React. Kinet. Catal. Lett., Vol. 34, No. 2, 273-276 (1987)

STUDY OF WELL-CHARACTERIZED Pt-Ru/C CATALYSTS BY OXYGEN ELECTROREDUCTION

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Received April 2, 1987
Accepted September 7, 1987

A series of well characterized Pt-Ru bimetallic catalysts supported on graphite has been studied by means of the electroreduction of oxygen in a supporting electrolyte of 1 N H_2SO_4. A synergetic effect is observed when the activity per gram of catalyst is considered. However, this effect disappears when the activity values are corrected by the active surface area.

Исследовали серии хорошо характеризуемых биметаллических катализаторов Pt-Ru, нанесенных на графит, с помощью электровосстановления кислорода в электролите 1N H_2SO_4. Принимая во внимание активность 1-ого грамма катализатора, наблюдали синергетический эффект. Однако, этот эффект исчезает, если величины активности исправлены на активную площадь поверхности.

INTRODUCTION

Platinum-ruthenium containing low atomic percentages of the metals indicated that such alloys could be more active for oxygen electroreduction than Pt itself [1]. These works were done with smooth electrodes and there is surprisingly little information about these reactions with dispersed Pt-Ru alloys suppported on graphitized carbon. Moreover, recent investigations on dispersed supported Pt showed the importance of the dispersion effect on the kinetics of the oxygen reaction [2]. In order to gain information about the dispersion effects, well characterized Pt-Ru/C catalysts were studied in the oxygen electroreduction reaction.

EXPERIMENTAL

Pt-Ru/C catalysts were prepared by impregnation of pure commercial graphite (Carbone Lorraine E.G.) with appropiate amounts of aqueous solutions of H_2PtCl_6 and $RuCl_3$ to obtain 2 of total metal content. The catalysts were dried and reduced under flowing hydrogen over 5 h at 400 °C. The dispersity values were determined by H_2-O_2 titration and CO chemisorption by means of a gravimetric method [3]. Catalysts were tested in an electrochemical cell where the electrolyte was an oxygen saturated solution of 1 N H_2SO_4. Catalyst activity for oxygen electroreduction was defined by the current measured at an electrode polarization of 0.25 V with respect to a calomel reference electrode.

RESULTS AND DISCUSSION

The mean particle size obtained from electron microscopy and chemisorption is reported in Table 1. Good agreement is observed between these two independent determinations. The results for surface metal concentrations of Table 1 show a preferential segregation of Pt in the bimetallic catalysts, since the nominal bulk composition does not correspond to that of the surface. This phenomenon was also observed by McNicol et al. [4] on Pt-Ru unsupported Adams-type catalysts.

The activity per gram of catalyst for oxygen electroreduction of the Pt-Ru/C catalysts as a function of the Pt bulk content is shown in Fig. 1, where a synergetic effect is observed. The activity, but now expressed per metallic atom is

Table 1

Surface composition and particle size ϕ(Å) for Pt-Ru/C

% Pt Bulk	0	15	34	61	100
% Pt Surface	0	18	51	75	100
CO^1	117	128	106	88	128
H_2-O_2^{1}	125	129	108	89	95
E.M.^{2}	126	98	101	95	118

1:Chemisorption; 2:Electron Microscopy ($\Sigma n_i d_i^3/\Sigma n_i d_i^2$)

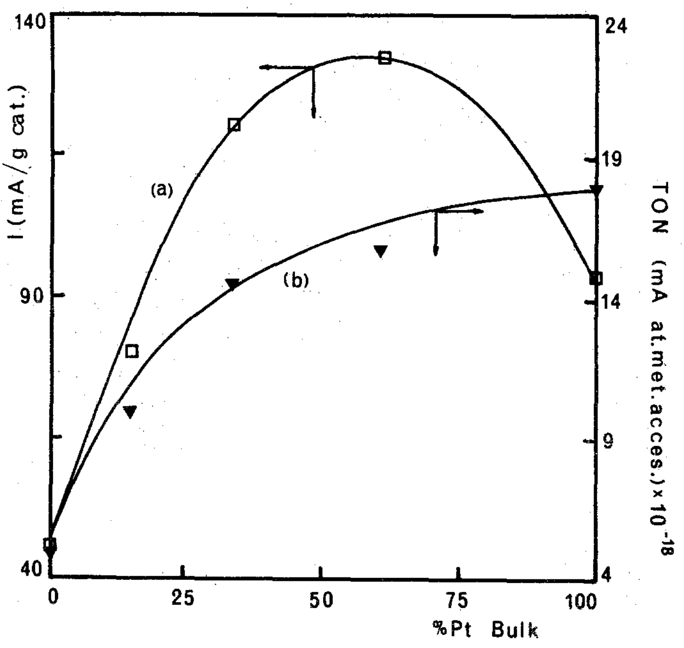

Fig. 1. Activity per gram of catalysts (□) and activity per surface atom (▼) as a function of the Pt bulk composition

shown in Figure 1 b. Here, an increase of the specific activity as a function of the Pt content is observed until the value of $17.7\text{x}10^{-18}$ mA/Pt site is reached. The results of Figure 1 b show that the catalytic behavior of Pt-Ru/C for oxygen electroreduction may be explained by a dispersion effect and, besides, by the Pt surface segregation, without any appreciable effect of an electronic interaction between both components. These results are in agreement with those obtained by Appleby [5] with smooth electrodes since in any case the bimetallic catalysts are more active than Pt itself.

Acknowledgement. This research was supported by OEA-CONACYT grant PROCYT 86-87.

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