors regenerated, by means of cleaning treatments with different acids to eliminate the poisons, and successfully reused the recovered Pd-, Pt-, Rh-still-containing carrier in the oxidation of VOCs such as benzene, toluene, and xylene [5,20,21]. The problem is that the noble metals are highly likely to have suffered irreversible damage or may even have disappeared from the exhausted converter. Therefore, it would neither be attractive for its use as an active catalyst for the oxidation of VOCs nor for the extraction of valuable metals, thus generating a waste with a high potential to affect the environment negatively. Nevertheless, it is still possible to exploit this waste if it is used as a catalytic support owing to its valuable honeycomb structure. In this work, we propose a new strategy for such a scenario based on the simple incorporation to the recycled TWC support of new chemical species which are less expensive than noble metals, but with high activity at low temperature and stability, considering the additional positive effect of residual metals in the discarded TWC for the sake of the economy of the process.

In previous studies, we demonstrated the potential of catalysts made of manganese oxides supported on clay honeycomb monoliths for VOCs’ decomposition (90% conversion of acetone and propane at 300 °C and 450 °C, respectively) [22,23]. Manganese oxides have a high activity in the oxidation of VOCs due to the possibility of changing the oxidation state of manganese, together with the presence of defects in its structure [23,24]. Thus, we used here the honeycomb recovered from an exhausted TWC, which was almost devoid of its initial noble metal loading, as a support of MnOx catalysts. The new structured devices were tested in the oxidation of acetone, selected as a VOC model, so as to evaluate the potential of this novel approach. Surprisingly, there are still not many publications reporting on the use of manganese-based catalysts supported onto cordierites for VOC abatement [24–28], the literature specifically focusing on acetone oxidation being much scarcer [29,30]. Therefore, our work can also contribute to fill this unexpected gap. According to preliminary surveys, the developed catalysts could be applied in the cleaning treatment of gasses emitted by workshops related to art crafts and low-size painting factories.

2. Results and Discussion

2.1. Characterization of the Monolithic Samples

The most serious damage in the raw exhausted TWC (M sample) seemed to be the channel blockage, due to attrition at the engine exhaust gas outlet (Figure 1a). That is why we selected a piece for the study from a different zone of the honeycomb; moreover, the cut applied for this selection did not cause any new damage (Figure 1b). From this slice, small prisms were further obtained (Sections 3.1 and 3.3). The weight loss after the subsequent chemical/thermal treatment (RM sample) was 0.7%.

Figure 1. Picture of the exhausted TWC employed in this work: (a) engine exhaust gas outlet section; (b) monolith sampling section (M).
Elemental analysis of M and RM revealed a carbon content of 0.12 and 0.7 wt.%, respectively. Interestingly, sulfur, which was present at a very low level in M (0.05 wt.%), was not detected in RM. This is the first piece of evidence of the positive effect of the cleaning treatment applied to the exhausted TWC. On the other hand, the active phase loading after impregnating the RM sample with manganese resulted in 1.6 wt.% for Mn/RM (one cycle) and 2.6 wt.% for Mn2/RM (two cycles); these loadings were reproducible for both cases. The adherence to the monolith substrate was estimated as 98% and 99%, respectively.

Figure 2 shows the results of the ATG study. In the case of the active phase precursor alone, studied first as a reference, the two major weight losses observed at approximately 100 °C and 200 °C must be related to the dehydration and decomposition of the manganese nitrate, respectively. According to this, manganese oxide formation takes place at a relatively low temperature, even slightly lower when supported. This analysis confirms the appropriateness of the calcination temperature selected as the final step of the catalysts preparation. It is also remarkable that the total weight loss is higher in the process leading to Mn2/RM, in good congruence with the double impregnation cycle applied in the preparation of this catalyst and the consequent higher amount of active phase incorporated.

The results of the study by XRD are shown in Figure 3. As it can be seen, the diffractograms are dominated by the peaks, which are characteristic of the cordierite support (Mg$_2$Al$_4$Si$_5$O$_{18}$ phase), including those of Ce$_2$Zr$_2$O$_7$ (pyrochlore), usually present in the cordierite washcoating of TWCs. However, in the case of Mn/RM, peaks attributable to Mn$_3$O$_4$ (hausmannite) (PDF codes = 000-24-0734) can be also detected, whereas both Mn$_3$O$_4$ and Mn$_2$O$_3$ (bixbyite) phases (PDF codes = 000-04-0732 and 000-41-1442, respectively) are identified in Mn2/RM. This proves that the active phase has been efficiently deposited over the RM support.
This is evidence that there are no significant differences between the derived BET surface area values (Table 1). Nevertheless, upon incorporation of the active phase over RM, there seems to be a small decrease in both porosity and surface area, which in any case is almost negligible considering the low percentage of active phase deposited (see the recovery of Mn2/RM).

The isotherms of M and RM are quite similar, which means that the chemical and thermal treatments applied to the raw support hardly affect its textural properties. This is evidence that there are no significant differences between the derived BET surface area values (Table 1). Nevertheless, upon incorporation of the active phase over RM, there seems to be a small decrease in both porosity and surface area, which in any case is almost negligible considering the low percentage of active phase deposited (see the recovery of Mn2/RM).

![X-ray diffractograms](image)

**Figure 3.** X-ray diffractograms obtained for the prepared catalysts.

The N₂ adsorption/desorption isotherms corresponding to all the studied samples are type II which are characteristic of macroporous solids, exhibiting a H3 hysteresis loop that can be related to aggregates of plate-shaped particles [31]. Figure 4 gathers the results for the M support and Mn2/RM catalyst as representative of the whole set of studied samples. The isotherms of M and RM are quite similar, which means that the chemical and thermal treatments applied to the raw support hardly affect its textural properties. This is evidence that there are no significant differences between the derived BET surface area values (Table 1). Nevertheless, upon incorporation of the active phase over RM, there seems to be a small decrease in both porosity and surface area, which in any case is almost negligible considering the low percentage of active phase deposited (see the recovery of Mn2/RM).

![Nitrogen adsorption/desorption](image)

**Figure 4.** Nitrogen adsorption/desorption representative isotherms of some of the studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S\textsubscript{BET} (m² g⁻¹)</th>
<th>V\textsubscript{total} (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>4.7</td>
<td>0.037</td>
</tr>
<tr>
<td>RM</td>
<td>4.2</td>
<td>0.029</td>
</tr>
<tr>
<td>Mn/RM</td>
<td>3.3</td>
<td>0.010</td>
</tr>
<tr>
<td>Mn2/RM</td>
<td>4.6</td>
<td>0.032</td>
</tr>
</tbody>
</table>

**Table 1.** Textural properties of the studied samples.
Special attention was paid to the recycled support (RM) by SEM-EDS analysis of different zones of the monolith channel walls. Figure 5a shows an SEM image of RM channel zones, and Figure 5b shows the elemental composition of these zones by EDS. As it can be seen in Figure 5, all the elements present in the structural cordierite (O, Al, Si and Mg) were detected, along with Zr, Ce, and Pr promoters. These results are consistent with those of XRD discussed above. The presence of Pt and Ni is also noticeable. These elements, like the three previous ones, are considered active species for the degradation of by-products in the autoengine combustion gases. Therefore, they could also be active in the decomposition of VOCs emitted by industrial processes. In any case, the absence of Pd and Rh signals and the trace level detected for Pt confirm the high degree of degradation of the exhausted TWC used in this work, which justifies the incorporation of manganese.

SEM-EDS mapping performed for Mn/RM and Mn2/RM catalysts shows how the added manganese is dispersed over the support (Figure 6). Notice the more intense coloration in the sample prepared from two impregnation cycles, with special Mn accumulation in the channels’ edges. This observation agrees with the active phase loading estimate results.

Figure 5. (a) SEM image of RM; (b) elemental composition obtained by EDS of the zones indicated in (a).

Figure 6. (a) SEM image of Mn/RM; (b) Mn distribution as obtained by EDS mapping in (a); (c) SEM image of Mn2/RM; (d) Mn distribution as obtained by EDS mapping in (c).
2.2. Catalytic Performance

Figure 7 shows the acetone conversion as a function of temperature for the supported catalysts and the recycled monolith without manganese. Data obtained of the raw M support are also included for comparative purposes. As it can be observed, the exhausted TWC exhibited some conversion when reaching a temperature of 150 °C, and a 92% conversion at 350 °C. This activity is attributed to the remaining active species present in the material, as suggested by XRD and EDS data, mainly due to the presence of mixed Ce and Zr compounds which are active in acetone oxidation because of their high oxygen storage capacity (OSC) and redox properties [24]. It is also noteworthy that the chemical and thermal treatment allowed, in general, a slight enhancement of the acetone conversion. This might be due to an effective removal of poisons such as the sulfur previously mentioned. In any case, the positive effect of manganese incorporation to the recycled monolith, especially above 200 °C, should be highlighted. This effect is increased by metal loading at 250 °C, the temperature at which 94% conversion is reached for Mn2/RM vs. 72% for Mn/RM, while that of M remains below 34%.

Figure 7. Catalytic activity of the studied samples in the acetone oxidation.

Noteworthily, the catalytic results obtained in this work are better than those obtained previously with manganese catalysts supported onto clay honeycomb monoliths [22,23]. Moreover, they are competitive with respect to Pt-loaded manganese oxide nanoarray-based catalysts coated onto honeycomb cordierite [29].

Finally, it must be indicated that the experimental quantitative data obtained by gas chromatography at the exit of the reactor confirmed, in all the cases, the total oxidation to CO2 even at 150 °C, with no by-products being detected.

3. Materials and Methods

3.1. Catalysts Preparation

The honeycomb monolithic support (with channels of 51 cm−2) was obtained from an exhausted TWC extracted from the converter of a gasoline-driver automobile (98,000 km mileage) provided by a Uruguayan local car workshop (Figure 1a). This was cut into adequate pieces to fit the catalytic reactor dimension. The sampled section (called M) was located at 2 cm of the engine exhaust gas inlet (Figure 1b). This avoids the area of structural deterioration of the sample. It was then chemically and thermally treated to remove possible remaining poisons [32–34]. The treatment consisted of submerging M in...
a 0.1 M citric acid (Sigma Aldrich, 98.5% pure) solution for 30 min and then leaving it in distilled water for 10 min. After this, it was dried at 100 °C for 24 h, and finally calcined at 750 °C also for 24 h. The resulting sample was called RM.

The MnO$_x$ active phase was incorporated by submerging RM in a 1 M Mn(NO$_3$)$_2$.4H$_2$O (Sigma Aldrich, 98.5% pure) solution, after which the excess was removed by blowing. In this way, two monoliths were impregnated, both being subjected to a further drying at 100 °C for 24 h. One of the dried monoliths was directly calcined at 450 °C for 2 h, to obtain the Mn/RM catalyst, while the other one was submitted to a second impregnation/drying cycle, followed by the same final calcination treatment, leading to the so-called Mn2/RM catalyst. The whole procedure followed for the preparation of the Mn-containing samples was inspired by our previous studies [23].

3.2. Catalysts Characterization

The active phase loading in the prepared supported catalysts was estimated from the weight difference between impregnated/dried/calcined and raw monoliths. In addition, the adherence of the manganese phase to the recycled honeycomb (RM) was evaluated from the weight loss after immersion in acetone under ultrasounds for 1 h [35]. Elemental analysis of M and RM samples was performed in a Carlo Erba EA1108 CHNS-O analyzer to see if there were carbon or sulfur deposits on their surface.

Thermogravimetric analysis (TGA) was carried out in Shimadzu DTG-60H equipment, using, in each case, 15 mg of the sample with a heating rate of 2 °C min$^{-1}$ up to 450 °C under air stream (50 mL min$^{-1}$), keeping this temperature for 2 h.

An X-ray diffraction (XRD) study was also carried out on a RIGAKU-Ultima IV (40 kV, 30 mA) diffractometer. The diffractograms were recorded using Bragg–Brentano geometry and CuK$\alpha$ radiation. The 2θ angle varied from 2° to 60°, with a step of 0.02° and a counting time per step of 10 s.

N$_2$ physisorption at −196 °C was performed in a Micromeritics ASAP2020. For this analysis, all the samples (monolith small pieces) were pre-evacuated at 200 °C for 2 h. The specific surface area was calculated by the BET method. Total pore volume (V$_{total}$) was estimated from the amount of nitrogen adsorbed at relative pressures of 0.99.

Small pieces of the monolithic samples were also studied by scanning electron microscopy (SEM). Digital micrographs were acquired at 20 kV in a JEOL JS M-5900LV microscope. Elemental composition of selected areas was determined by means of an energy dispersion spectroscopy (EDS) probe (NORAN Instruments).

3.3. Catalytic Tests

The catalytic tests were carried out in a U-shaped glass reactor where the monoliths, 2 cm high and 1.3 cm in diameter, were placed. Samples were pre-treated at 450 °C for 30 min in Ar stream. The light-off curves were obtained at atmospheric pressure through experiments in which the temperature increased from 150 °C in steps of 50 °C, staying at each step for 30 min. The reaction mixture was Ar/O$_2$/acetone with an excess of more than 10% of O$_2$. A 3.43 mL/min stream of O$_2$ passed through an acetone saturator, immersed in a 0 °C bath. The acetone-saturated O$_2$ was then diluted in a stream of 120 mL min$^{-1}$ of Ar, leading to a contact time of 0.5 s. In this way, the concentration of acetone was kept at approximately 1500 ppm. Quantification of reagents and reaction products was carried out by gas chromatography on Shimadzu GC 2014 equipment, using HAYESEP R 60/80 mesh (diameter 1/8 mm and length 4.5 m) and serial FID and TCD detectors.

4. Conclusions

An exhausted TWC was successfully recycled by means of a chemical/thermal treatment, recovering the honeycomb to be used as a catalytic support in the total oxidation of acetone. The support by itself showed some activity in this reaction but it was significantly improved (60% increase at 250 °C) by just depositing by impregnation 2.6 wt.% of manganese as the active phase. The results obtained demonstrate that it is possible to
provide value to the residues of the automotive industry by means of a simple procedure (not adequate for the noble metals extraction or regeneration), enhancing their efficiency to eliminate atmospheric organic pollutants such as VOCs, which can be generated in many different industrial processes.

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**References**


