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Methanol Electrooxidation on PtRu Modified Zeolite X**Z. Mojović^{*)}, T. Mudrinić, A. Abu Rabi-Stanković, A. Ivanović-Šašić,
S. Marinović, M. Žunić, D. Jovanović**University of Belgrade, Institute of Chemistry, Technology and Metallurgy,
Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade,
Republic of Serbia**Abstract:**

Zeolite NaX (faujasite type) was used as a support for platinum-ruthenium catalyst. A procedure for thermal decomposition of noble metal acetylacetonates to deposit noble metal clusters on the surface of solid support was adapted by authors to introduce noble metal clusters in zeolite cavities. The effectiveness of this composite material for methanol electrooxidation from alkaline solution was investigated by cyclic voltammetry. The influence of the concentration of supporting electrolyte, scan rate and rotation rate on the reaction of methanol oxidation was investigated. The obtained activity was compared with literature data for similar catalysts.

Key words: *Modified Zeolites, Methanol Electrooxidation, Alkaline Solution*

1. Introduction

Methanol electrooxidation runs through several parallel pathways [1]. The direct reaction goes via adsorbed CO, while the other pathways include formation of formaldehyde and formic acid. Regardless the pathway, initial dehydrogenation of methanol must occur. Therefore, the catalyst for methanol oxidation should be able to dissociate C-H bond and to facilitate the oxidation of the resulting residue [2].

Platinum is the most active metal for dehydrogenation reaction. However, it is well known the platinum has large affinity for CO adsorption leading to rapid deactivation of platinum electrode [3]. The addition of second element enhance the electroactivity of platinum for methanol electrooxidation [4]. This metal added to platinum must fulfill the requirement of forming O-containing surface species at low potential. Among others Sn, Re, Ru, Ge, Mo, Bi, Pb, In were suggested [5]. The enhanced catalytic activity of bimetallic surfaces is usually ascribed to the bifunctional or ligand effect, or their combination [6].

Pt-Ru alloy is regarded as the most active electrocatalyst for both CO and methanol oxidation and a number of studies of this alloy have already been published [1, 7-11]. Even so, the properties of PtRu alloys are still extensively studied. Different support materials for PtRu alloys such as conventional Vulcan XC carbon black [12], graphite [13], carbon nanotubes [14], zeolite material [15] were investigated in order to obtain more efficient electrocatalyst for methanol electrooxidation. Nano-structured materials are a topic of a great interest [16, 17].

The zeolite has acidic protonic entities on its surface providing more hydrophilic

^{*)} **Corresponding author:** zoricam@nanosys.ihtm.bg.ac.rs

surface, and therefore, lower resistance and less ohmic drop than the carbon support. In this work, zeolite NaX (faujasite type) was used as a support for platinum-ruthenium catalyst and the effectiveness of this composite material for methanol electrooxidation was investigated. A procedure for thermal decomposition of noble metal acetylacetonates to deposit noble metal clusters on the surface of solid support [18] was adapted by authors to introduce noble metal clusters in zeolite cavities [19,20]. The aim of this work was to investigate the possibility of using zeolite as a support for Pt/Ru catalyst for methanol oxidation.

2. Experimental

Platinum(II) acetylacetonate [Pt(acac)₂] and ruthenium(II) acetylacetonate [Ru(acac)₃] were synthesized. The zeolite NaX, alternatively labeled 13X (Linde Co.) was heated at 350 °C to remove adsorbed water and cooled to room temperature in dry atmosphere. Then, the sample was soaked with diluted acetone solution of acetylacetonate salt. Wet sample was previously dried to 90 °C, to evaporate acetone, and further to 350 - 400 °C with the purpose to both decompose acetylacetonate salt and to remove its gaseous decomposition products. The impregnation/decomposition procedure was repeated until the following weight ratios were reached: Pt/zeolite 0.1 and PtRu/zeolite 0.2. Pt and Pt/Ru modified samples were designated as 13XPt and 13XPtRu, respectively. Thermal degradation of mixture of Pt(acac)₂ and Ru(acac)₃ was done under the hydrogen atmosphere, since thermal analysis of these salts has shown that Pt(acac)₂ sublimates under the nitrogen atmosphere and gives incomplete metal yield under the oxygen atmosphere [21].

In order to use the modified zeolite as an electrode material, the zeolite sample was homogeneously dispersed in a solution of Nafion (5 wt. %) in a mixture of isopropyl alcohol and distilled water by means of an ultrasonic bath (40 mg of sample in 1 ml of mixture). 10 wt. % of carbon black Vulcan XC72 (Cabot Corp.) was added to the initial suspension to provide the electronic conductivity of the sample. The droplet (10 μl) of this suspension was placed on the surface of a glassy carbon disc rotating electrode (disc area = 0.0314 cm²). After the solvent removal by evaporation at 90 °C, the zeolite particles properly dispersed in a form of thin layer finally resulted as pasted deposit on the glassy carbon support.

For electrochemical investigations in a three-electrode all glass cell compartment, glassy carbon disc, covered by a layer of homogeneous mixture of modified zeolite along with 10 wt. % carbon black, was used as a working electrode. The reference electrode was Ag/AgCl in 1M KCl, while a platinum foil served as a counter electrode. The performance of 13XPtRu electrode for methanol oxidation was evaluated in a solution 0.5 M CH₃OH + 0.5M NaOH. The device used for electrochemical measurements was 757 VA Computrace Metrohm. The geometric surface area of an electrode was used to calculate current density.

The results of samples characterization performed by X-ray diffraction analysis, nitrogen adsorption-desorption measurements and Raman spectroscopy are presented elsewhere [20]. In short, XRD measurements showed that impregnation/decomposition procedure affected zeolite crystal structure in a small degree, causing amorphisation of crystal structure only at local level. The Raman spectroscopy confirmed partial destruction of zeolite framework after incorporation of metal in zeolite.

3. Results and Discussion

The cyclic voltammograms of 13XPtRu electrode in alkaline solution with and without methanol are presented at Fig 1. In methanol free solution the peak at -0.9 V (corresponding to hydrogen desorption) is followed by double layer potential region, until at potential of 0.0 V oxide formation started. In methanol containing solution hydrogen

desorption peak is shifted about 30 mV toward more negative potentials. This peak is followed with methanol oxidation peak at -0.23 V, and oxide formation at 0.0 V. In backward sweep another oxidation peak appeared at -0.3 V corresponding to oxidation of products formed in forward sweep.

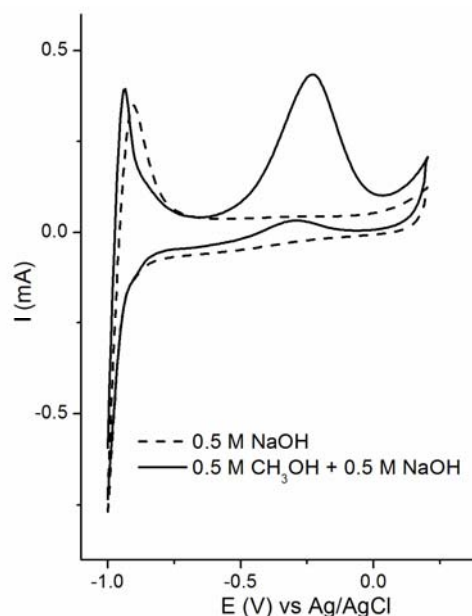
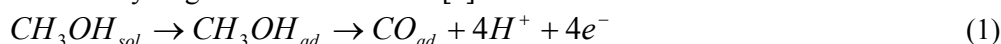
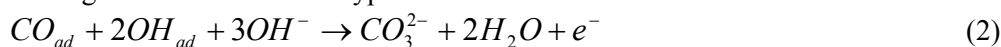


Fig. 1. Cyclic voltammograms of 13XPtRu electrode in alkaline solution with and without methanol recorded at polarization rate of 20 mV s^{-1} .

The peak of methanol oxidation is symmetric indicating that activation and deactivation of electrode run with similar rate with potential increase. Current maximum is formed at the potentials where the kinetics are optimized by a delicate balance between the rate of dehydrogenation of methanol [1]:



and the rate of oxidation of dehydrogenation products (CO_{ad}) with oxygen-containing species in Langmuir – Hinshelwood type reaction :



Methanol adsorption on the pure platinum surface commences after complete hydrogen desorption and is neglectable at potentials below 0.1V vs RHE. Methanol does not adsorb on pure ruthenium at low potentials and small degree of adsorption is noticed for PtRu alloy with Pt/Ru atomic ration of 1. Much better results are achieved with Pt/Ru alloys where surface composition is 10 atomic % Ru [22].

However, the bulk alloy composition is not necessarily identical to its surface composition. McNicol et al. [23] investigated electrocatalytical activity of PtRu catalyst dispersed on carbon toward methanol electrooxidation and came to the conclusion that heating of catalyst at the hydrogen atmosphere lead to platinum enriched surface, while by heating in the air ruthenium enriched surface was obtained. Miura et al. [24] established that surface of PtRu alloy dispersed on alumina is platinum rich if at the end of synthetic procedure reduction in hydrogen atmosphere at elevated temperatures is performed. Since modification of zeolite by Pt/Ru at this work was performed under the hydrogen atmosphere we expect that surface of metal clusters formed on zeolite is platinum rich.

3.1. The influence of the concentration of the supporting electrolyte

The influence of the concentration of the supporting electrolyte was investigated for two values of the concentration of NaOH solution: 0.1 and 0.5 M (Fig.2), while the concentration of methanol was 0.5 M. The onset potential for the methanol oxidation shifted toward lower values, while the peak current was slightly increase in the solution with higher concentration of NaOH. The observed pH dependence of methanol oxidation is in accordance with literature data [25]. Tripković et al. [26] investigated this dependence for Pt₂Ru₃/C in broader concentration range of NaOH and concluded that reaction order with respect to the OH⁻ ion is ≈ 0.5. We roughly estimated reaction order with respect to the OH⁻ ion using two investigated concentrations and found that the obtained result is approximately 0.5.

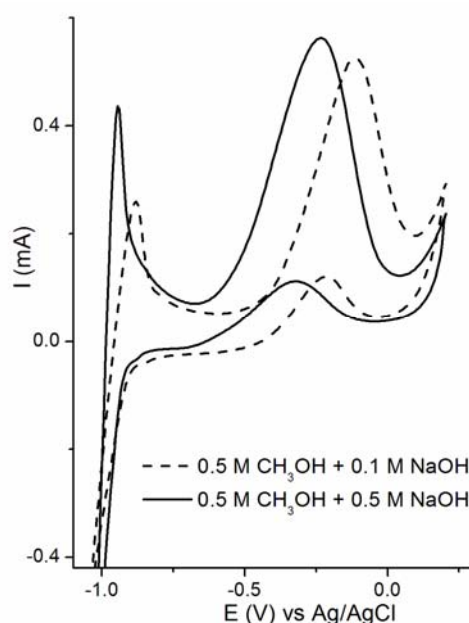


Fig. 2. Cyclic voltammograms of methanol oxidation on 13XPtRu electrode in 0.1 M and 0.5 M solution NaOH recorded at polarization rate of 20 mV s⁻¹.

3.2. The influence of the scan rate

The dependence of methanol oxidation peak current on the scan rate was studied in the range of 5 – 500 mV s⁻¹(Fig.3a). The curve of I_p vs. $v^{1/2}$ exhibited a dual linear region with different slopes (Fig. 3b). The slope in the lower scan-rate region (5 -100 mVs⁻¹) was greater than that in the higher scan-rate region (100 – 500 mVs⁻¹). Shen et al. observed similar behavior on Pt-WO₃ electrode [27]. They explained this effect in the term of decreased adsorption of methanol molecules on the electrode surface. The possible reasons for decreased methanol adsorption were the accumulation of the reaction products in the vicinity of the electrode at higher scan rates or the increased amount of adsorbed hydrogen whose re-oxidation was not fast enough at higher scan rates. Plot of peak potential (E_p) of the methanol oxidation peak vs logarithm of scan rate (v) (Fig. 3c) also exhibited a dual linear region with different slopes $dE_p/d(\log v) = 18$ and 51 mV dec⁻¹. The shift of the peak potential E_p is given by

$$\frac{dE_p}{d\log v} = \ln(10) \times \frac{RT}{2\alpha F} \quad (3)$$

for processes with electrochemically irreversible kinetics [26]. The existence of two values of slopes indicated transition from quasi-reversible to irreversible behavior [28].

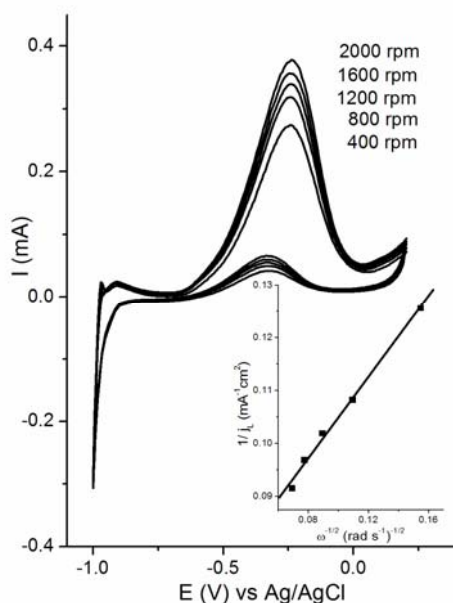


Fig. 3. (a) Cyclic voltammograms recorded for 13XPtRu electrode in 0.5 M CH₃OH + 0.5 M NaOH at various scan rates, 5-500 mVs⁻¹; (b) Dependence of peak current on square root of scan rate; (c) Dependence of peak potential on logarithmic value of scan rate.

3.3. The influence of rotation rate

In order to evaluate the effect of mass transport, assuming a diffusion coefficient of CH₃OH, D_i of $1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, a viscosity of solution of ca 1.0, 800 rpm rotating rate and methanol concentration C_i , 0.5 M, so the limitation current densities can be approximately calculated and given as follows:

$$j_d = 0,62nFD_i^{2/3} \omega^{1/2} \nu^{-1/6} C_i \approx 150 \text{ mA cm}^{-2} \quad (4)$$

The limitation current density, j_d , is significantly higher than the current density of methanol electrooxidation (about 10 mA cm^{-2} in this work for the rotation rate of 800 rpm), so the mass transport limitation could be completely ignored. Accordingly, methanol dehydrogenation on bare Pt electrode showed no dependence on rotation speed of the electrode [29]. Gojković and Vidaković [29] investigated influence of rotation rate on methanol oxidation on Pt electrode, nafion covered Pt electrode and Pt supported electrode from acidic solution. They noticed that stirring of the solution caused a decrease of the methanol oxidation current, but the currents were the same for different rotation rate.

Contrary to this zeolite-modified electrode showed linear dependence of the peak current on the square root of rotation speed of the electrode (Fig. 4). This result indicated that the methanol electro-oxidation process on zeolite-modified electrodes is controlled by the diffusion of methanol to the electrode surface and/or through the zeolite cavities. It is important to notice that above calculated value of limitation current was calculated for diffusion coefficient and methanol concentration in bulk solution. These values can be significantly decreased in the zeolite film applied on the surface of carbon glass electrode leading to much lower values of the limiting current.

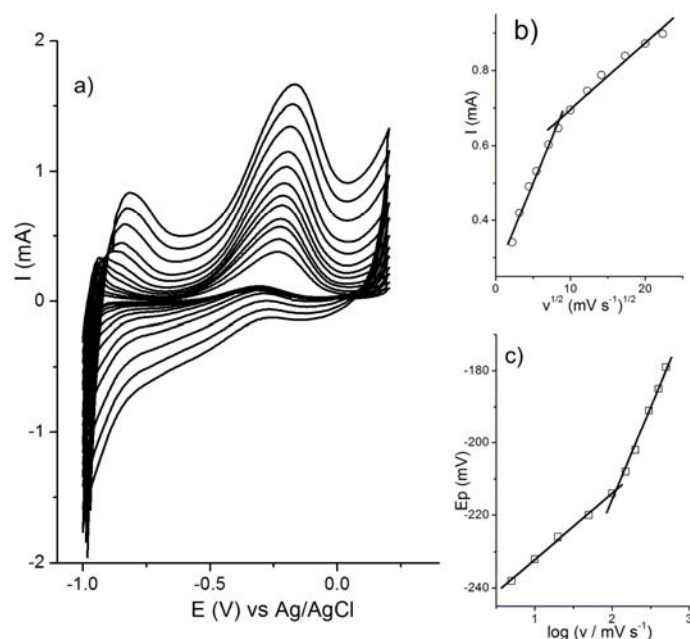


Fig. 4. Cyclic voltamograms for 13XPtRu in methanol 0.5 M CH_3OH + 0.5 M NaOH, recorded at polarization rate of 5 mV s^{-1} and various rotation rates 400 -2000 rpm.

Inserted figure: Koutecky – Levich plot for methanol oxidation.

3.4. Tafel analysis

Tafel slope for methanol electrooxidation, obtained in this work, could be best fitted with two Tafel slopes. The value of the Tafel slope fitted at low overpotentials ($< -0.60 \text{ V}$) was 97 mV dec^{-1} , while the value of the Tafel slope fitted at high overpotentials (-0.60 to -0.45 V) was 219 mV dec^{-1} . The latter slope was double the first one. This can indicate a possible change of reaction mechanism or at least a change of rate-determining step at different potential range [30].

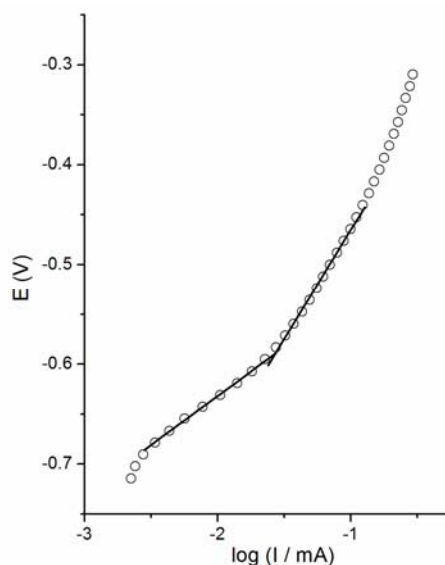


Fig. 5. Tafel plot for methanol oxidation on 13XPtRu electrode.

3.5. The activity of 13XPtRu for methanol oxidation

The comparison of the activity of investigated catalyst with literature data involves numerable difficulties. The activity of catalyst is influenced, beside the nature of the catalyst itself, by the composition of used electrolyte, temperature of the electrolyte, conditions of electrochemical investigation (sweep rate, for example). Another important feature is presentation of activity results in the literature: the results were read for different potentials or presented in different manners (mAcm^{-2} of catalyst; mAcm^{-2} of metal; mAcm^{-2}).

The electrocatalytic activity for the catalyst in this paper was evaluated using mass specific activity (MSA) and peak potential for methanol electrooxidation. The MSA was calculated by integration of the charge density corresponding for methanol oxidation divided by metal loading according to the following equation [31]:

$$MSA = \frac{Q_{MOR}}{L_{PtRu}} \quad (5)$$

where the MSA is the mass specific activity for MOR (mCmg^{-1}), Q_{MOR} is the charge density for methanol oxidation peak (mC) and L_{PtRu} is the loading of PtRu in the electrode (mg). The obtained value of activity was 170 mCmg^{-1} . This value is comparable with the values for carbon supported PtRu nanocatalyst with PtRu loading of 18 wt. % [31].

4. Conclusion

Impregnation/thermal decomposition technique was used in order to obtain Pt/Ru metal nanodispersion on zeolite NaX (faujasite type). The effectiveness of this composite material for methanol electrooxidation from alkaline solution was investigated by cyclic voltammetry. Methanol oxidation on 13XPtRu electrode exhibited expected pH dependence. The dependence of methanol oxidation peak current on square root of scan rate exhibited a dual linear region with different slopes. Plot of peak potential (E_p) of the methanol oxidation peak vs logarithm of scan rate also exhibited a dual linear region with slopes with values 18 and 51 mVdec^{-1} . The existence of two values of slopes indicated transition from quasi-reversible to irreversible behavior. The zeolite-modified electrode showed linear dependence of the peak current on the square root of rotation speed of the electrode, unlike conventional electrode that does not show dependence on rotation rate. Tafel slope for methanol electrooxidation on 13XPtRu electrode be best fitted with two Tafel slopes with values 97 and 219 mVdec^{-1} . The electrocatalytic activity for 13XPtRu electrode was determined to be 170 mCmg^{-1} .

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5. References

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Садржај: *Зеолит NaX (фожазитног типа) коришћен је као носач за платина-рутенијумски катализатор. Аутори су прилагодили процедуру термалне декомпозиције племенитих металних ацетилацетоната којом су наношени кластери племенитих метала на површину чврсте подлоге, како би се кластери племенитих метала су увели у шупљине зеолита. Ефикасност ових композитних материјала за реакцију електрооксидације метанола је испитана цикличном волтаметријом. Испитан је утицај концентрације инертног (основног) електролита, брзине поларизације и брзине ротације електроде на реакцију оксидације метанола. Добијена активност је упоређена са литературним подацима за сличне катализаторе.*

Кључне речи: *Модификовани зеолити, електрооксидација метанола, алкални раствор*
