NO AND CO OXIDATION WITH PT RECOVERED FROM SPENT CATALYTIC CONVERTERS

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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/Al₂O₃ catalyst powder samples. Catalytic activity comparison between catalysts based on recovered platinum and commercial Pt/Al₂O₃ catalysts showed that the 2wt% Pt(recovered)/Al₂O₃ exhibited a slightly higher peak combustion temperature (Tp=561°C) compared with the commercial 2 wt% Pt/Al₂O₃ (Tp=555°C). Shifting our attention towards the NO oxidation to NO₂, 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 (CO₂) and water (H₂O). 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 (Al₂O₃ as a support) and commercial Pt/Al₂O₃ catalysts.

Materials and Methods

For Pt recovering, 250g of a spent catalytic converter was treated with 1 liter of aqua regia (HCl/HNO₃ = 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/Al₂O₃ 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

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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 CO/CO_2 NDIR analyzer (ABB).

The same catalysts were also tested for the oxidation of NO towards NO_2 with the same apparatus according to the following conditions, gas mixture: 93 ppmv NO; 15 vol.% 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 NO/NO_2 chemiluminescence analyzer (Eco Physics) and a N_2O 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 Al_2O_3 with platinum cluster having an average diameter of 10-20 nm finely dispersed onto the surface for the 2 wt% Pt(recovered)/ Al_2O_3 (Fig. 2).

Figure 2: SEM view of 2 wt% Pt(recovered)/ Al_2O_3 with a magnification of 4 KX

An higher platinum cluster average diameter was observed for the 2 wt% Pt/ Al_2O_3 commercial sample (not reported).

The catalytic activity tests (Fig. 3) concerning the carbon combustion showed that the 2wt% Pt(recovered)/ Al_2O_3 exhibited a slightly higher peak combustion temperature ($T_p=561^{\circ}\text{C}$) compared with the commercial 2 wt% Pt/ Al_2O_3 ($T_p=555^{\circ}\text{C}$). Shifting our attention towards the

NO oxidation to NO_2 , both catalysts showed a similar performance, reaching the highest conversion ($\sim 61\%$) at 310°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°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 CO_2 and NO conversion to 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- Al_2O_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

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