

# NO AND CO OXIDATION WITH Pt RECOVERED FROM SPENT CATALYTIC CONVERTERS

N. Russo\*, J. C. Caroca, D. Fino, S. Bensaid, G. Saracco and V. Specchia

Materials Science and Chemical Engineering Department, Politecnico di Torino,

C.so Duca degli Abruzzi 24, 10129 Torino, Italy. e-mail: nunzio.russo@polito.it

## Summary

A selective recovery process of recovery platinum from spent automotive catalytic converters using a strong basic ion exchange resin was developed. Recovered Pt was characterized by FESEM-EDS technique and used for the preparation of 2wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst powder samples. Catalytic activity comparison between catalysts based on recovered platinum and commercial Pt/Al<sub>2</sub>O<sub>3</sub> catalysts showed that the 2wt% Pt(recovered)/Al<sub>2</sub>O<sub>3</sub> exhibited a slightly higher peak combustion temperature (T<sub>p</sub>=561°C) compared with the commercial 2 wt% Pt/Al<sub>2</sub>O<sub>3</sub> (T<sub>p</sub>=555°C). Shifting our attention towards the NO oxidation to NO<sub>2</sub>, both catalysts showed a similar performance, reaching the highest conversion (~61%) at 310°C with no production of nitrous oxide.

## Keywords

Sustainability, Environmental Reaction Engineering.

## Introduction

Automotive catalysts today make almost 50% of the global demand for the Platinum Group Metals (PGM) due to emission limits enforced by international legislation. The catalysts contain either platinum or platinum/palladium combinations to oxidize carbon monoxide (CO) and unburnt hydrocarbons (HC) to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). The recovery of these precious metals present in spent automobile catalytic converters [1] is an important topic not only from the economic point of view but also for recycling rare natural resources. The main purpose of this work is to develop a selective recovery process of recovery platinum from a spent catalytic converter using a strong basic ion exchange resin and then to carry out catalytic activity comparison between catalysts based on recovered platinum from spent catalytic converters (Al<sub>2</sub>O<sub>3</sub> as a support) and commercial Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.

## Materials and Methods

For Pt recovering, 250g of a spent catalytic converter was treated with 1 liter of aqua regia (HCl/HNO<sub>3</sub> = 3:1) as leaching solution [2]. With continued stirring, the mixture was heated at 70°C for 3 h. The obtained solution was then processed by means of the Column ion-exchange procedure [3] to recover the platinum (Fig 1). During the

process, absorption atomic analysis was carried out to measure the platinum concentration in the solution.

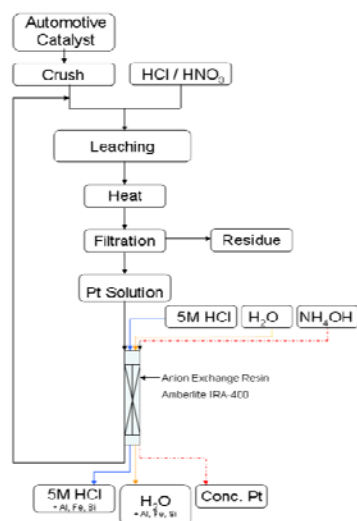


Figure 1: Process for platinum recovery

Two 2wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst powder samples were synthesized via incipient wetness impregnation IWI [5]. The first sample was prepared by using the recovered platinum, whereas the second one was prepared by using

\* To whom all correspondence should be addressed

an aqueous solution of hydrogen hexachloroplatinate (IV) provided by Sigma-Aldrich. The activity of the prepared catalysts towards the carbon oxidation was analyzed by means of Temperature-Programmed Combustion (TPC), carried out in a fixed-bed micro-reactor under standard operating conditions (air flow rate of  $50 \text{ Nml}\cdot\text{min}^{-1}$ , carbon/catalyst 1:9 mass basis,  $W/F = 0.05 \text{ g}\cdot\text{s}\cdot\text{cm}^{-3}$ , GHSV of  $9,000 \text{ h}^{-1}$ , heating rate of  $5 \text{ }^\circ\text{C}/\text{min}$ ). The outlet gas was monitored by a  $\text{CO}/\text{CO}_2$  NDIR analyzer (ABB).

The same catalysts were also tested for the oxidation of NO towards  $\text{NO}_2$  with the same apparatus according to the following conditions, gas mixture: 93 ppmv NO; 15 vol.%  $\text{O}_2$ ,  $\text{N}_2 = \text{balance}$ ; flow rate of  $350 \text{ Nml}\cdot\text{min}^{-1}$ ,  $W/F = 0.02 \text{ g}\cdot\text{s}\cdot\text{cm}^{-3}$ , GHSV of  $40,000 \text{ h}^{-1}$ , heating rate of  $5 \text{ }^\circ\text{C}/\text{min}$ ). The outlet gas was monitored by both a  $\text{NO}/\text{NO}_2$  chemiluminescence analyzer (Eco Physics) and a  $\text{N}_2\text{O}$  NDIR analyzer (ABB).

## Results and discussion

After the leaching with aqua regia, a solution containing an elevated concentration of platinum (640 ppm) and several undesirable compounds (Al, Fe, Si, among others) was obtained. The column ion-exchange procedure with a strong anionic resin (Amberlite IRA - 400) was used to separate the platinum complex  $[\text{PtCl}_6]^{2-}$ , recovering 71% of the present platinum, with high pureness. The SEM analysis carried out with the BSE detector showed a ceramic matrix of  $\text{Al}_2\text{O}_3$  with platinum cluster having an average diameter of 10-20 nm finely dispersed onto the surface for the 2 wt% Pt(recovered)/ $\text{Al}_2\text{O}_3$  (Fig. 2).

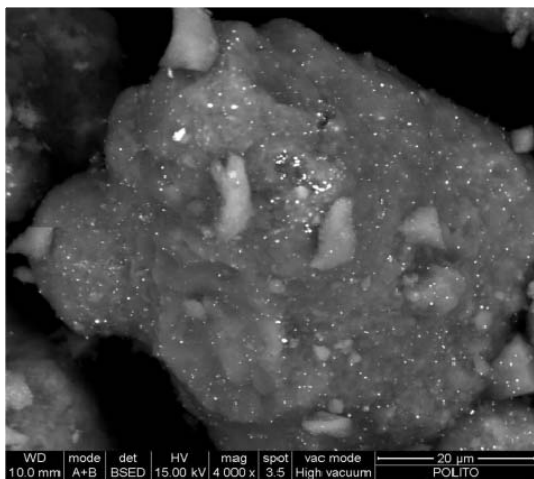


Figure 2: SEM view of 2 wt% Pt(recovered)/ $\text{Al}_2\text{O}_3$  with a magnification of 4 KX

An higher platinum cluster average diameter was observed for the 2 wt% Pt/ $\text{Al}_2\text{O}_3$  commercial sample (not reported).

The catalytic activity tests (Fig. 3) concerning the carbon combustion showed that the 2wt% Pt(recovered)/ $\text{Al}_2\text{O}_3$  exhibited a slightly higher peak combustion temperature ( $T_p=561^\circ\text{C}$ ) compared with the commercial 2 wt% Pt/ $\text{Al}_2\text{O}_3$  ( $T_p=555^\circ\text{C}$ ). Shifting our attention towards the

$\text{NO}$  oxidation to  $\text{NO}_2$ , both catalysts showed a similar performance, reaching the highest conversion ( $\sim 61\%$ ) at  $310^\circ\text{C}$  with no production of nitrous oxide. The residual part of solution deriving by Pt recovering from a spent DOC converter has been calcined at  $400^\circ\text{C}$  and characterized by an FESEM-EDS analysis. The EDS result brings out the presence of pure Platinum. No other elements were observed.

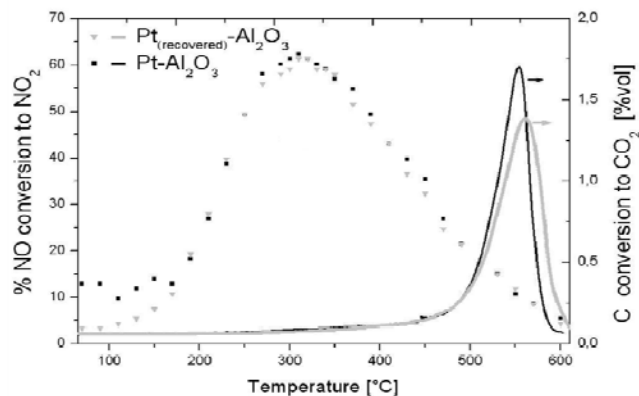


Figure 3: Activity results regarding the C conversion to  $\text{CO}_2$  and NO conversion to  $\text{NO}_2$

## Conclusions

The work has established the catalytic activity towards soot combustion and NO oxidation of platinum recovered from a spent DOC. The activity results were quite similar to the commercial and fresh Pt- $\text{Al}_2\text{O}_3$  catalyst. The SEM-EDS analysis has demonstrated that the morphology of this platinum could be interesting for a new utilization and confirmed the strength relationship between chemi-physical properties and catalytic activity. Further studies are necessary to complete the scenario for a right recycling of spent after-treatment devices

## References

- (1) Benson, M.; Bennett, C. R.; Harry, J. E.; Patel, M. K.; Cross, M. The recovery mechanism of platinum group metals from catalytic converters in spent automotive exhaust systems. *Conservation and recycling* **2000**, *1*, 31.
- (2) Barakat, M. A.; Mahmoud, M. H. H. Recovery of platinum from spent catalyst. *Hydrometallurgy* **2004**, *72*, 179.
- (3) Gaita, R; Al-Bazi, J. An ion-exchange method for selective separation of palladium, platinum and rhodium from solutions obtained by leaching automotive catalytic converters. *Talanta* **1995**, *42*, 249.
- (4) Cauda, E.; Fino, D.; Saracco, G; Specchia, V. Nanosized Pt-perovskite catalyst for the regeneration of a wall-flow filter for soot removal from diesel exhaust gases. *Topics in Catalysis* **2004**, *30/31*, 299.