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Al,Cu-pillared clays as catalysts in environmental protection

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ABSTRACT

In order to perform water purification from toluene Al,Cu-pillared clay (PILC) was synthesized and tested as catalyst in the oxidation of toluene. Two different catalytic reactions at moderate temperatures were investigated: catalytic wet peroxide oxidation (CWPO) using Al,Cu-PILC and electrooxidation in acidic solution using Al,Cu-PILC based electrode. X-ray diffraction analysis confirmed that pillaring was successful. Chemical analysis confirmed the incorporation of Al^{3+} and Cu^{2+} species in the PILCs. The Cu^{2+} species were proven to be the active ones in both reactions. CWPO in the presence of Cu containing PILC resulted in efficient catalytic degradation of toluene. Steady state voltammograms for Al,Cu-PILC based electrode in acidic toluene solution showed broad anodic peak at about 1.7 V vs. Ag/AgCl ascribed to the electrooxidation of toluene. Another peak ascribed to toluene oxidation products occurred at 0.5 V. Anodic peak currents corresponding to these peaks linearly increased with the initial toluene concentration. Both CWPO and electrooxidation confirmed the possibility of use of the synthesized Al,Cu-PILC in the toluene oxidation and might be employed in the environmental protection.

1. Introduction

Toluene is a pollutant classified into the group of extremely dangerous compounds to the environment. Toluene is a common contaminant in waters in the vicinity of oil refineries. It is suggested by Environmental Protection Agency that the amount of toluene in drinking water should not exceed 1 ppm [1]. Therefore, preventing toluene from getting to water streams is an important task. The techniques usually adopted to achieve water purification from toluene are largely based on the use of phase separation methods and/or adsorption on active suspended materials, as well as biodegradation [2]. There are several drawbacks of these methods, including the inability of quantitative removal of pollutants or the fact that they are time consuming and effective only at low concentration levels [2,3]. Oxidation of toluene into nontoxic carbon dioxide and water might be the optimal solution.

Catalytic wet peroxide oxidation (CWPO) appears to be a promising method for the removal of BTEX (which stands for benzene, toluene, ethylbenzene, o-, m- and p-xylene) from water under mild temperature and pressure conditions. CWPO is based on the presence of hydrogen peroxide as a source of highly reactive radicals generated on transition metal cation sites within employed catalysts [2,4]. Possible leaching of active metal cations can be overcome if pillared interlayered clay (PILC) is used as a catalyst. Metal oxide PILCs represent a new class of materials that have found a wide range of potential applications in catalytic, adsorption and separation processes [5]. The CWPO of phenol using Al,Cu-PILCs at room temperature and atmospheric pressure was shown to be successful heterogeneous catalytic reaction [6–8]. According to literature this reaction has not been tested thoroughly in the case of degradation of less water soluble BTEX compounds, although the CWPO performance of Cu-doped alumina-pillared montmorillonite has been tested for toluene [9].

Catalysts in the form of electrode surfaces provide additional dimension of the electrode potential which can be used to control the catalyst reactivity and, in some cases, selectivity. Electrochemical oxidation of toluene has been performed on platinum and glassy carbon surfaces, by using different electrolytes [10–12]. Due to the electrolyte decomposition, toluene did not react when mixture of alcohol and sulfuric acid was used as electrolytic medium. However, it produces carbon dioxide and water when the reaction is carried out in sulfuric acid [13]. Many experimental results regarding electrooxidation of toluene on different surfaces in organic media have been published [14], while the same reaction in aqueous solution has been seldom reported [15,16]. Treimer et al. have investigated Fe(III)-β-PbO_2, Bi(V)-β-PbO_2 and β-PbO_2 electrodes for electrooxidation of toluene in acidic media [17]. Adsorption interaction of aromatic molecules at the Fe(III) sites is stronger than at the Bi(V) and Pb(IV) sites which results in faster reaction kinetics on the Fe(III)-β-PbO_2 electrode. D'Elia et al. have tested vanadium pentoxide, titanium dioxide and cerium oxide as anodes for the electrooxidation of toluene. TiO_2 showed some activity for the electrooxidation of toluene while CeO_2 was totally inactive in

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this reaction. V_2O_5 was not active in this reaction under the experimental conditions [15,16].

In this work Al,Cu-PILC was synthesized and tested as catalyst in the oxidation of toluene in order for water purification to be performed. The obtained PILC was employed as catalyst in the CWPO, and as electrode material in the electrocatalytic toluene oxidation in acidic solution. Al-PILC was synthesized and used for comparison purposes in order to prove catalytic activity of Cu species.

2. Experimental

2.1. Materials

Starting material was domestic clay from Bogovina which had been previously characterized [18,19]. The fraction of this clay with particle diameters $\leq 2\ \mu m$ and cation exchange capacity (estimated by ammonium acetate method) of 765 mmol kg^{-1} was used in further experiments and denoted as raw clay. The raw clay was submitted to the Na-exchange procedure by repeated stirring with 1 M NaCl followed by filtering. Thus obtained filtration cake was rinsed with distilled water in order to remove NaCl and other exchangeable cations excess from the sample. Rinsing was repeated until the filtrate was Cl^- free (confirmed by $AgNO_3$ precipitation test). The Na-exchanged clay was dried at 110 °C.

2.2. Synthesis

The process of pillaring was carried out according to a common procedure [20]. Pillaring solutions were adjusted to have the atomic ratio $OH^-/Me^{n+} = 2.0$ (where $Me^{n+} = Al^{3+}$ or Cu^{2+}) and Me^{n+}/clay ratio of 20 mmol/g. In the case of Al,Cu-PILC $Cu^{2+}/(Al^{3+} + Cu^{2+})$ atomic ratio was 0.1. The procedure included continuous stirring at 60 °C for 3 h followed by stirring at room temperature overnight. In the next step the pillaring solutions were slowly added into Na-exchanged bentonite dispersion in distilled water. After being rigorously stirred at 80 °C for 3 h the final suspension was stirred at room temperature overnight. The suspension was filtered through a Büchner funnel while hot. The obtained cake was rinsed with hot distilled water until the filtrate was NO_3^- free (tested by UV–vis spectrophotometry), and finally air-dried overnight at 110 °C. It was then calcined at 300 °C for 2 h. The materials made from solutions containing only Al^{3+} cations, or those with Al^{3+} and Cu^{2+} cations were referred to as Al-PILC and Al,Cu-PILC, respectively.

2.3. Characterization

The X-ray diffraction (XRD) patterns for powders of raw, Na-exchanged and pillared clays were obtained using a Philips PW 1710 X-ray powder diffractometer with a Cu anode ($\lambda = 0.154178$ nm).

A Spectro Spectroflame M—inductively coupled plasma optical emission spectrometer (ICP-OES) and atomic absorption spectrometer (AAS), were used for the chemical analysis of the raw and pillared clays. ICP was also used to determine potential leaching of pillaring cations from the catalysts.

Nitrogen adsorption–desorption isotherms were determined on Sorptomatic 1990 Thermo Finningen at −196 °C. Samples were outgassed at 160 °C, during 20 h. WinADP software was used to analyze obtained isotherms. Specific surface area of the samples, S_{BET}, was calculated according to Brunauer, Emmett, Teller method [21,22].

2.4. Catalytic test

The reaction of toluene oxidation was carried out in the manner analogue to the procedure previously used for phenol degradation [23] and described below. A 500 cm^3 thermostated Pyrex reactor equipped with a stirrer was used. The reaction temperature was regulated with circulation of thermal fluid at 310 K using Julabo MC 4 heating circulator. The reactor contained 150 cm^3 of aqueous toluene solution (2×10^{-3} mol dm^{-3}). The quantity of hydrogen peroxide that corresponds to 20 mol of H_2O_2 per mole of toluene was introduced to it. In this manner stoichiometric quantity needed for total transformation of toluene into CO_2, being 18 mol H_2O_2 per mole of toluene, was slightly exceeded. The moment when solid catalyst (0.75 g) was introduced to the vessel was taken as zero time of the reaction. The obtained suspension was continuously stirred at atmospheric pressure. Aliquots of 3 cm^3 were taken at predetermined periods of time. After filtration (Cole-Palmer nylon syringe filters with PP housing; pore size = 0.20 μm) filtrates were analyzed by gas chromatography. Shimadzu GC-9A gas chromatograph equipped with Supelco SPB-1, 30 m × 0.25 mm capillary column was used for this purpose.

2.5. Electrocatalytic test

In order to use the PILCs as electrode materials, the PILC samples were dispersed in 5 wt.% Nafion solution in a mixture of isopropyl alcohol and water. Homogenous dispersion was obtained using ultrasonic bath. The electronic conductivity of the samples was enhanced by adding 10 wt.% of carbon black Vulcan XC72 (Cabot Corp.) into the initial suspension. Droplets of these suspensions were placed onto the surface of a glassy carbon rotating disc electrode. After the solvent removal by evaporation at 90 °C, the PILC particles were uniformly distributed on the glassy carbon support in a form of thin layer. Analogous way of preparation of this type of powdered materials for electrochemical investigations was already published elsewhere, for instance, in the investigation of galvanostatic charging and discharging of the Li-intercalate powders [24].

For the electrochemical investigations a three-electrode glass cell was used. Glassy carbon disc, covered with a layer of homogeneous mixture containing carbon black with either Al or Al,Cu-PILC, was used as a working electrode. The reference electrode was Ag/AgCl in 1 M KCl, while a platinum foil served as a counter electrode. Toluene degradation was investigated for starting concentrations of toluene ranging from 0 to 5 mmol dm^{-3} in 0.1 M H_2SO_4. The toluene/electrolyte solutions were purged by nitrogen stream. Device used for the electrochemical measurements was 757 VA Computrace Metrohm.

3. Results and discussion

3.1. XRD

According to X-ray diffraction patterns (Fig. 1) the following phases were identified in the investigated samples: smectite, quartz, feldspar and calcite [25].

Small hump between 19° and 30° 2θ attributed to X-ray amorphous matter was also observed. The (0 0 1) smectite peak around $2\theta = 6°$ shifts during different stages of the pillaring process. The process of Na-exchange lowered corresponding basal spacing, d_{001}, from 1.53 nm ($2\theta = 5.78°$) for the starting clay, to 1.28 nm ($2\theta = 6.92°$). The Na-exchanged clay retained swelling properties. The pillaring process increased and fixed the basal spacing of the clay. This resulted in the shift of the (0 0 1) smectite peak to $2\theta = 5.52°$ ($d_{001} = 1.60$ nm) for Al-PILC, $2\theta = 5.58°$ ($d_{001} = 1.58$ nm) for Al,Cu-PILC.

3.2. Chemical composition

Chemical composition of the raw, Na-exchanged and pillared clays is presented in Table 1.

The observed decrease of CaO content is caused by the Na-exchange process—the preceding step to the synthesis of PILCs. In

Table 1
Chemical composition.

Sample	Oxide content [mass%]								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CuO	CaO	MgO	Na_2O	K_2O
Raw clay	55.0	24.6	8.6	1.2	<0.1	2.6	3.0	2.5	2.5
Na-exchanged	37.5	26.8	8.9	1.2	<0.1	0.4	2.5	20.0	2.7
Al-PILC	40.1	43.8	9.1	1.0	<0.1	<0.1	2.8	0.7	2.5
Al,Cu-PILC	39.7	43.4	8.6	1.1	1.6	<0.1	1.8	1.4	2.4

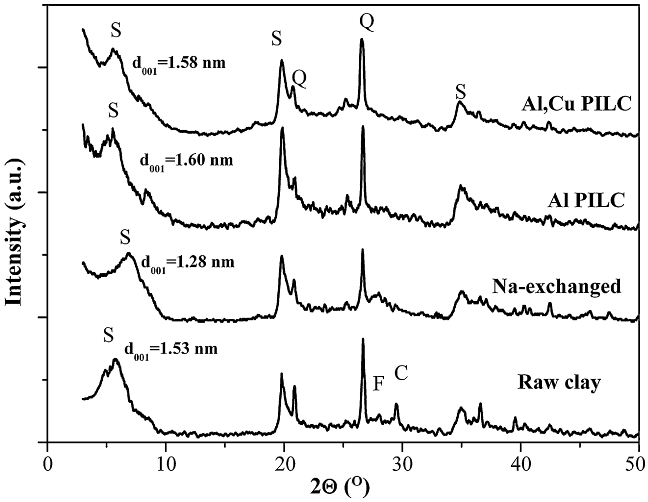

Fig. 1. X-ray diffractograms (S, smectite; Q, quartz; F, feldspar; C, calcite).

further pillaring steps Na^+ undergoes cation exchange by polioxocationic pillar precursors. The remaining sodium in the pillared samples might be ascribed to accompanying species such as feldspar. The increase of the Cu^{2+} content after pillaring is lower than stoichiometric but in correspondence with previously published data [23].

3.3. CWPO test

After the synthesis and characterization the obtained Al,Cu-PILC was tested in the CWPO of toluene under above defined conditions. For the purpose of comparison a control reaction was conducted under the same conditions using Al-PILC. This enabled the determination of the influence of the presence of Cu species in the investigated process. Toluene removal using Al,Cu-PILC and Al-PILC in the presence of H_2O_2 is presented in Fig. 2.

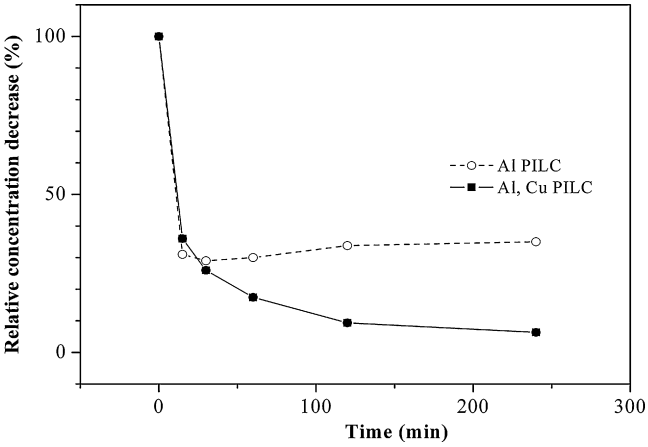

Fig. 2. Toluene concentration decrease vs. time.

It can be observed that toluene degradation curves obtained for Al and Al,Cu-PILC follow different trends, which leads to conclusion that different processes governed the behavior of the two reaction systems. The application of Al-PILC apparently lead to adsorption followed by slow desorption. In the case of Al,Cu-PILC, continuous decrease of toluene concentration suggests that it underwent catalytic degradation. This was confirmed by washing of the used catalyst with water when only insignificant amount of toluene was released from it. The efficiency of CWPO using Al,Cu-PILC can be illustrated by the toluene removal after 4 h of the reaction, when only 6.3% of the introduced toluene remained (corresponding to 11 ppm of toluene).

In general, pillaring is performed in order to improve the catalytic efficiency of the process. The idea is to combine a porous support and active sites for the adsorption of organic compounds and for the activation of H_2O_2, thus enabling complete oxidation [6]. PILC's are expected to have both increased specific surface area and greater number of active sites. In our previously published work S_{BET} value for Na-exchanged clay was determined to be 99 $m^2\,g^{-1}$ [26]. Comparing to this result the pillaring process lead to expected increase of S_{BET}. Here obtained specific surface area for Al-PILC was 179 $m^2\,g^{-1}$. For Al,Cu-PILC S_{BET} was determined to be 135 $m^2\,g^{-1}$, which is in agreement with data published by other authors [8]. It can be observed that, although Al-PILC has greater specific surface area than Al,Cu-PILC, it is less efficient in the toluene removal. Therefore, the efficiency of toluene removal by Al,Cu-PILC should be ascribed to the presence of new species, namely Cu^{2+}, that are catalytically active. Such behavior is expected since Cu^{2+} is a strong one-electron oxidant from the first transition metal row which can initiate homolytic degradation of H_2O_2. On the other hand Al^{3+} does not fulfill criteria neither for homolytic nor for heterolytic peroxide degradation [27].

Al-PILC was also shown to be reasonably effective in the removal of toluene. However, adsorption as the means of pollutant removal requires adsorbent recovery. Besides, the adsorbed molecules remain intact within solid phase being a possible threat to the environment. These facts make this method less desirable for water purification. The CWPO reaction, on the other hand, showed higher degree of toluene removal and is a method that provides permanent elimination of polluting molecules.

In order to check the chemical stability of the synthesized materials in the investigated system, the presence of inorganic cations in the reaction mixture was analyzed. The obtained ICP-OES spectra confirmed that the Al^{3+} and Cu^{2+} ion concentrations in the filtrates taken after 24 h of the reaction did not exceed 0.01 ppm. These results show that leaching is negligible confirming that the pillaring cations are well incorporated in the pillar structure. Consequently, the reaction of catalytic degradation of toluene can be regarded as heterogeneous.

3.4. Electrocatalytic test

Blank experiment was carried out using a composite electrode containing clay pillared only with Al. Cyclic voltammogram (CV) in 0.1 M H_2SO_4 was recorded at the polarization rate of 10 $mV\,s^{-1}$ in the potential range of −1 to +2 V. The electrode was then transferred

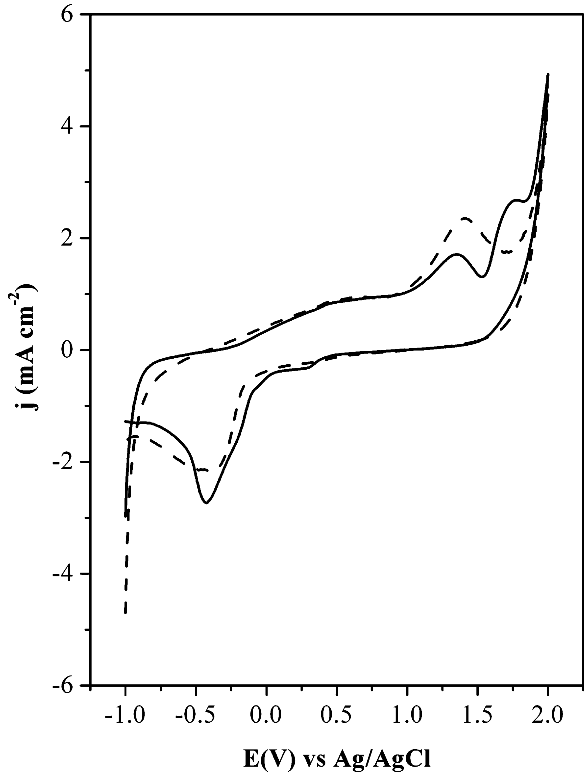

Fig. 3. CVs of Al-PILC electrode: 0.1 M H_2SO_4 (dotted line) and 3 mM toluene +0.1 M H_2SO_4 (solid line) at polarization rate of 10 mV s^{-1}.

into a toluene/H_2SO_4 containing solution. The first cycle registered in the presence of toluene is presented in Fig. 3 together with steady state CV obtained for toluene free solution.

Hydrogen and oxygen evolution reactions are visible at the limits of this range. At the potential of +1.4 V oxides formation occurs. Cathodic peak at −0.5 V may be attributed to oxygen reduction reaction, involving oxygen that evolved at high anodic potential and remained within clay pores. This conclusion is supported by the fact that this peak significantly decreases if the rotation of the electrode is applied. Such behavior is already noticed at metal-impregnated zeolite electrodes [28].

When the electrode was transferred to toluene containing solution oxide formation peak was reduced, but new anodic peak at higher potential appeared (+1.7 V). Cycling within the investigated potential range lead to complete electrode deactivation after only ten cycles. In this case toluene oxidation products were not formed.

CVs recorded using Al,Cu-PILC electrode in 0.1 M H_2SO_4 in the presence and without toluene are presented in Fig. 4a. The effect of successive cycling of the Al,Cu-PILC electrode in toluene containing solution is shown in Fig. 4b.

Voltammogram of the Al,Cu-PILC electrode in acidic solution shows anodic peak at potential of 70 mV vs. Ag/AgCl and its corresponding cathodic peak at potential of −40 mV. These peaks can be observed in the embedded diagram within Fig. 4a, which represents enlarged potential region around 0 V. This diagram is given in order to show the processes occurring at these potentials, which would otherwise be invisible due to significantly lower current densities. The pair of peaks in the embedded graph probably corresponds to Cu^{2+}/Cu^{+} oxidation/reduction processes [29].

The Al,Cu-PILC electrode exhibited approximately five times higher current densities then the Al-PILC electrode. In the voltammograms obtained for both investigated electrodes can be observed hydrogen evolution, oxygen evolution, oxide formation and toluene oxidation processes. However, in the case of Cu containing electrode the oxide formation and toluene oxidation waves overlap. Toluene oxidation wave appears at potential of +1.7 V. The presence of toluene reduces the current of oxygen evolution at +2.0 V and consequently the current of oxygen reduction at −0.5 V.

Rapid electrode failure occurs in five cycles (Fig. 4b), but at potential around 0.5 V new pair of oxidation/reduction peaks appears corresponding to some species formed during toluene oxidation in the first cycle. Electrode failure is partially a consequence of forming polymeric products of toluene oxidation, but the main reason for this effect is the electrode instability at such high potentials. This conclusion is supported by the fact that prolonged cycling in toluene free solution also lead to electrode deactivation, although less pronounced.

In further investigation the influence of toluene concentration on the intensity of anodic peak at 1.7 V was investigated. The obtained results for the polarization rate of 10 mV s^{-1} are given in Fig. 5a and b.

Due to previously observed electrode deactivation a freshly prepared electrode was used for each experiment. The first CVs and enlarged anodic sweeps for each toluene concentration are presented in Fig. 5a. Currents obtained at 1.7 V for toluene containing solution were diminished for the current value obtained at the same potential for toluene free solution. In this manner the current contributing to toluene oxidation was evaluated. These values were used to establish the current dependence on the toluene concentration and are given in Fig. 5b. The obtained linear dependence has the coefficient of correlation (R) equal to 0.9916. It can be presented as:

$$j = 8.972 + 1.391 \cdot C_{\text{toluene}} \tag{1}$$

where j is reduced current density at 1.7 V, expressed in mA cm^{-2} and C_{toluene} concentration in mmol dm^{-3}.

In Fig. 4b beside toluene oxidation peak another peak at 0.5 V was observed. In order to investigate the nature of this process, cycling in shorter potential range where electrode activation remains stable was performed. Since the electrode deactivation does not occur up to anodic potential of 1.5 V and some toluene oxidation products are formed in successive cycles, the investigation was performed within this range.

It was also found that the measured current densities were independent on the electrode rotation rate. This behavior indicates that the electrode reaction is not controlled by the diffusion of the reactant outside the electrode film [30].

In this work toluene oxidation reaction was investigated at different scan rates in the range of 10–1000 mV s^{-1} (Fig. 6a). The dependences of the logarithm of current density (j) and peak potential at 0.5 V (E_p) on the logarithm of scan rate (v) are presented in Fig. 6b and c, respectively.

From the data presented in Fig. 6b the following linear dependence (R = 0.9978) was derived:

$$\log j = -0.574 + 0.750 \cdot \log v \tag{2}$$

The slope of this linear regression is close to 0.7 indicating combined adsorption/diffusion controlled process [31].

The dependence of the peak potential on the scan rate also provides kinetic information. A peak potential that is independent on the scan rate indicates reversible charge-transport process. On the other hand, irreversible charge-transfer process causes the peak potential to vary with the scan rate [30]. A shift in the potential of the peak at 0.5 V is observed with increase of the scan rate (Fig. 6c). This indicates irreversible charge-transfer process. At higher scan rates peak potentials linearly depend on the logarithm of the scan rate. The corresponding equation (R = 0.9950) is:

$$E_p = -0.419 + 0.406 \cdot \log v \tag{3}$$

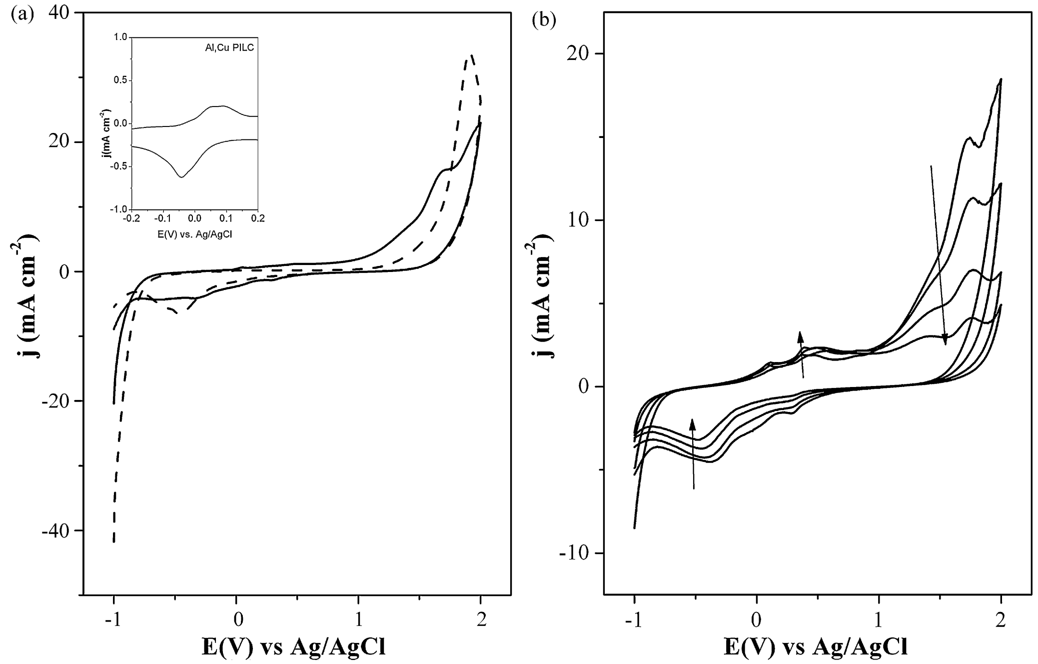

Fig. 4. (a) CVs of Al,Cu-PILC electrode in 0.1 M H_2SO_4 (dotted line) and the first cycle (solid line) in 3 mM toluene +0.1 M H_2SO_4. (b) Successive cycling of Al,Cu-PILC electrode in 3 mM toluene +0.1 M H_2SO_4, at polarization rate of 10 mV s^{-1}.

The peak at 0.5 V related to toluene oxidation products was further investigated in order to establish the influence of the concentration of toluene on the formation of its oxidation products. Porous electrodes like the PILC based ones show high values of capacitive currents due to high specific surface area. As mentioned above, in here presented investigation the specific surface area of Al,Cu-PILC was 135 m^2 g^{-1} and consequently it exhibits high capacitive currents. On the other hand the capacitive currents are directly proportional to the scan rate. Therefore, low scan rates are usually applied in the investigation of porous electrodes. However, low intensity currents for toluene oxidation products were obtained and therefore the analysis had to be performed at higher polarization rates. The CVs were registered at the polarization rate of 50 mV s^{-1}, in the potential range from −1.0 to +1.5 V, and toluene concentrations of 1–5 mmol dm^{-3} (Fig. 7a).

The values of current densities were acquired from the 0.5 V peak by subtracting the corresponding current densities for the solution without toluene. They are presented in Fig. 7b as the dependence on the toluene concentration. A linear dependence (R = 0.9960) was obtained in the following form:

$$j = 0.307 + 1.195 \cdot C_{\text{toluene}} \tag{4}$$

Comparing the CVs for the Al-PILC and Al,Cu-PILC based electrodes it can be concluded that the process of toluene oxidation follows different reaction paths. Toluene oxidation products can not be observed in the Al-PILC related voltammograms, while in the case of Al,Cu-PILC they are formed. The fact that the only structural difference is the presence of Cu^{2+} ions in Al,Cu-PILC indicates that the occurrence of new Lewis sites is responsible for the expressed electrocatalytic activity of the material [32]. In addition, despite

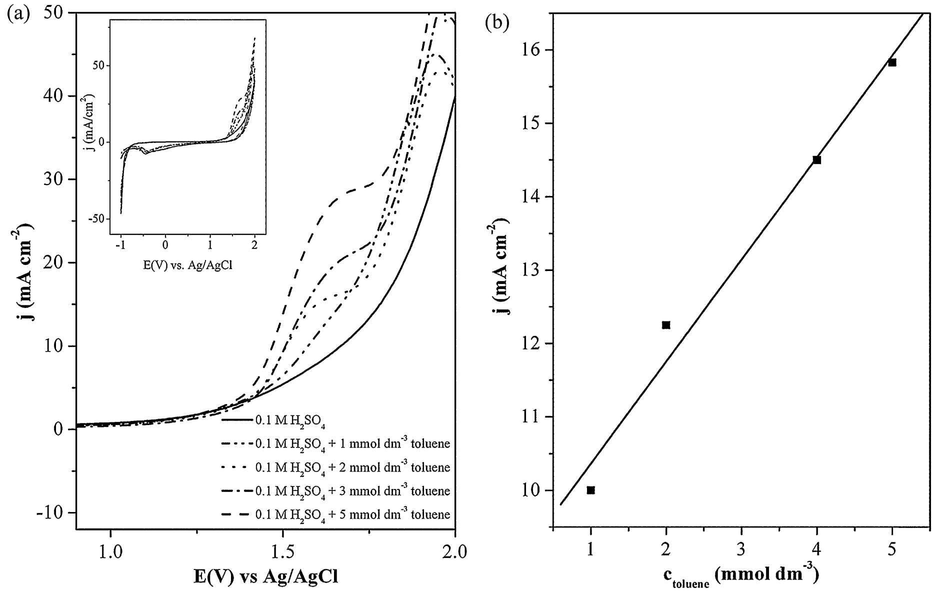

Fig. 5. (a) CVs and enlarged anodic sweeps for Al,Cu-PILC for different C_{toluene}. (b) Anodic peak current at potential 1.7 V vs. C_{toluene}.

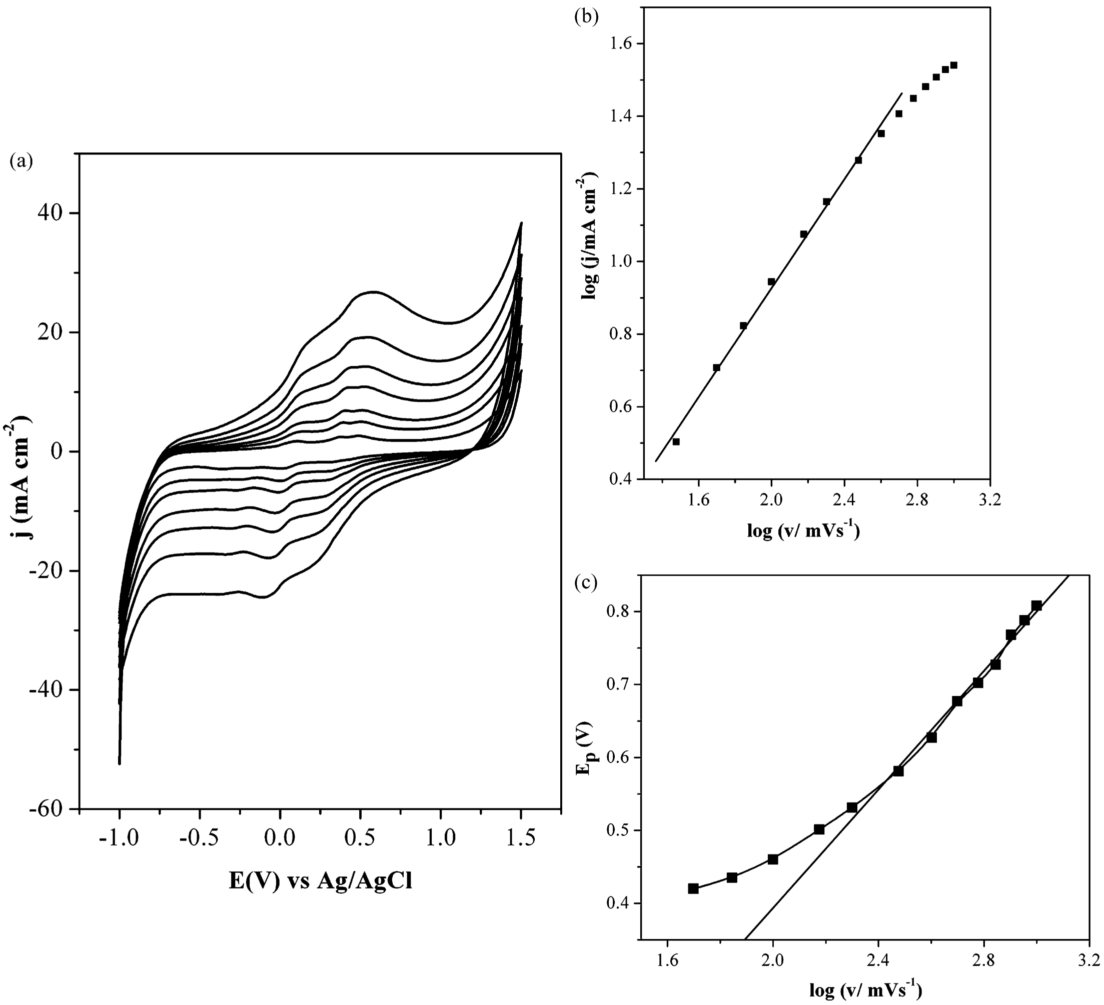

Fig. 6. (a) CVs of Al,Cu-PILC electrode in 3 mM toluene +0.1 M H_2SO_4 at different scan rates. The presented scan rates from inside to outside are 10–150 mV s^{-1}. The 0.5 V peak dependence on scan rate (v): (b) log$j$ vs. log$v$ and (c) variation of peak potential vs. log$v$.

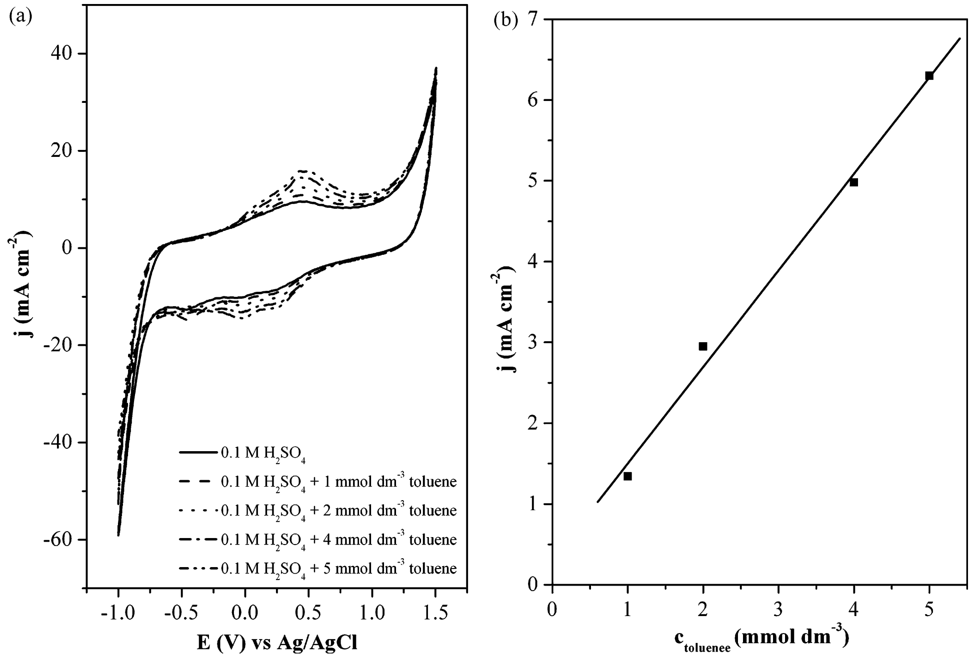

Fig. 7. (a) CVs for Al,Cu-PILC for different C_{toluene} and (b) anodic peak current at potential of 0.5 V vs. C_{toluene}.

smaller specific surface area of Al,Cu-PILC comparing to that of Al-PILC the toluene oxidation current densities for the latter are approx. five times smaller. This supports previous claim that the incorporation of Cu^{2+} ions is a driving force for a new type of electrocatalytic reaction.

Based on the results presented in Figs. 4–7, described electrochemical processes on Al,Cu-PILC based electrodes can be applied in the monitoring, detection and quantification of both toluene and toluene oxidation products.

4. Conclusion

Al and Al,Cu-pillared clays were synthesized from bentonite clay. XRD analysis confirmed successfulness of the pillaring procedure. Chemical analysis confirmed the incorporation of Al^{3+} and catalytically active Cu^{2+} species in the PILCs. Leaching of these species was below 0.01 ppm. Al-PILC showed adsorption while Al,Cu-PILC showed efficient catalytic wet peroxide degradation of toluene. Voltammograms for the Al,Cu-PILC based electrode in acidic toluene containing solutions showed broad anodic peak at about 1.7 V vs. Ag/AgCl ascribed to the electrooxidation of toluene and anodic peak at 0.5 V ascribed to toluene oxidation products. It was concluded that in both CWPO and electrocatalytic oxidation Cu^{2+} has decisive role in the toluene degradation. Both investigated methods confirmed the possibility of application of Al,Cu-PILCs in the oxidative degradation of toluene and can be employed in the environmental protection. The CWPO might be considered as a method of water purification, or as a preceding step to biodegradation in a two-stage purification method. On the other hand electrocatalysis should be considered as a method for monitoring, detection and quantification of toluene and its oxidation products.

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