

SHORT COMMUNICATION

DETERMINATION AND DELINEATION OF THE AMOUNT OF PLATINUM IN VARIOUS SEGMENTS OF AN AUTOMOTIVE CATALYST USING CARBON PASTE ELECTRODE TECHNIQUE WITH ELECTROLYTIC BINDER

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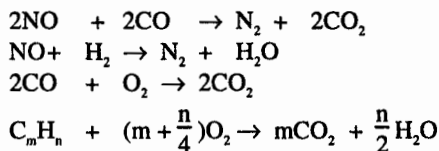
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ABSTRACT. Analytical determination of platinum in an automotive catalyst has been undertaken using carbon paste electrode technique. The catalyst had a priori been subjected to high temperature vaporization treatment as a means of extracting platinum from the catalyst. We have been able to demonstrate by this study that the delineation of the various levels of platinum in the various segments of the catalyst is possible. To this end, a diagram for the reconstitution of the catalyst vis-a-vis the distribution pattern of the platinum has been proposed. Platinum is found to exist in the same form, Pt(IV) as in the untreated catalyst. The average value of platinum in the untreated catalyst was found to be 2.20 mg g⁻¹ using carbon paste electrode technique. While the average value of 0.84 mg g⁻¹ in platinum was obtained for the treated catalyst indicating that about 60% of platinum must have been extracted during the high temperature vaporization treatment. The catalyst was found to be richer in platinum at the exit region than at the entrance portion of the catalyst.

INTRODUCTION

Platinum-bearing catalysts have the ability to transform atmospheric pollutants such as carbon monoxide, the products of incomplete combustion of hydrocarbon fuel and the oxides of nitrogen into non-toxic products according to the chemical reaction given below [1]:



The automotive post-combustion catalysts (APCC) contain the platinum groups elements such as platinum or palladium or/and rhodium as deposit on the surface of γ -alumina substrate. Some of the previous publications on the carbon paste electrode and the electrochemical behaviour of some platinum compounds [2,5] have demonstrated that in addition to the quantitative determination of platinum group elements, this method also provides additional information on the oxidation state of the platinum group elements contained in the automotive catalysts.

Adekola *et al.* [3,5] have recently demonstrated the suitability of carbon paste electrode for the electrochemical study of some selected automotive catalysts. The present study is an

extension of that work. We have attempted to delineate the various levels of platinum metal contained in a particular automotive catalyst as a function of the axial radius (from the centre towards the outer layer) on one hand, and also as a function of the length of the catalyst (from the entrance to the exit) on the other hand. The catalyst used in the present study has been subjected to high temperature vaporization treatment as a means of extracting the precious metals. The present study therefore provides a means of assessing the efficacy of this high temperature extracting technique.

High temperature vaporization technique has been extensively discussed by Tajmouati and co-workers [4]. This is a method for direct recovering/extracting metals from their parent solid matrices without dissolving the solid in solution. It is based on the principle of vaporization, followed by recondensation of the precious metals at high temperature with the aid of a carrier gas, which is usually an oxidizing gas such as O_2 . The plasma torch is employed as a source of heat. The exit temperature is usually lower than the temperature at the entrance by about 200 K.

EXPERIMENTAL

The carbon paste was prepared by mixing about 60 mg of ultra-pure grade graphite powder (Johnson-Matthey, UK), about 20 mg of the catalyst to be studied and about 70 μL of electrolytic binder (HCl , 6 mol dm^{-3}). Other procedures especially with respect to the tracing of current-potential curves and the exploitation of the voltamperogram for the determination of the number of coulombs are as discussed in the previous papers [2,3]. The studied catalyst was kindly provided by Comptoir Lyon Alemand Louyot (CLAL), France. The catalyst was used as provided without any further pre-treatment.

RESULTS AND DISCUSSION

Untreated automotive catalyst. Studies are carried out on both the treated and untreated catalysts. This is necessary so as to be able to observe any morphological differences in their respective voltamperograms. The typical voltamperogram obtained for the untreated catalyst including the identification or the assignment of all the peaks have been completely discussed in our earlier paper on the electrochemical behaviour of automotive catalysts [3]. The large peak (C_1) has been identified with the simultaneously reduction of CeO_2 and Pt(IV) contained in the catalyst into Ce and Pt , respectively [3]. The reduction of CeO_2 is irreversible, and this implies that its influence could be eliminated after the first cathodic potential scan. We also found that the number of coulombs calculated using either the large peak C_1 or the peak C_2 obtained from the second cathodic potential scan increases linearly with the quantity of the catalyst introduced into the carbon paste (Figure 1). This clearly indicates that the peak C_1 could be exploited for analytical determination of both CeO_2 and platinum while peak C_2 could be used for the determination of the quantity of platinum without experiencing interference from CeO_2 . About the same quantity of platinum (an average of 2.2 mg g^{-1}) is obtained using carbon paste electrode technique irrespective of the portion of the automotive catalyst analyzed. This indicates that there is even distribution of platinum in the catalyst before treatment.

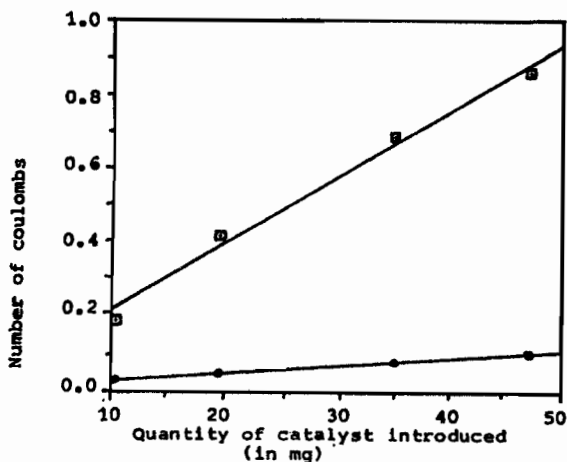


Figure 1. Variation of the number of coulombs as a function of the catalyst used (□ = first cathodic scan and ● = second cathodic scan).

Automotive catalyst obtained after flash thermic treatment. The same type of catalyst as described in the preceding section was subjected to the treatment of vaporization at high temperature (flash thermic or plasma torch).

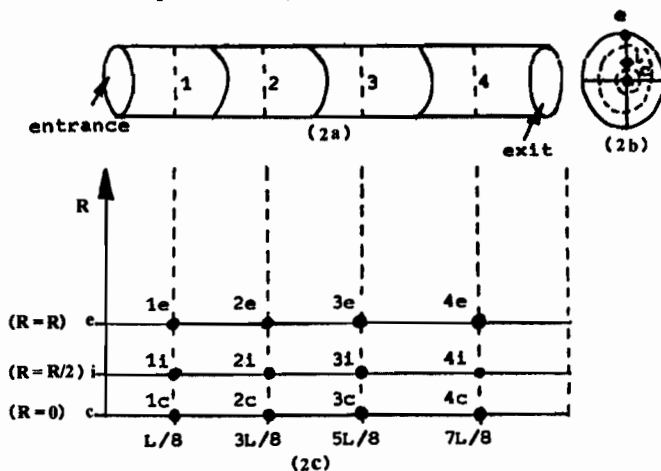


Figure 2. Delineation of an automotive catalyst subjected to flash thermic treatment. (a) vertical, (b) radial section and (c) indication of co-ordinates of various segments.

The studied automotive catalyst was of cylindrical shape with radius 5 mm and length 30 mm. It was divided into four portions of the same thickness ($L/4$) perpendicular to the revolutionary axis. The portions were numbered from 1 to 4 starting from the entrance face through the middle part to the exit face (Figure 2a). On each portion, 3 zones have been delineated: central zone (index c), the intermediate zone (index i) and the exterior zone (index e) (Figure 2b). The different fractions were then subjected to electrochemical analysis after grinding them into powder form ($<200 \mu\text{m}$) with the aid of carbon paste electrode technique

in 6 mol/L HCl medium. Three different analyses were carried out for each fraction. The results obtained are summarized in Table 1.

Table 1. Concentration of platinum(IV) in mg/ g in different fractions.

Fractions	Central zone, c	Intermediate zone, i	Exterior zone, e
1 (entrance)	1c : 0.95	1i : 1.02	1e : 0.72
2	2c : 1.14	2i : 1.15	2e : 0.92
3	3c : 1.34	3i : 1.24	3e : 0.97
4 (exit)	4c : 1.33	4i : 1.39	4e : 1.11

The result of each fraction is considered to be representing the average level of platinum at the neighbourhood of the coordinate points (L/8, c or i or e) (3L/ 8, c or i or e) etc. The current-potential curves are of the same form as the voltamperogram obtained in the case of the untreated automotive catalyst [3]. Different kinds of diagrams can be put up to indicate the trend of variation of the experimental results. Figure 3 shows that the variation of the quantity of platinum as a function of radius for a given slice while (Figure 4) on its own, illustrates the variation of the amount of platinum as a function of the distance covered for a given slice, that is, at a given radial axis, R.

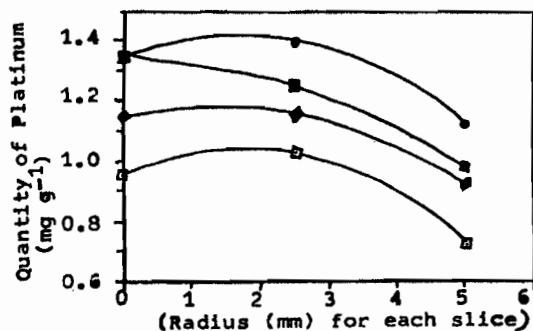


Figure 3. Quantity of platinum (in mg/g) as a function of radius (at constant length L). (□ = slice 1, ♦ = slice 2, ■ = slice 3, and ● = slice 4).

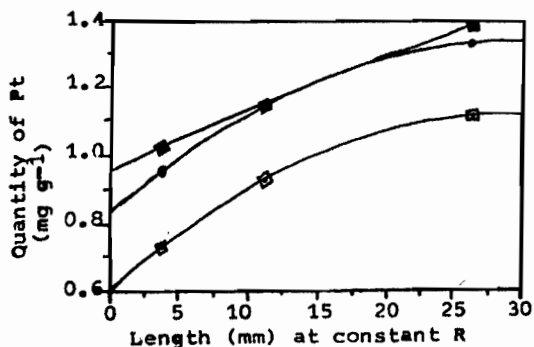


Figure 4. Quantity of platinum (in mg/g) as a function of length, L (at constant radius r). (□ = exterior zone, ● = central zone, and ■ = intermediate zone).

Lastly, a more concise and imaginary manner enables to sketch approximately the diagram of reconstitution of the automotive catalyst. This is obtained by tracing the iso-concentration curves for platinum as illustrated in Figure 5.

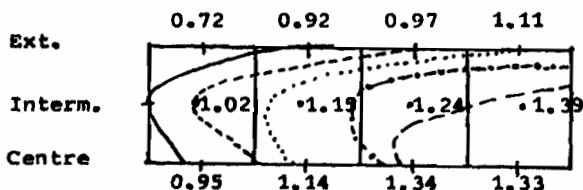


Figure 5. Iso-concentration curves for platinum in the catalyst (— 0.9, --- 1.0, ... 1.1, --- 1.2, --- 1.3).

It is evident from our results that the automotive catalyst is richer in platinum at the exit region than at the entrance portion of the catalyst. In other words, for each slice, the exterior layer is poorer in platinum than the intermediate layer or even the central layer. The intermediate and the central layers have about the same composition in platinum. As the temperature is higher at the entrance of the vaporization reactor than at the exit, greater amount of platinum must have been vaporized at the entrance than at the exit. It is most probable that there could be recondensation of platinum metal on the cooler part, that is, at the back of the sample. Our results agree satisfactorily with the results obtained by Tajmouati *et al.* [4] who analyzed platinum metal in the same catalyst by thermogravimetric technique. The average value of 0.84 mg g^{-1} in platinum was obtained if all the fractions are homogeneously mixed together. We have also demonstrated from the current-potential curves that platinum is most probably present as Pt(IV). We will recall that an oxidizing gas (O_2) has been used for the vaporization treatment of the material at high temperature. We can also estimate from our results that about 60% of the platinum must have been extracted through vaporization process from the automotive catalyst during this treatment.

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