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E-05-P

ELECTROOXIDATION OF *P*-NITROPHENOL ON TMA-BENTONITE MODIFIED ELECTRODES

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Abrstract

A natural bentonite, modified with tetramethylammonium (TMA), was used as an electrode material in a *p*-nitrophenol (*p*-NP) electrooxidation. The influence of TMA loading into the bentonite layers on the electrochemical properties TMA-bentonite (TMA-B) electrodes toward *p*-NP electrooxidation was examined. Electrode sensitivity toward *p*-NP was performed. The detection limit of $1 \cdot 10^{-8}$ mol dm^{-3} was obtained.

Introduction

Nitrophenols are mainly used in the productions of pesticides, herbicides, explosives, dyes and plasticizers [1] causing severe environmental contamination. Due to the carcinogenic risk for humans, methods for phenol detection are highly relevant in environmental sciences. Electrochemical phenol determination may be accomplished by oxidation on modified solid electrodes [2]. The present study was carried out in order to investigate the electrochemical behavior of *p*-NP on bentonite electrode modified by tetramethylammonium (TMA) cation with different TMA/bentonite ratios.

Experimental

The series of organobentonites with different TMA/bentonite ratios (0.127, 0.317, 0.633 and 1.266 mmol/g) was synthesized. The amount of TMA cations was expressed in multiples of CEC with values 0.2, 0.5, 1.0, and 2.0, hence the samples were denoted as 0.2 TMA-B etc.

Nitrogen adsorption-desorption isotherms were determined using a Sorptomatic 1990 Thermo Finningen at -196 °C. Specific surface area of the samples (S_{BET}), total pore volume, volume of meso- and micropores were calculated according to different methods [3,4,5,6].

For electrochemical investigations in three-electrode all glass cell the reference electrode was Ag/AgCl in 1M KCl, while a platinum foil served as a counter electrode. Para-nitrophenol behavior was investigated in 10 mM *p*-NP + 0.1 M H_2SO_4 at room temperature. The device used for the electrochemical measurements was 757 VA Computrace Metrohm.

Results and Discussion

X-ray diffractograms showed that the incorporation of TMA led to increase of d_{001} basal spacing, from 1.28 nm for Na-B, up to 1.40 nm for 2.0 TMA-B. The values of d$_{001}$ basal spacing obtained for all TMA-B samples corresponded to monolayer arrangements of TMA between smectite layers [7].

Textural properties of sintetized TMA-bentonites were calculated from the adsorption isotherms and presented in Table 1.

Sample	Na-B	0.2 TMA-B	0.5 TMA-B	1.0 TMA-B	2.0 TMA-B
S_{BET} (m^2g^{-1})	84	69	96	146	149
$V_{0.98}$	0.088	0.078	0.098	0.102	0.104
V_{μ}^{D} (cm^3g^{-1})	0.033	0.027	0.037	0.060	0.060
V_{meso} (cm^3g^{-1})	0.084	0.080	0.083	0.068	0.070

Table 1. The textural properties of the samples based on the analysis of nitrogen adsorption isotherms (S_{BET}-specific surface area, $V_{0.98}$-total pore volume according to Gurvitch method for $p/p_0=0.98$, VμD - micropore volume calculated according to Dubinin-Radushkevich method, V_{meso}- volume of mesopores calculated according to Barrett, Joyner, Halenda method)

With increase of TMA loading the values of textural parameters increased with exception of 0.2 TMA-B. In this sample most probably more significant portion of exchangeable hydrated Na^+ remained in the smectite interlayer and lower outgasing temperature was not sufficient to eliminate water from pores. Textural properties for 1.0 TMA-B and 2.0 TMA-B slightly differed. Specific surface area (S_{BET}) increased from 84 m^2g^{-1} for Na-B up to 149 m^2g^{-1} for 2.0 TMA-B. Total pore volume ($V_{0.98}$) followed the same trend. Significant increase in pore volume was found in microporous region (d< 2nm), while mesopore volume slightly decreased. Therefore, the intercalation of TMA into smectite interlayer lead to development of microporosity.

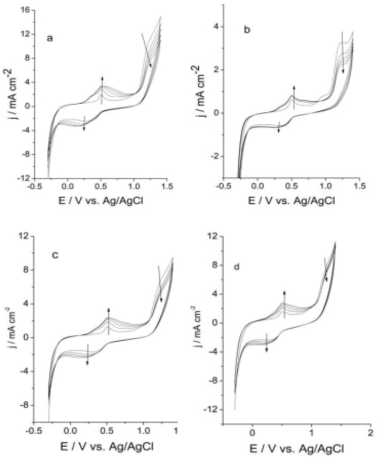

Figure 1. Cyclovoltammograms of organobentonite modified electrodes in 10 mM *p*-NP +0.1 M H_2SO_4 , at 10 mV s^{-1} for a) 0.2 TMA-B, b) 0.5 TMA-B, c) 1.0 TMA-B, d) 2.0 TMA-B. Arrows indicate changes during cycling.

Electrochemical behavior of TMA-B based electrodes in *p*-NP solution is presented in Figure 1. All the investigated electrodes registered a wave at about 1.2 V, which decreased with cycling. The peaks at 0.47 V and 0.54 V, which increased during cycling, were assigned to p-benzoquinone and hydroquinone [8]. The cyclic voltammograms of the investigated electrodes differ only in current density of corresponding peaks. The current density for p-NP oxidation wave at ~1.2 V increased in following order: 0.5 TMA-B< Na-B <1.0 TMA-B ≈ 2.0 TMA-B < 0.2 TMA-B. With the increase of specific surface area of the investigated TMA-bentonites the electrode activity toward p-NP oxidation increased. Therefore, the similar electrochemical behavior of 1.0 TMA-B and 2.0 TMA-B electrodes might be ascribed to similar textural properties. The enhanced current density in 0.2 TMA-B based electrodes might be induced by better accessibility to active sites for p-NP oxidation.

The sensitivity of 0.2 TMA-B electrode toward p-NP was investigated using the technique of square wave voltammetry. Anodic peak currents were linearly related to concentration of p-NP over the range from $2{\cdot}10^{-7}$ to $2{\cdot}10^{-4}$ mol dm^{-3}. The detection limit (DL) was estimated by gradually decreasing the concentracion of *p*-NP and it is considered to be $1{\cdot}10^{-8}$ mol dm^{-3}.

Conclusions

A series of tetramethylammonium bentonites (TMA–B) was prepared from domestic bentonite with different TMA/bentonite ratios. X-ray diffraction technique and nitrogen adsorption/desorption isotherms were used for caracterization of the samples. X-ray diffractograms confirmed the increase of d_{001} basal spacing upon the incorporation of TMA. The intercalation of TMA into smectite interlayer also lead to development of microporosity. Among all investigated samples, 0.2 TMA-B showed the best activity toward p-NP suggesting that the textural properties did not have dominant role in the electro–oxidation process. Using square wave voltammetry technique calibration plot was determined and detection limit of $1{\cdot}10^{-8}$ mol dm $^{-3}$ was calculated.

Acknowledgements

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