

SHORT COMMUNICATION

**Kinetic study of methanol oxidation on  
Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst in the alkaline media**

A. V. TRIPKOVIĆ<sup>\*#</sup>, K. DJ. POPOVIĆ<sup>#</sup> and J. D. LOVIĆ<sup>#</sup>

*ICTM – Institute of Electrochemistry, University of Belgrade, Njegoševa 12,  
P.O. Box 473, 11000 Belgrade, Serbia*

(Received 20 June, revised 6 August 2007)

**Abstract:** The electrochemical oxidation of methanol in NaOH solution was examined on a thin film Pt<sub>2</sub>Ru<sub>3</sub>/C electrode. The XRD pattern revealed that the Pt<sub>2</sub>Ru<sub>3</sub> alloy consisted of a solid solution of Ru in Pt and a small amount of Ru or a solid solution of Pt in Ru. It was shown that in alkaline solution, the difference in activity between Pt/C and Pt<sub>2</sub>Ru<sub>3</sub>/C is significantly smaller than in acid solution. It is proposed that the reaction follows a quasi bifunctional mechanism. The kinetic parameters indicated that the chemical reaction between adsorbed CO<sub>ad</sub> and OH<sub>ad</sub> species could be the rate limiting step.

**Keywords:** platinum–ruthenium alloy, supported nanocatalyst; XRD analysis, methanol oxidation, alkaline solution.

INTRODUCTION

There is a general consensus at present that Pt/Ru offers the most promising results in methanol oxidation in acid solution. The catalytic effect has been observed using different Pt/Ru electrodes, including Pt/Ru alloys,<sup>1–3</sup> electrochemical and spontaneously deposited Ru on Pt<sup>4–6</sup> and carbon supported Pt/Ru.<sup>7–10</sup> When discussing the reason for the catalytic effect of the Pt–Ru surface in the reaction of methanol oxidation, the bifunctional mechanism is often invoked,<sup>11</sup> which suggest the joint activities of both metals. The Pt sites acting as adsorption and dehydrogenation centers produce various adsorbed carbonaceous species and the Ru sites adsorb oxygen-containing species at lower potentials than a pure Pt surface.

The bifunctional mechanism is related to low potentials ( $E < 0.5$  V) and low temperatures ( $t < 60$  °C), since at high potentials Pt dissociates water and at high temperatures Ru adsorbs methanol.<sup>2,12</sup>

There is lack of data dealing with methanol oxidation on PtRu catalyst in alkaline solution<sup>10,13</sup> although from a fundamental viewpoint, the study of the ki-

\* Corresponding author. E-mail: amalija@tmf.bg.ac.yu

# Serbian Chemical Society member.

doi: 10.2298/JSC0711095T

netics of methanol oxidation in alkaline solution may provide some new insight into developing new catalysts.

In this work, the kinetics of methanol oxidation on a Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst in alkaline solution was investigated and compared with a Pt/C catalyst.

## EXPERIMENTAL

### *Electrode preparation*

The platinum–ruthenium and platinum electrocatalysts supported on high area carbon (Pt<sub>2</sub>Ru<sub>3</sub>/C and Pt/C) with 54 wt % alloy and 47.5 wt % Pt (Tanaka Precious Metal Group) were applied to a glassy carbon substrate in the form of a thin film using the procedure described elsewhere.<sup>9</sup> The mass transfer resistance through the Nafion<sup>®</sup> film was negligible.<sup>10</sup>

### *Electrode characterization*

The electrodes were characterized by X-ray diffraction analysis.

### *Electrochemical measurements*

All electrochemical measurements were conducted at 22 °C in a thermostated three-compartment electrochemical cell with a Pt spiral as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The potentials refer to the reversible hydrogen electrode (RHE). The thin film rotating disk method was used.

All measurements were performed in a nitrogen purged sodium hydroxide solution. Methanol was added to the solution while holding the electrode potential at  $E = 0.05$  V (RHE) for 3 min. The catalytic activity was measured either by recording the potentiodynamic polarization curves (sweep rate 50 mV s<sup>-1</sup>) or quasi-steady state curves (sweep rate 1 mV s<sup>-1</sup>).

## RESULTS AND DISCUSSION

### *Electrode characterization*

In the diffraction pattern of the Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst (Fig. 1), two phases were found: a solid solution of ruthenium in platinum (fcc) and a phase associated with an overlapped peak at 43.7° and a weak peak at 58° assigned to the hexagonal phase of ruthenium or a solid solution of platinum in ruthenium (hcp). Pt–Ru fcc reflections in the Pt<sub>2</sub>Ru<sub>3</sub>/C pattern are systematically shifted towards higher angles in relation to the platinum peaks in the Pt/C pattern due to the incorporation of smaller ruthenium atoms into platinum crystal lattice. It was assumed in the calculations that the second phase is Ru hcp. The two structures, *i.e.*, Pt–Ru fcc and Ru hcp were refined using the Rietveld method. The presence of the carbon support was not taken into account. The crystallite sizes determined with the TOPAS program were 3.9 nm for Pt–Ru fcc and 2.8 nm for Ru hcp. The crystallite size determined using the Scherrer method based on the (220) breadth was 3.5 nm for the Pt–Ru fcc phase.

### *Methanol oxidation on Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst*

The polarization curve for methanol oxidation on Pt<sub>2</sub>Ru<sub>3</sub>/C in alkaline media and the corresponding basic curve for Pt<sub>2</sub>Ru<sub>3</sub>/C are presented in Fig. 2.

According to the phase diagram<sup>14</sup> as well as the analysis of the XRD spectra, the Pt<sub>2</sub>Ru<sub>3</sub>/C catalyst has a complex structure consisting mostly of a solid solu-

tion of Ru in Pt, with a small contribution of pure Ru or a solid solution of Pt in Ru. Consequently, electrochemical characterization by cyclic voltammetry can provide only the general characteristics of the surface structure, such as the hydrogen adsorption/desorption region ( $0.05 \text{ V} < E < 0.3 \text{ V}$ ) followed by the reversible and irreversible formation of oxygen-containing species ( $\text{RuOH}$ ,  $\text{Ru}_2\text{O}$ ,  $\text{RuO}_x \cdot \text{H}_2\text{O}$ )<sup>15,16</sup> at  $E > 0.3 \text{ V}$ . The continuous and fast transition from reversible to irreversible state of oxides results in a broad capacitive feature of a Ru rich alloy such as Pt<sub>2</sub>Ru<sub>3</sub>.

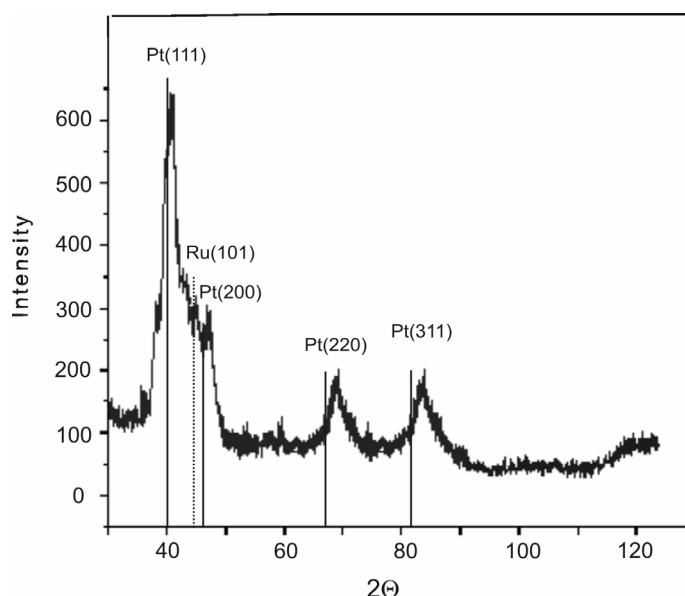


Fig. 1. XRD Pattern of Pt<sub>2</sub>Ru<sub>3</sub>/C (54 wt. % alloy) catalysts. Vertical lines represent the position of the peaks of pure Pt and pure Ru.

The onset of the methanol oxidation reaction at  $E_{\text{in}} = 0.35 \text{ V}$  coincides with the beginning of surface oxidation. The current densities increase with potential up to  $0.9 \text{ V}$  and then sharply decrease. The current maximum is attained at potentials where the kinetics is optimized by a balance between the rate of methanol dehydrogenation and the rate of oxidation of dehydrogenated products with  $\text{OH}_{\text{ad}}$  species.<sup>10,17</sup> This balance is rapidly disturbed immediately upon reaching the maximum reaction rate, probably due to the fast transformation of the reversible to the irreversible state of oxygenated species.<sup>18,19</sup>

The quasi steady state polarization curve for methanol oxidation on Pt<sub>2</sub>Ru<sub>3</sub>/C recorded at a slow sweep of  $1 \text{ mV s}^{-1}$ , shown in Fig. 3, has a Tafel slope of  $\approx 120 \text{ mV dec}^{-1}$ .

The influence of the methanol concentration was examined in  $0.1 \text{ M NaOH}$  containing  $0.05\text{--}1 \text{ M}$  methanol. In the entire concentration range, the reaction

rate increases with increasing methanol concentration. The current density at several potentials in the linear Tafel region as a function of the methanol concentration is shown in Fig. 4a. Parallel lines with a slope of about 0.55 imply that methanol oxidation follows half-order kinetics with respect to methanol. The same value was reported for a carbon-supported PtRu catalyst in  $\text{HClO}_4$ <sup>7</sup> as well as for a bulk PtRu catalyst.<sup>12</sup>

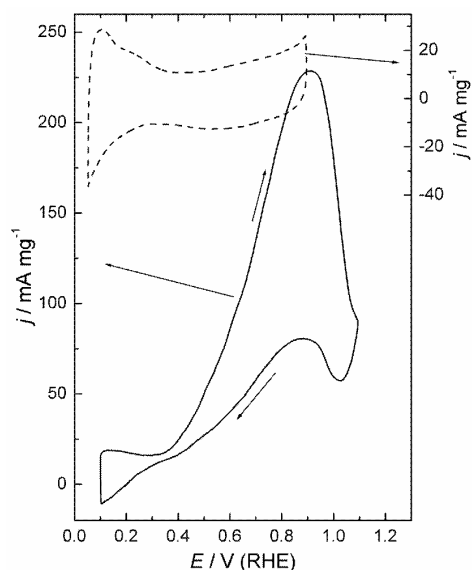


Fig. 2. Cyclic voltammograms for the oxidation of 0.5 M  $\text{CH}_3\text{OH}$  in 0.1 M NaOH at a  $\text{Pt}_2\text{Ru}_3/\text{C}$  electrode and the corresponding basic curve. Sweep rate:  $50 \text{ mV s}^{-1}$ ;  $T = 295 \text{ K}$ .

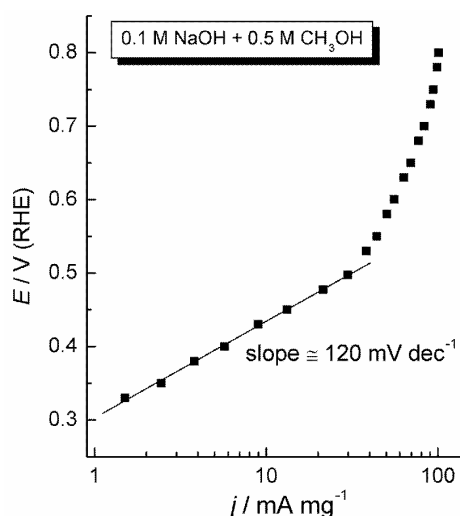


Fig. 3. Tafel plot for the oxidation of 0.5 M  $\text{CH}_3\text{OH}$  at  $\text{Pt}_2\text{Ru}_3/\text{C}$  in 0.1 M NaOH solution. Sweep rate:  $1 \text{ mV s}^{-1}$ ;  $T = 295 \text{ K}$ .

The pH dependence of methanol oxidation was investigated in electrolytes containing 0.5 M  $\text{CH}_3\text{OH}$  and 0.05–1 M NaOH. The reaction rate increases with increasing  $\text{OH}^-$  ion concentration. The estimated reaction order with respect to the  $\text{OH}^-$  ion is  $\approx 0.5$  (Fig. 4b).

#### *Comparison of methanol oxidation at $\text{Pt}_2\text{Ru}_3/\text{C}$ and $\text{Pt}/\text{C}$ catalysts and the reaction mechanism*

The polarization curves for methanol oxidation at  $\text{Pt}/\text{C}$  and  $\text{Pt}_2\text{Ru}_3/\text{C}$  in 0.1 M NaOH recorded at the slow sweep of  $1 \text{ mV s}^{-1}$  are shown in Fig. 5.

Methanol oxidation commences at  $\text{Pt}_2\text{Ru}_3/\text{C}$  at less positive potentials compared to  $\text{Pt}/\text{C}$  and proceeds at a higher reaction rate up to  $\approx 0.55 \text{ V}$ .  $\text{Pt}_2\text{Ru}_3/\text{C}$  is more active than  $\text{Pt}/\text{C}$  by a factor of two at  $E = 0.5 \text{ V}$ . At higher potentials  $\text{Pt}/\text{C}$  is more active than  $\text{Pt}_2\text{Ru}_3/\text{C}$ , since the oxide covered Ru leads to a decrease of the  $\text{Pt}_2\text{Ru}_3/\text{C}$  activity.<sup>13</sup>

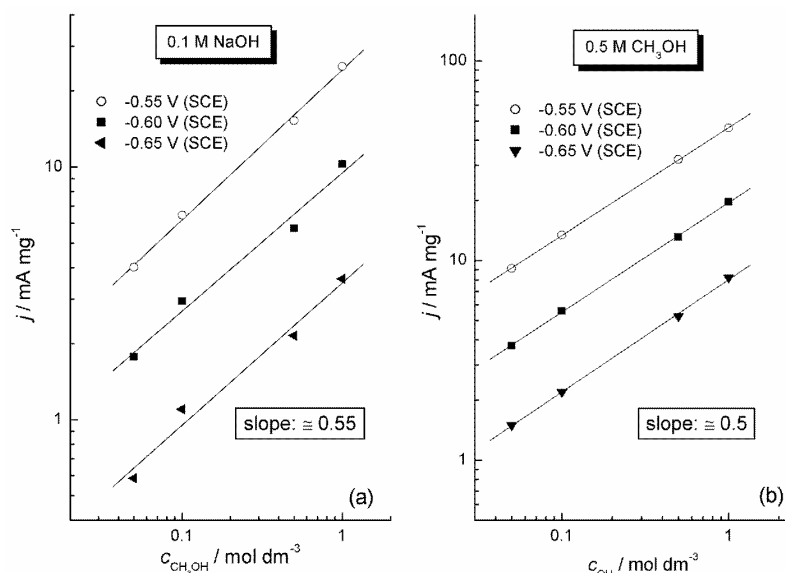


Fig. 4. Dependence of the methanol oxidation rate on the  $\text{CH}_3\text{OH}$  and  $\text{NaOH}$  concentrations at a  $\text{Pt}_2\text{Ru}_3/\text{C}$  electrode.

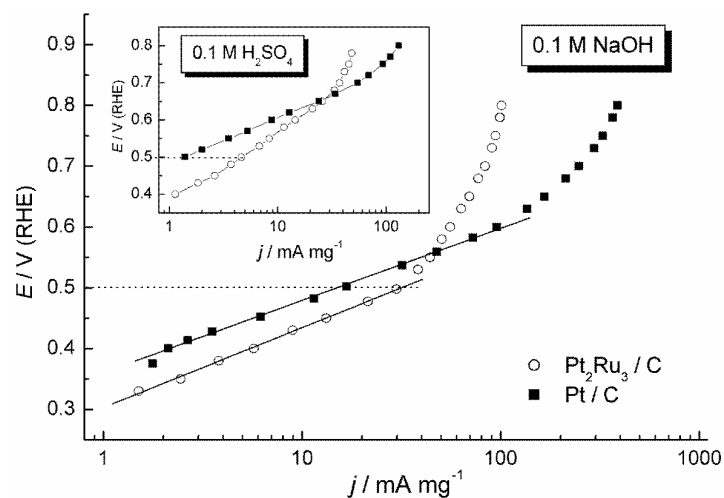
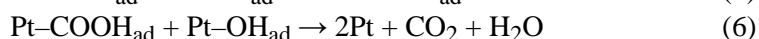
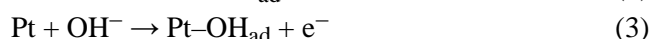
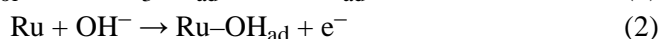
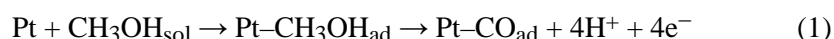


Fig. 5. Tafel plots for the oxidation of  $0.5 \text{ M CH}_3\text{OH}$  at  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{Pt}/\text{C}$  electrodes in  $0.1 \text{ M NaOH}$  solution. Inset: Tafel plots for the oxidation of  $0.5 \text{ M CH}_3\text{OH}$  at  $\text{Pt}_2\text{Ru}_3/\text{C}$  and  $\text{Pt}/\text{C}$  electrodes in  $0.1 \text{ M H}_2\text{SO}_4$  solution. Sweep rate:  $1 \text{ mV s}^{-1}$ ;  $T = 295 \text{ K}$ .

The enhanced activity of the  $\text{PtRu}$  catalyst for methanol oxidation compared to  $\text{Pt}$  can be explained by the bifunctional mechanism as was done in acid solution.<sup>10</sup> However, in alkaline solution,  $\text{Pt}$  is able to adsorb  $\text{OH}$  species at almost as low potentials as  $\text{Ru}$  causing the reaction also on  $\text{Pt}$ . For this reason the difference in activity between  $\text{Pt}/\text{C}$  and  $\text{Pt}_2\text{Ru}_3/\text{C}$  electrodes is smaller in alkaline

than in acid solution, as is shown in Fig. 5. In this sense, it could be concluded that Ru in alkaline media is not the only donor of  $\text{OH}_{\text{ad}}$  species as is the case in acid solution.

In fact, oxidation of methanol in alkaline solution proceeds through a quasi-bifunctional mechanism, summarized as follows:



In view of the kinetic parameters obtained by this study of methanol oxidation at  $\text{Pt}_2\text{Ru}_3/\text{C}$ , the chemical reaction between adsorbed  $\text{CO}_{\text{ad}}$  and  $\text{OH}_{\text{ad}}$  species is proposed as the rate-limiting step (Eqs. (4) or (5)). The kinetic expression for the rds has the form:

$$j = k_1 \theta_{\text{CO}} \theta_{\text{OH}} \quad (7)$$

Based on the experimental data (Tafel slope of  $\approx 120 \text{ mV dec}^{-1}$  and the reaction orders with respect to methanol and  $\text{OH}^-$  ions of 0.5), the current density of methanol oxidation for the overall reaction can be summarized as:

$$j = nFk c_{\text{CH}_3\text{OH}}^{0.5} c_{\text{OH}^-}^{0.5} \exp\left(\frac{\alpha FE}{RT}\right) \quad (8)$$

assuming that the adsorption of methanol and OH species obey Temkin isotherm.

*Acknowledgement:* This work was financially supported by the Ministry of Science of the Republic of Serbia, Contract No. N-142056.

#### ИЗВОД

#### КИНЕТИКА ОКСИДАЦИЈЕ МЕТАНОЛА НА $\text{Pt}_2\text{Ru}_3/\text{C}$ КАТАЛИЗАТОРУ У АЛКАЛНОЈ СРЕДИНИ

А. В. ТРИПКОВИЋ, К. Ђ. ПОПОВИЋ И Ј. Д. ЛОВИЋ

*ИХТМ – Центар за електрохемију, Универзитет у Београду, Њеђошева 12, ил. бр. 473, 11000 Београд*

Електрохемијска оксидација метанола испитивана је на нанокатализатору  $\text{Pt}_2\text{Ru}_3$  диспергованом на активном угљу као носачу у алкалној средини. Катализатор је карактерисан дифракцијом X-зрака (XRD) и добијени резултати су показали да се легура  $\text{Pt}_2\text{Ru}_3$  састоји од две фазе: чврстог раствора Ru у Pt и од малих количина чистог Ru или чврстог раствора Pt у Ru. Поређењем активности Pt/C и  $\text{Pt}_2\text{Ru}_3/\text{C}$  катализатора у оксидацији метанола у алкалној средини, показано је да је та разлика знатно мања него у киселој средини. Предложен је квази-бифункционални механизам реакције. Добијени кинетички параметри указују на то да је хемијска реакција између адсорбованих  $\text{CO}_{\text{ad}}$  и  $\text{OH}_{\text{ad}}$  честица спори ступањ у оксидацији метанола на  $\text{Pt}_2\text{Ru}_3/\text{C}$  катализатору у алкалној средини.

(Примљено 20. јуна, ревидирано 6. августа 2007)

## REFERENCES

1. N. M. Marković, H. A. Gasteiger, P. N. Ross, X. Jiang, I. Villegas, M. J. Weaver, *Electrochim. Acta* **40** (1995) 91
2. D. Kardash, C. Korzeniewski, N. Marković, *J. Electroanal. Chem.* **500** (2001) 518
3. A. Kabbibi, R. Faure, R. Durand, B. Beden, F. Hahn, J. M. Leger, C. Lamy, *J. Electroanal. Chem.* **444** (1998) 41
4. T. Frelnik, W. Visscher, A. P. Cox, J. A. R. van Veen, *Electrochim. Acta* **40** (1995) 1537
5. Y. Morimoto, E. B. Yeager, *J. Electroanal. Chem.* **444** (1998) 95
6. W. Chrzanowski, H. Kim, A. Wieckowski, *Catal. Lett.* **50** (1998) 69
7. S. Lj. Gojković, T. R. Vidaković, D. R. Đurović, *Electrochim. Acta* **48** (2003) 3607
8. A. S. Arico, A. K. Shukla, K. M. El-Khatib, P. Creti, V. Antonucci, *J. Appl. Electrochem.* **29** (1999) 671
9. T.J.Schmidt, H.A.Gasteiger, R.J.Behm, *Electrochem. Comm.* **1** (1999) 1
10. A. V. Tripković, K. Dj. Popović, B. N. Grgur, B. Blizanac, P. N. Ross, N. M. Marković, *Electrochim. Acta* **47** (2002) 3707
11. M. Watanabe, S. Motoo, *J. Electroanal. Chem.* **60** (1975) 267
12. H. A. Gasteiger, N. Marković, P. N. Ross Jr., E. J. Cairns, *J. Electrochem. Soc.* **141** (1994) 1795
13. A. V. Tripković, S. Štrbac, K. Dj. Popović, *Electrochem. Comm.* **5** (2003) 484
14. V. Radmilović, H. A. Gasteiger, P. N. Ross Jr., *J. Catal.* **154** (1995) 98
15. A. H. C. Sirk, J. M. Hill, S. K. Y. Kung, V. I. Birss, *J. Phys. Chem. B* **108** (2004) 689
16. G. Wu, L. Li, B.-Q. Xu, *Electrochim. Acta* **50** (2004) 1
17. A. V. Tripković, K. Dj. Popović, J. D. Lović, V. M. Jovanović, A. Kowal, *J. Electroanal. Chem.* **572** (2004) 119
18. A. V. Tripković, K. Dj. Popović, J. D. Lović, *Electrochim. Acta* **46** (2001) 3163
19. A. V. Tripković, S. Lj. Gojković, K. Dj. Popović, J. D. Lović, *J. Serb. Chem. Soc.* **71** (2006) 1333.