



Beneficial effect of Ni in pillared bentonite based electrodes on the electrochemical oxidation of phenol



T. Mudrinić^{a,*}, Z. Mojović^a, A. Milutinović-Nikolić^a, P. Banković^a,
B. Dojčinović^b, N. Vukelić^c, D. Jovanović^a

^a University of Belgrade-Institute of Chemistry, Technology and Metallurgy, Center for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia

^b University of Belgrade-Institute of Chemistry, Technology and Metallurgy, Center for Chemistry, Njegoševa 12, 11000 Belgrade, Serbia

^c University of Belgrade, Faculty of Physical Chemistry, Studenski trg 12-16, 11000 Belgrade, Serbia

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ABSTRACT

The influence of Ni on the electrochemical performance of Fe containing bentonite-based electrode materials was investigated in the electrochemical oxidation of phenol in acidic solution. Clay originated from Mečji Do, Serbia, was submitted to pillaring. Mixed pillaring solutions containing Al^{3+} and Fe^{3+} or Al^{3+} , Fe^{3+} and Ni^{2+} were used for this purpose. The XRD, chemical and FTIR analysis and nitrogen physisorption at -196°C were used for sample characterization. The electrochemical behavior of the pillared clay-based electrodes was tested by cyclic voltammetry. The results confirmed that the pillaring was successful. The presence of Ni in the electrode material enhanced the electrode stability. It is possible that the presence of Ni restricted the electrode fouling caused by the formation of polymeric products during the electrooxidation of phenol.

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1. Introduction

Electrochemical oxidations have shown to be promising in the treatment of wastewaters containing organic molecules. They possess several technologically important characteristics, which make them advantageous over other conventional technologies such as versatility, energy efficiency, environmental compatibility, cost-effectiveness, etc. [1–4]. The electrooxidation processes could be used as a pre-treatment technology in order to increase the biodegradability of pollutants in wastewater before bio-treatment or in the ideal case for the complete mineralization of organic compounds to carbon dioxide and water [5–8].

Phenol has been extensively investigated as a model organic compound in electrooxidation processes due to its classification as a priority contaminant [9] whose oxidation mechanisms are well-known [10,11]. Summarized literature results [3,12,13] show that the nature of electrode material strongly affects the selectivity and efficiency of electrochemical processes of oxidation of organic compounds. One of the major problems that appear during the electrooxidation of phenol is the formation of insulating polymeric film. Such film can prevent electron transfer between phenol

and electrical conductor and restrain further oxidation. Complete organic oxidation to CO_2 is favored on antimony-doped tin oxide, lead or boron-doped diamond electrodes. Unfortunately, these electrodes encounter several problems such as short service life, the release of toxic ions and high cost, respectively.

One of the promising ways to overcome these problems is the modification of electrode surface. Clay minerals have been recognized as electrode surface modifiers due to their availability, well-defined layered structure, thermal and chemical stability and low cost [14,15]. It was previously shown that electrodes based on bentonite–clay rich in smectite–are active toward the oxidation of phenol [16]. Smectites are aluminosilicates that consist of $[\text{AlO}_3(\text{OH})_3]^{6-}$ octahedral sheet sandwiched between two opposing $[\text{SiO}_4]^{4-}$ tetrahedral sheets [17]. In smectites some of structural Si^{4+} and Al^{3+} cations are isomorphously substituted with different cations. The isomorphous substitution by oxidation/reduction electroactive cations (like iron cations) is very important feature from the electrochemical standpoint. Structural iron can be either employed as electron acceptor/donor to relay electrons between species adsorbed in the interlayer space and the conductive substrate [18,19] or for the generation of hydroxyl radicals, as occurs in the electro-Fenton's reaction [2]. Unfortunately natural smectites are limited by their chemical composition, since they do not contain significant amounts of electroactive cations other than Fe [14]. Therefore, either clay modifications [16,20,21] or designed

* Corresponding author. Tel.: +381 11 2630213; fax: +381 11 2637977.
E-mail address: tihana@nanosys.ihm.bg.ac.rs (T. Mudrinić).

clay synthesis [18,19] are used for the preparation of clay-modified electrodes.

Pillaring is one of the common techniques of clay modification [22]. It was shown [16] that the electrocatalytic activity and stability depend on the type of incorporated metals. Among investigated pillaring species (Al, Al-Fe, Al-Cu and Al-Co) the highest current density for phenol oxidation was obtained on the Al,Co pillared clay (PILC) electrode. Unfortunately, this electrode was easily and irreversibly deactivated. The Al,Fe-PILC electrode was found to be the most optimal choice among the investigated ones.

Xiang and Villemure [18] tested electrode materials based on synthetic smectite clays containing iron or nickel, as well as their combination, in sodium sulfate electrolytes. They found that certain particular amount of nickel incorporated in the lattice of the synthetic iron smectite enhanced the wave attributed to direct electron transfer between redox-active iron sites in the smectite lattice and the conductive substrate. Moreover, clay-modified electrode based on Fe and Ni showed better electrochemical performance than those containing either pure iron or pure nickel.

The goal of this work was to examine possible beneficial effect of Ni on Fe containing bentonite based electrode materials in the electrooxidation of phenol. In order to investigate the effect, a series of modified bentonite based materials was synthesized. Clay from seldom investigated deposit Mečji Do in Serbia was characterized and used for further investigations. The clay was modified by pillaring, which was performed using the following combinations of pillaring cations: Al^{3+} and Fe^{3+} or Al^{3+} , Fe^{3+} and Ni^{2+} . The synthesized materials were used to obtain glassy carbon electrode (GCE) coatings.

2. Experimental

2.1. Materials

Bentonite clay from seldom investigated deposit Mečji Do, Serbia was used as a raw material. The fraction of this clay with particle diameters $\leq 74 \mu\text{m}$ and cation exchange capacity (estimated by ammonium acetate method [23]) of 79.5 mmol/100 g of clay was used in further experiments and denoted as raw clay. The raw clay was subjected to the common Na-exchange procedure [22,24]. The excess of Na^+ , Cl^- and exchangeable cations was removed from the sample by dialysis using deionized water with the resistance of 12 M Ω . The dialysis was repeated until the dialysate was free of chloride (confirmed by precipitation test with AgNO_3 and UV-Vis spectrophotometry). Sodium-enriched clay was dried at 110 °C, ground in agate mortar and denoted as Na-MD.

All chemicals used for Na exchange and pillaring were analytic grade. NaCl and NaOH were supplied by Moss Belgrade, $\text{Al}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$ and AgNO_3 by Kemika Zagreb and $\text{Fe}(\text{NO}_3)_3$ by Centrohem Belgrade.

The Dialysis Tubing: SERVAPOR[®], Prod. No. 44148 with a pore diameter of 2.5 nm was used for dialysis.

Nafion[®] solution (5 mass % in lower aliphatic alcohols and water, with water content of 15–20%, Sigma-Aldrich) and carbon black Vulcan XC72 (Cabot Corporation) were used in GCE surface modification.

2.2. Synthesis

The process of pillaring was carried out according to previously established procedure [16,22]. The only step that was altered was the rinsing procedure. Instead of rinsing the suspension was dialysed until free of NO_3^- (tested by UV-Vis spectrophotometry). Pillaring solutions were adjusted to have the molar ratio of $\text{OH}^-/\text{Me}^{n+} = 2.0$ (where $\text{Me}^{n+} = \text{Al}^{3+}$, Fe^{3+} , Ni^{2+}) and metal

cation/clay ratio of 20 mmol Me^{n+}/g . The pillaring solutions contained the following molar ratios of each species: a) 90% Al, 10% Fe, b) 85% Al, 10% Fe, 5% Ni, and c) 90%Al, 5% Fe, 5% Ni. Accordingly, the obtained pillared samples were denoted: AlFe10-MD, AlFe10Ni5-MD and AlFe5Ni5-MD, respectively.

2.3. Characterization

The XRD analyses were performed using a Philips PW 1710 X-ray powder diffractometer with a Cu anode ($\lambda = 0.154178 \text{ nm}$). First the XRD patterns of raw clay were obtained in wide 2θ range (3–70°) and the mineral composition was identified. The XRD technique provided the confirmation of smectite swelling properties. Oriented samples were prepared for this purpose by slow sedimentation from aqueous raw clay suspension onto a quartz plate, followed by drying at room temperature. X-Ray diffractograms of air-dried oriented sample, sample saturated with ethylene glycol vapor for 24 h and oriented sample heated at 450 °C for 1 h were registered in the 2θ range from 3 to 15°. Finally, the XRD analysis in the 2θ interval from 3 to 40°, with 0.02° step was performed for Na-MD and pillared clays (PILCs) in order to confirm successful pillaring.

A Thermo Scientific iCPA 6500 Duo ICP Spectrometer was used for the chemical analysis of all investigated samples. Prior to the analysis the samples were prepared by microwave digestion (ETHOS1, Advanced Microwave Digestion System).

Fourier transformed infrared (FTIR) spectra were obtained in the 4000–400 cm^{-1} wavenumber range with the resolution of 2 cm^{-1} using a Thermo Nicolet 6700 FTIR spectrometer. The spectra were registered in the transmission mode using KBr pressed discs. The KBr discs were prepared by mixing 2 mg of clay samples and 200 mg of KBr. All the clay samples were dried at 120 °C for 6 h and cooled in a desiccator before recording the spectrum.

Nitrogen adsorption-desorption isotherms were determined using a Sorptomatic 1990 Thermo Finnigan at -196 °C. Samples were outgassed at 160 °C during 20 h. The WinADP software was used to analyze the obtained isotherms and textural parameters were calculated according to common methods [25–27]. Specific surface area, S_{BET} [m^2g^{-1}], was calculated according to the Brunauer, Emmett, Teller method. The total pore volume was calculated according to the Gurvich method at $p/p_0 = 0.98$. The volume of mesopores was calculated according to the Barrett, Joyner, Halenda model. Dubinin and Raduskevich method was used for the calculation of micropore volume, while specific surface of micropores was obtained using the Horvath–Kawazoe method.

2.4. Electrocatalytic test

In order to use the investigated clay-based materials as electrode materials, the samples were homogeneously dispersed in original Nafion[®] solution using an ultrasonic bath. The electronic conductivity of the samples was enhanced by adding 10 mass % of carbon black into the initial suspension. Droplets (10 μl) of these suspensions were placed on the surface of a glassy carbon rotating disc electrode (disc area = 0.0314 cm^2). After solvent evaporation, the clay was uniformly distributed on the glassy carbon support in the form of a thin layer [16,28]. In this manner working electrodes were obtained. The electrochemical investigations were performed in a three-electrode glass cell. Reference electrode was Ag/AgCl in 3 M KCl, while a platinum foil served as a counter electrode. Phenol degradation was investigated at room temperature for the starting phenol concentration of 10 mM in 0.1 M H_2SO_4 . The device used for the electrochemical measurements was a 797 VA Computrace Metrohm. The geometric surface area of electrode was used to calculate current density.

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