



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)

Editors: Ž. Čupić and S. Anić

Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia

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: 6+ 441; **Format:** B5; Printing finished in September 2014.

Text and Layout: "Jovan"

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*12th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Organized by
The Society of Physical Chemists of
Serbia*

*in co-operation
with*

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PHENOL ELECTROOXIDATION USING ELECTRODES BASED ON ACID-TREATED AND Ni-IMPREGNATED BENTONITE

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ABSTRACT

Electrooxidation of phenol in acidic solution was investigated on modified bentonite-based glassy carbon electrode (GCE). The modification of bentonite was performed in two steps. First bentonite was acid treated and then nickel species were incorporated in acid-treated bentonite. Incorporation of nickel species was achieved by either impregnation with $\text{Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ or by impregnation-decomposition method using nickel acetylacetonate $[\text{Ni}(\text{acac})_2]$. The change in phase and chemical composition was monitored by XRD. The electrochemical behavior was tested by cyclic voltammetry. The higher current density and lower potentials of phenol oxidation wave were obtained for acid-treated bentonite based GCE, while presence of nickel led to better stability of modified GCE regarding electrode fouling.

INTRODUCTION

Electrochemical oxidation processes have been recognized as an alternative method for treating wastewaters containing organic molecules. The oxidation of various organic pollutants at different electrode materials has been extensively investigated [1]. Phenol is the most commonly investigated compound as model organic compound in electrooxidation processes [2, 3]. Many electrode materials suffer from electrode fouling by formation of insulating polymeric film during electrooxidation of phenol. Modification of the electrode surface is one of approaches to overcome the problem of electrode fouling. Clays modified using oxidation/reduction species have proven to be good electrode surface modifiers [4, 5].

The goal of this work was to incorporate nickel in acid treated bentonite and apply these materials as GCE modifiers in the electrochemical oxidation of phenol.

EXPERIMENTAL

Bentonite from seldom investigated deposit Mečji Do Serbia ($< 75 \mu\text{m}$) was used as raw material (MD). First bentonite was treated with 1 M HCl at 70°C for 30 min and designed as MD_A. Incorporation of nickel species into the acid-treated bentonite was performed by either impregnation with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or by impregnation-decomposition method using nickel acetylacetonate $[\text{Ni}(\text{acac})_2]$ [4]. The sample was impregnated with 0.5 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 300°C for 2h and designed as MD_A/ $\text{Ni}(\text{NO}_3)_2$. The impregnation-decomposition procedure with $\text{Ni}(\text{acac})_2$ was performed at 430°C in order to transform $\text{Ni}(\text{acac})_2$ into NiO. The procedure was repeated until mass ratio of Ni/MD_A of 0.1 was reached. This sample was designed as MD_A/ $\text{Ni}(\text{acac})_2$.

The XRD analyses were performed using Philips PW 1710 X-ray powder diffractometer with a Cu anode ($\lambda=0.154178 \text{ nm}$). The GCE surface was coated with 10 μl of homogeneous mixture of each modified bentonite and carbon black dispersed in Nafion® solution and applied as working electrode [4]. The reference electrode was Ag/AgCl, KCl (3M), while a platinum foil served as a counter electrode. The electrooxidation of phenol was investigated in 10 mM phenol + 0.1 M H_2SO_4 . The device used for electrochemical measurements was 797 VA Computrace Metrohm.

RESULTS AND DISCUSSION

The main minerals identified in all samples were smectite (S), cristobalite (Cb), quartz (Q) and feldspar (F) (Fig. 1) [6]. In the Ni containing samples d_{001} value was 0.97 nm characteristic for dehydrated smectites caused by applied heat treatment. Among impregnated samples only MD_A/ $\text{Ni}(\text{acac})_2$ showed new reflections at around 43.1° and 37.1° 2θ characteristic for nickel oxide [6].

Cyclic voltammograms (CV)s were obtained for GCE modified with each of modified bentonite in acidic phenol solution. The polarization rate was 10 mVs^{-1} in the range of potential from hydrogen evolution at -0.3 V to oxygen evolution at 1.1 V . CVs were first obtained in 0.1 M H_2SO_4 . The freshly prepared electrodes were then tested under the same conditions

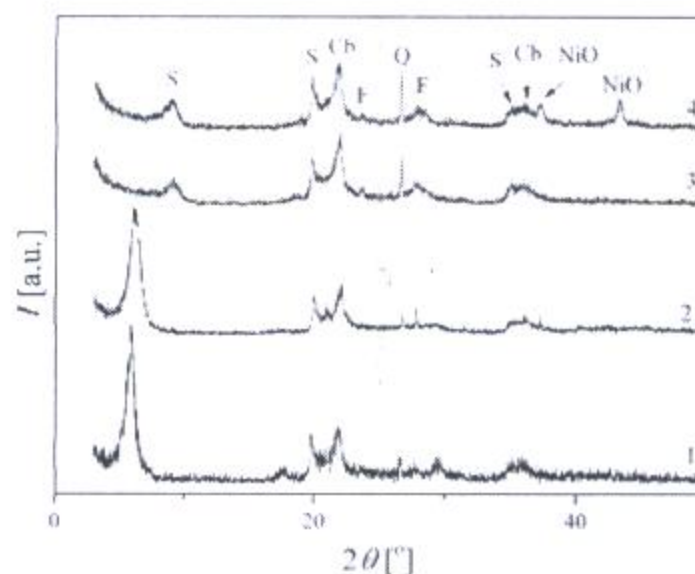


Figure 1. XRD patterns of: (1) MD; (2) MD_A; (3) MD_A/ $\text{Ni}(\text{NO}_3)_2$ and (4) MD_A/ $\text{Ni}(\text{acac})_2$.

in 10 mM phenol + 0.1 M H₂SO₄. CVs were similar for all investigated electrodes and for clarity sake only CVs for MD_A/Ni(acac)₂ are presented in Figs. 2. The CV obtained in the supporting electrolyte (dashed line in Fig. 2a) is presented together with the first cycle recorded in phenol containing solution (solid line in Fig. 2a). In Fig. 2b ten successive cycles in phenol containing solution are presented.

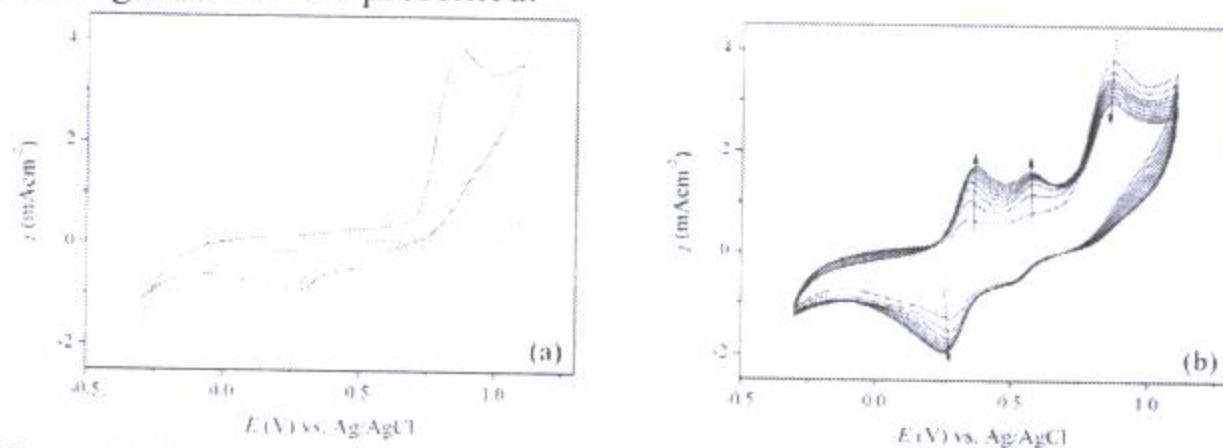


Figure 2. CVs of the MD_A/Ni(acac)₂: (a) 0.1 M H₂SO₄ (dashed line) and the first cycle in phenol containing solution (solid line); (b) Successive cycles in phenol containing solution. Arrows indicate changes during cycling.

During electrooxidation of phenol in the first cycle the phenol oxidation wave and pair of waves that correspond to the reduction of hydroquinone and catechol were obtained for all synthesized electrode materials. During successive cycling additional pair of waves that correspond to hydroquinone and catechol oxidation was registered [5]. Successive cycling increased the current density of waves associated with phenol oxidation products. On the other hand, successive cycling resulted in decreased intensity of the phenol oxidation wave for all investigated electrodes. Differences between electrochemical parameters obtained for GCE coated with different materials are summarized in Table 1.

Table 1. Electrochemical parameters of investigated modified electrodes.

Modifier	E [mV]	j_1 [mAcm ⁻²]	j_x [mAcm ⁻²]	$(j_1 - j_x)/j_1$ [%]
MD	939	1.06	0.24	77.4
MD _A	863	3.40	2.18	35.9
MD _A /Ni(NO ₃) ₂	878	2.07	1.49	28.0
MD _A /Ni(acac) ₂	868	3.87	2.99	22.7

Where: E – potential of phenol oxidation peak, j_1 and j_x – current density at phenol oxidation peak, in the first and tenth cycle, respectively.

The current density for phenol oxidation wave increased in following order MD < MD_A/Ni(NO₃)₂ < MD_A < MD_A/Ni(acac)₂. The higher current densities for MD_A based electrodes might be induced by better accessibility to active sites for phenol oxidation. Also, potential at phenol oxidation wave shifts

toward lower potentials in MD_A based electrodes. Such finding indicates better electrode activity. Incorporation of nickel in modified bentonite based GCE resulted in improvement of the stability of these electrodes. The introduction of nickel by impregnation/decomposition method in MD_A was found to be the most promising modification regarding the use of investigated modified bentonites in surface coating of GCE.

CONCLUSION

Electrooxidation of phenol was investigated on glassy carbon electrode (GCE) coated with raw (MD), acid-treated bentonite (MD_A) and acid-treated bentonite impregnated with either Ni(NO₃)₂ (MD_A/Ni(NO₃)₂) or nickel acetylacetonate (MD_A/Ni(acac)₂). Phenol oxidation process on all synthesized electrode materials showed similar response with difference in electrochemical parameters. The higher current density and lower potentials of phenol oxidation wave were obtained for MD_A based GCE. The incorporation of nickel species into MD_A caused better stability of modified GCE regarding electrode fouling. The GCE modified with MD_A/Ni(acac)₂ was more stable than GCE modified MD_A/Ni(NO₃)₂. The presence of nickel has important role in the stability of the GCE in the phenol electrooxidation process and further investigation of this phenomenon is still in progress.

ACKNOWLEDGEMENT

This work was partially supported by the Ministry of Education, Science and Technology Development of the Republic of Serbia (Project Nos. III 45001 and ON 172026).

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