PHYSICAL CHEMISTRY 2010

10th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Proceedings

The Conference is dedicated to the
100th Anniversary of the academician Pavle Savić birthday
and
20th Anniversary of the Society of Physical Chemists of Serbia

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21-24 September 2010
BELGRADE

ISBN 978-86-82475-17-0
Title: Physical Chemistry 2010. (Proceedings)
Editors: S. Anić and Ž. Čupić
Published by: Society of Physical Chemists of Serbia, Studentski trg 12-16
P.O.Box 47, 11158 Beograd, 218, Srbija
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: “Jovan” Printing and Publishing Company; 200 Copies;
Number of pages 16 + 388, **Format:** B5; Printing finished in September 2010.

Text and Layout: “Jovan”

200 - *Copy printing*

The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis, Bulgarian Academy of Sciences

Boreskov Institute of Catalysis, Siberian Branch of
the Russian Academy of Sciences

Faculty of Physical Chemistry, University of Belgrade, Serbia

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METHANOL ELECTROOXIDATION FROM ALKALINE SOLUTION ON Pt AND PtRu MODIFIED ZEOLITE X

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Abstract

Zeolite NaX was modified by Pt and Pt/Ru nanodispersed metallic clusters. This modification was achieved by zeolite impregnation with acetylacetonate salt/acetone solution, followed by acetone evaporation and thermal decomposition of organometallic complex. The mixture of modified zeolite and 10 wt.% of carbon black, in a form of thin layer, was pasted to a glassy carbon surface by nafion. Electrocatalytic properties of metal-modified zeolites were tested in methanol electrooxidation reaction.

Introduction

Pt-Ru alloy is considered as the most active electrocatalyst for both CO and methanol oxidation. However, even PtRu still suffers from a significant overpotential for the oxidation of organic fuels and from poisoning by sulfur-containing compounds, each of which results in loss of catalytic efficiency. Therefore, properties of PtRu alloys, possible improvements of their catalytic activity and application for methanol electrooxidation are still subject of investigation. One approach to the problem was to investigate different support materials such as conventional Vulcan XC carbon black [1], graphite or carbon nanotubes [2]. The zeolite material, as pointed out by Samant and Fernandes [3], is more hydrophilic than carbon due to acidic protonic entities on its surface. Therefore, zeolite support provides lower resistance and less ohmic drop than carbon support.

In this work, zeolite NaX (faujasite type) was used as a support of platinum and platinum-ruthenium catalyst. A procedure of thermal decomposition of noble metal acetylacetonates to deposit noble metal clusters on the surface of solid support [4], was adapted by some of the present authors to introduce noble metal clusters in zeolite cavities. Metal acetylacetonates were used as zeolite impregnation agents very rarely, but were not decomposed to metals. Zeolites are expected to both enable to obtain effective catalyst in a form of nano-dispersion and prevent the occurrence of agglomeration. There is the evidence that solid aluminosilicate framework hinders the metal nanocluster agglomeration [5].

Experimental

Pt-acetylacetonate and Ru-acetylacetonate were dissolved in acetone. Zeolite 13X was soaked by the solution, dried to evaporate acetone and heated to 350^0C in air in order to decompose the complex compounds and desorb the decomposition products. In this way nanodispersed PtRu clusters were incorporated into the zeolite cages. Procedure was repeted until Pt/zeolite PtRu/zeolite weight ratios of 0.1 and 0.2, respectively, were reached.

Powdered mixture of the sample and 10 % carbon black, was homogenously dispersed in a solution of Nafion (5 wt.%), at Nafion solution/powder wt. ratio 2.5, and a droplet of the suspension was applied on glassy carbon disc of rotating electrode. Solvent evaporation resulted in a thin film of modified zeolite bonded, by a Nafion film, to glassy carbon support. The electrochemical performance of this material was investigated in 0.1M NaOH solution using rotating disc technique.

Results and Discussion

Methanol electrooxidation on 13XPt and 13XPtRu was examined in 0.5M CH_3OH + 0.5M NaOH. Steady state voltammograms recorded at scan rate of 10 mV/s for modified zeolites are presented at the Fig 1 in comparison with bare Pt recorded under the same conditions.

Methanol electrooxidation peak is visible at forward scan at all three electrodes at potential arround -0.2V. At the reverse scan another oxidation peak appear at -0.3 corresponding probably to oxydatation of residual species adsorbed on the surface of the electrode after methanol electrooxidation. The onset for methanol electrooxidation is shifted to somewhat lower potential on 13XPtRu in comparison to Pt electrodes, bare and zeolite modified. The peak is symethric 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 [6]:

$$CH_3OH_{sol} \rightarrow CH_3OH_{ad} \rightarrow CO_{ad} + 4H^+ + 4e^-$$

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

$$CO_{ad} + 2OH_{ad} + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + e^-$$

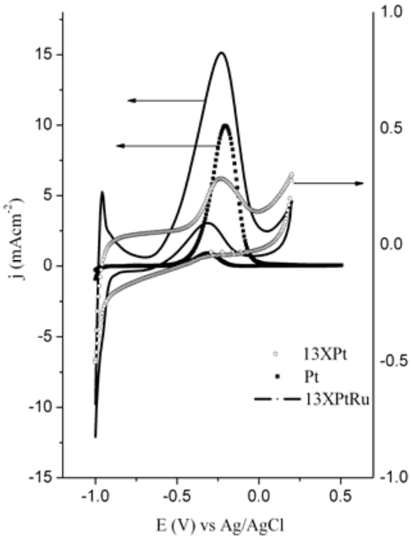

Fig.1.. Cyclic volammograms of 13XPt (–), 13XPtRu (---) and bare Pt (!) in 0.5M CH_3OH + 0.5M NaOH at scan rate of 10mV/s

Pt-modified electrode shows the lowest activity toward methanol electrooxidation. Since three adjacent Pt sites are initially needed for dissociative methanol adsorption to COH_{ads} [7] it is reasonable to assume that Pt is dispersed over the inner surface of zeolite. 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 [8].However, the bulk alloy composition is not necesseraly identical to its surface composition. McNicol et al [9] investigated electrocatalytical activity of PtRu catalyst disperged 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 [10] established that surface of PtRu alloy disperged 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. Methanol dehydrogenation on bare Pt electrode shows no dependence on rotation speed of the electrode [11]. Contrary to this zeolite-modified electrodes show linear dependence of the peak current with rotation speed of the electrode. These results indicate that the methanol electro-oxidation process on zeolite-modified electrodes is controlled by the diffusion of methanol to the electrode surface and/or through zeolite cavities.

Conclusion

Impregnation/thermal decomposition technique was used in order to obtain Pt and Pt/Ru metal nanodispersion on zeolite. The mutual influence between Pt and Ru atoms enhanced electroactivity of Pt/Ru-modified zeolite toward methanol electrooxidation in comparison to Pt-modified zeolite.

Acknowledgments

This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (Projects 166001B and 142019).

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