SHORT COMMUNICATION

Kinetic study of methanol oxidation on Pt₂Ru₃/C catalyst in the alkaline media

A. V. TRIPKOVIĆ*[#], K. DJ. POPOVIĆ[#] and J. D. LOVIĆ[#]

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

Abstract: The electrochemical oxidation of methanol in NaOH solution was examined on a thin film Pt₂Ru₃/C electrode. The XRD pattern revealed that the Pt₂Ru₃ 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 Pt₂Ru₃/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_{ad} and OH_{ad} 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,[1−3] electrochemical and spontaneously deposited Ru on Pt[4−6] and carbon supported Pt/Ru.[7−10] 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,[11] 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.[2,12]

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

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_2Ru_3/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_2Ru_3/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.[9] The mass transfer resistance through the Nafion® film was negligible.[10]

Electrode characterization

The electrodes were characterized by X-ray diffraction analysis.

Electrochemical measurements

All electrochemical measurements were conducted at 22 ºC 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^{-1}) or quasi-steady state curves (sweep rate 1 mV s^{-1}).

RESULTS AND DISCUSSION

Electrode characterization

In the diffraction pattern of the Pt_2Ru_3/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_2Ru_3/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 Scherer method based on the (220) breadth was 3.5 nm for the Pt–Ru fcc phase.

Methanol oxidation on Pt_2Ru_3/C catalyst

The polarization curve for methanol oxidation on Pt_2Ru_3/C in alkaline media and the corresponding basic curve for Pt_2Ru_3/C are presented in Fig. 2.

According to the phase diagram[14] as well as the analysis of the XRD spectra, the Pt_2Ru_3/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 ($0.05 \text{ V} < E < 0.3$ V) followed by the reversible and irreversible formation of oxygen-containing species (RuOH, Ru$_2$O, RuO$_x$·H$_2$O)[15,16] at $E > 0.3$ 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$_2$Ru$_3$.
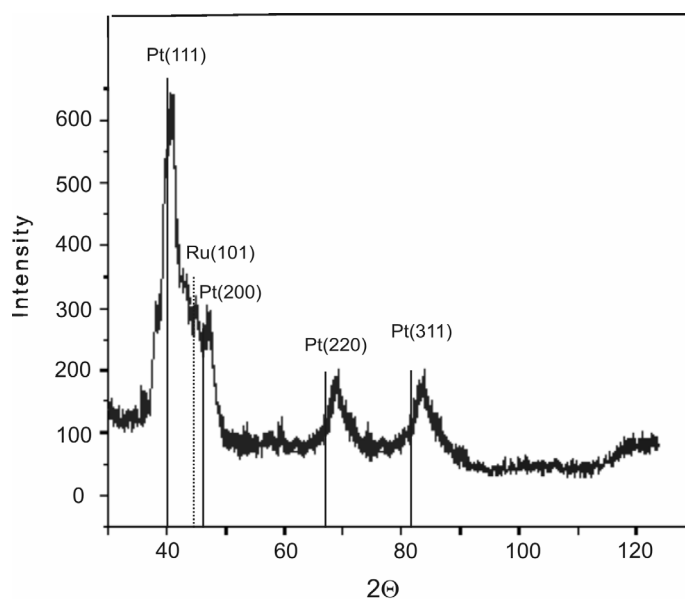

Fig. 1. XRD Pattern of Pt$_2$Ru$_3$/C (54 wt. % alloy) catalysts. Vertical lines represent the position of the peaks of pure Pt and pure Ru.

The onset of the methanol oxidation reaction at $E_{in} = 0.35$ V coincides with the beginning of surface oxidation. The current densities increase with potential up to 0.9 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 OH$_{ad}$ species.[10,17] 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.[18,19]

The quasi steady state polarization curve for methanol oxidation on Pt$_2$Ru$_3$/C recorded at a slow sweep of 1 mV s^{-1}, shown in Fig. 3, has a Tafel slope of ≈ 120 mV dec^{-1}.

The influence of the methanol concentration was examined in 0.1 M NaOH containing 0.05−1 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 $HClO_4$[7] as well as for a bulk PtRu catalyst.[12]
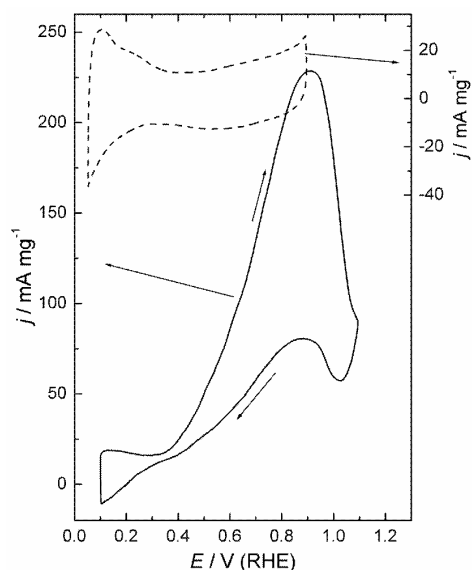

Fig. 2. Cyclic voltammograms for the oxidation of 0.5 M CH_3OH in 0.1 M NaOH at a Pt_2Ru_3/C electrode and the corresponding basic curve. Sweep rate: 50 mV s^{-1}; T = 295 K.
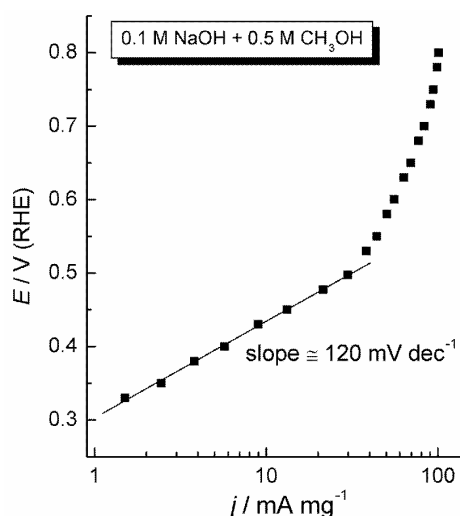
Fig. 3. Tafel plot for the oxidation of 0.5 M CH_3OH at Pt_2Ru_3/C in 0.1 M NaOH solution. Sweep rate: 1 mV s^{-1}; T = 295 K.

The pH dependence of methanol oxidation was investigated in electrolytes containing 0.5 M CH_3OH and 0.05−1 M NaOH. The reaction rate increases with increasing OH^- ion concentration. The estimated reaction order with respect to the OH^- ion is ≈ 0.5 (Fig. 4b).

Comparison of methanol oxidation at Pt₂Ru₃/C andPt/C catalysts and the reaction mechanism

The polarization curves for methanol oxidation at Pt/C and Pt_2Ru_3/C in 0.1 M NaOH recorded at the slow sweep of 1mV s^{-1} are shown in Fig. 5.

Methanol oxidation commences at Pt_2Ru_3/C at less positive potentials compared to Pt/C and proceeds at a higher reaction rate up to ≈ 0.55 V. Pt_2Ru_3/C is more active than Pt/C by a factor of two at E = 0.5 V. At higher potentials Pt/C is more active than Pt_2Ru_3/C, since the oxide covered Ru leads to a decrease of the Pt_2Ru_3/C activity.[13]
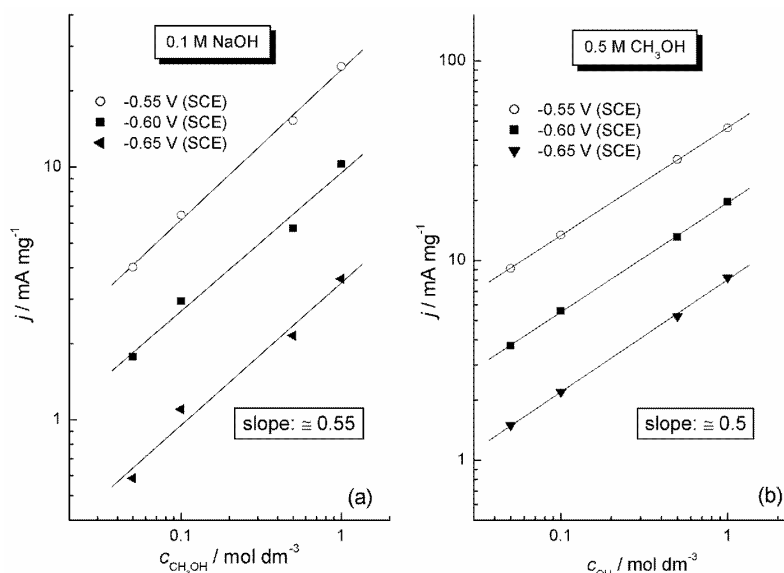
Fig 4. Dependence of the methanol oxidation rate on the CH_3OH and $NaOH$ concentrations at a Pt_2Ru_3/C electrode.
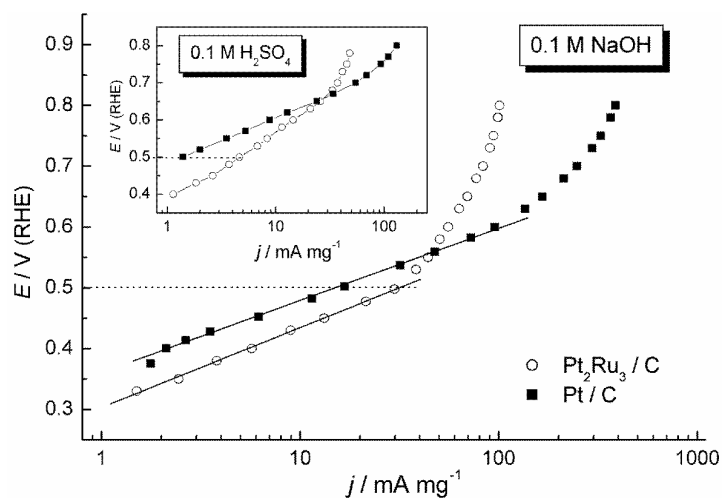

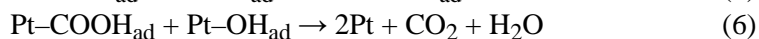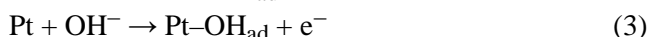Fig. 5. Tafel plots for the oxidation of 0.5 M CH_3OH at Pt_2Ru_3/C and Pt/C electrodes in 0.1 M NaOH solution. Inset: Tafel plots for the oxidation of 0.5 M CH_3OH at Pt_2Ru_3/C and Pt/C electrodes in 0.1 M H_2SO_4 solution. Sweep rate: 1 mV s^{-1}; $T = 295$ K.

The enhanced activity of the PtRu catalyst for methanol oxidation compared to Pt can be explained by the bifunctional mechanism as was done in acid solution.[10] However, in alkaline solution, Pt is able to adsorb OH species at almost as low potentials as Ru causing the reaction also on Pt. For this reason the difference in activity between Pt/C and Pt_2Ru_3/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 OH_{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:

$$Pt + CH_3OH_{sol} \rightarrow Pt–CH_3OH_{ad} \rightarrow Pt–CO_{ad} + 4H^+ + 4e^- \tag{1}$$

$$Ru + OH^- \rightarrow Ru–OH_{ad} + e^- \tag{2}$$

$$Pt + OH^- \rightarrow Pt–OH_{ad} + e^- \tag{3}$$

$$Pt–CO_{ad} + Ru–OH_{ad} \rightarrow Pt–COOH_{ad} + Ru \tag{4}$$

$$Pt–CO_{ad} + Pt–OH_{ad} \rightarrow Pt–COOH_{ad} + Pt \tag{5}$$

$$Pt–COOH_{ad} + Pt–OH_{ad} \rightarrow 2Pt + CO_2 + H_2O \tag{6}$$
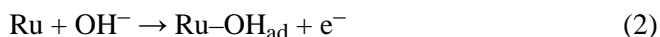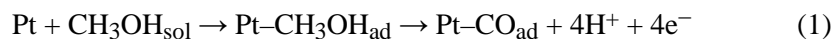
In view of the kinetic parameters obtained by this study of methanol oxidation at Pt_2Ru_3/C, the chemical reaction between adsorbed CO_{ad} and OH_{ad} species is proposed as the rate-limiting step (Eqs. (4) or (5)). The kinetic expression for the rds has the form:

$$j = k_1 \theta_{CO} \theta_{OH} \tag{7}$$

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

$$j = nFkc_{CH_3OH}^{0.5} c_{OH^-}^{0.5} \exp\left(\frac{\alpha FE}{RT}\right) \tag{8}$$

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

ИЗВОД

КИНЕТИКА ОКСИДАЦИЈЕ МЕТАНОЛА НА Pt_2Ru_3/C КАТАЛИЗАТОРУ У АЛКАЛНОЈ СРЕДИНИ

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

ИХТМ – Центар за електрохемију, Универзитет у Београду, Његошева 12, п. пр. 473, 11000 Београд

Електрохемијска оксидација метанола испитивана је на нанокатализатору Pt_2Ru_3 дисперго-ваном на активном угљу као носачу у алкалној средини. Катализатор је карактерисан дифракцијом X-зрака (XRD) и добијени резултати су показали да се легура Pt_2Ru_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 Pt_2Ru_3/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 CO_{ad} и OH_{ad} честица спори ступањ у оксидацији метанола на Pt_2Ru_3/C катализатору у алкалној средини.

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, *Electrocim. 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.