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Mixed pillared bentonite for electrooxidation of phenol

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ABSTRACT

Bentonite was pillared with Al, Al-Cu, Al-Fe or Al-Co poly(hydroxo metal) cations for electrochemical oxidation of phenol in acidic solution. Multisweep cyclic voltammetry was applied to analyze the behavior of the bentonite modified glassy carbon electrode. The influence of pillaring on the electrocatalytic properties was investigated. Reactivation of the electrodes after prolonged phenol oxidation was performed by cathodisation at -2 V.

1. Introduction

Heavy metal ions and toxic organic compounds are common pollutants in wastewaters from many industrial sectors. Among organic pollutants phenols are considered to be extremely dangerous since they are harmful to organisms even at low concentrations. A large number of advanced oxidation processes was applied to degrade and destroy aromatic organics including photochemical reactions, Fenton oxidation, ozonation, and supercritical water oxidation (Brillas et al., 1998). Electrochemistry is another alternative way (Comninellis, 1994; Chen, 2004; Maluleke and Linkov, 2003). Previously investigated electrodes - Pt (Boscoletto et al., 1994), thin metal oxide layers like SnO_2 (Li et al., 2005; Feng and Li (2003), PbO_2, RuO_2 and IrO_2 deposited on a base metal (Chopra et al., 1983) showed certain drawbacks, such as electrode fouling or leaching of Pb from the anode. Complete phenol oxidation to CO_2 at low phenol concentrations was achieved with a boron-doped diamond electrode (Iniesta et al., 2001). Investigation of phenol adsorption by different types of activated bentonites showed that the pillaring process considerably increased phenol adsorption (Al-Asheh et al., 2003). Therefore, the use of pillared clays as electrode materials might be of great interest. In this study, bentonite from the „Bogovina" deposit was pillared with Al, Al-Cu, Al-Fe and Al-Co poly (hydroxo cations). These materials were used as electrode materials for the phenol electooxidation in acidic solution.

2. Experimental

Starting material was a domestic bentonite from Bogovina (Vuković et al., 2006). The fraction of particles < 2 μm ("raw bentonite") was used. The raw bentonite (cation exchange capacity determined by ammonium acetate method was 76.5 meq/100 g) was submitted to Na-exchange by repeated stirring with 1 M NaCl followed by filtering and washing until the filtrate was Cl^- free (confirmed by $AgNO_3$ precipitation test). The obtained Na-enriched bentonite was dried at 110 °C and denoted Na-B. The process of pillaring was carried out according to the common procedure (Kaloidas et al., 1995). Pillaring solutions were adjusted to have the molar ratio $M^{n+}/(Al^{3+}+M^{n+})$ 0.1 (where $M^{n+}=Cu^{2+}$, Co^{2+} or Fe^{3+}), $OH^-/(Al^{3+}+M^{n+})=2.0$ and the metal ion/Na-B ratio of 20 mmol M^{n+}/g. Another sample was synthesized using only Al^{3+} as pillaring species denoted as Al-PILC and used as reference. The procedure included continuous stirring at 60 °C for 3 h and at room temperature overnight. The appropriate amount of the pillaring solutions was slowly added to the Na-B dispersion in distilled water. After stirring at 80 °C for 3 h the dispersion was stirred at room temperature overnight, filtered, washed with hot distilled water until the filtrate was NO_3 free (tested by UV-Vis spectrophotometry), and finally air-dried overnight at 110 °C. The products were calcined at 300 °C for 2 h and referred to as Al,Cu-PILC, Al,Co-PILC and Al,Fe-PILC. The chemicals used for the Na^+ exchange and pillaring were NaCl, NaOH and Al(III), Fe(III), Cu (II) and Co(II) nitrate.

X-ray diffraction powder patterns 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, together with atomic absorption spectrometer, was used for the chemical analysis.

Nitrogen adsorption-desorption isotherms were determined using a Sorptomatic 1990 Thermo Finningen at -196 °C. The samples were outgassed at 160 °C, during 20 h. Specific surface area of the samples,

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S_{BET}, total pore volume and volume of micropores were calculated according to standard methods (Gregg and Sing, 1967; Rouquerol et al., 1999; Dubinin, 1975). Pore size distribution for mesopores was calculated according to Barrett, Joyner, Halenda method (Webb and Orr, 1997).

In order to use the PILCs as electrode materials, the samples were homogeneously dispersed in 5 mass % Nafion solution in mixture of isopropyl alcohol and water using ultrasonic bath. The electronic conductivity of the samples was enhanced by adding 10 mass % of carbon black Vulcan XC72 (Cabot Corp.) into the initial suspension. Droplets (10 μl) of these suspensions were placed on the surface of a glassy carbon rotating disc electrode. After the solvent removal by evaporation at 90 °C, the clay mineral particles (Bergaya and Lagaly, 2006) were uniformly distributed on the glassy carbon support in a form of thin layer (Mojović et al., 2009). For the electrochemical investigations in a three-electrode glass cell, as a working electrode was used a glassy carbon rotating disc electrode covered with a layer of homogeneous mixture containing carbon black combined with each of the following clay based samples separately. The reference electrode was Ag/AgCl in 1 M KCl, while a platinum foil served as a counter electrode. Phenol degradation was investigated for starting concentration of phenol of 10 mM in 0.1 M H_2SO_4 at room temperature. The device used for the electrochemical measurements was 757 VA Computrace Metrohm.

3. Results and discussion

3.1. Sample characterization

According to X-ray diffraction patterns (Fig. 1) the following phases were identified: smectite, quartz, feldspar and a small amount of amorphous phase (McClune, 1990).

The basal spacings d_{001} were: 1.28 nm for Na-B; 1.60 nm for Al-PILC; 1.64 nm for Al,Fe-PILC, 1.58 nm for Al,Cu-PILC and 1.72 nm for Al,Co-PILC.

During pillaring the ions were exchanged by poly(hydroxo metal) cations (Table 1). The sodium ions remaining in the pillared samples might be ascribed to associated minerals like feldspar. The incorporation of Al^{3+} species was very pronounced in all PILCs. Also, a significant increase of the Fe_2O_3 content was observed in Al,Fe-PILC. The Cu^{2+} and particularly Co^{2+} contents after pillaring were much lower, which in the case of Cu^{2+} corresponded to previously published data (Barrault et al., 2000).

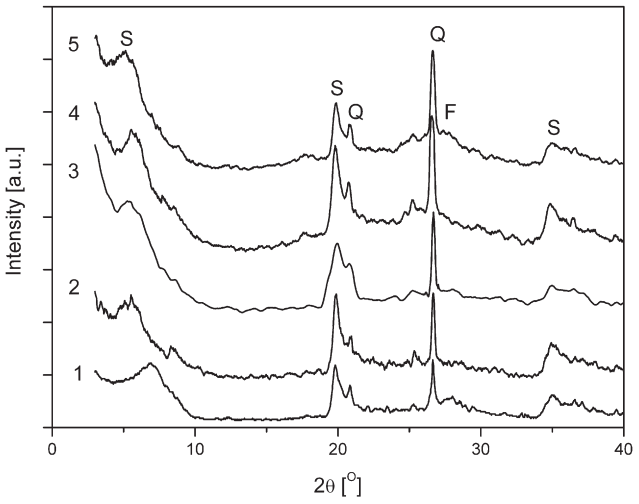

Fig. 1. X-ray diffraction patterns of:1- Na-B; 2- Al-PILC; 3- Al,Fe-PILC; 4- Al,Cu-PILC; 5- Al, Co-PILC (S = smectite, Q = quartz, F = feldspar).

Table 1
Chemical composition of investigated samples.

Sample	Oxide content, [mass %]									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	CuO	CoO
Na-B	37.5	26.8	8.9	1.2	0.4	2.5	20.0	2.7	<0.1	<0.1
Al-PILC	40.1	43.8	9.1	1.0	<0.1	2.8	0.7	2.5	<0.1	<0.1
Al,Co-PILC	40.8	43.5	8.0	1.3	<0.1	2.0	1.9	2.3	<0.1	0.2
Al,Cu-PILC	39.7	43.4	8.6	1.1	<0.1	1.8	1.3	2.4	1.6	<0.1
Al,Fe-PILC	20.1	43.1	29.7	1.3	<0.1	2.0	1.6	2.2	<0.1	<0.1

The pillared samples showed the expected increase of the specific surface area, total pore volume and volume of micropores (Table 2). The S_{BET} increased in the following order: Al-PILC, Al,Fe-PILC, Al,Cu-PILC, Al,Co-PILC. The D_{max} and D_{med} values indicated grater mesopore diameters.

3.2. Electrochemical behavior

3.2.1. Behavior in 0.1 M H_2SO_4

Steady state voltammograms of pillared bentonite electrodes in the support electrolyte were obtained after 20-30 cycles and recorded at scan rate of 10 mV/s (Fig. 2).

All bentonite based electrodes showed hydrogen evolution at a potential of -0.3 V and oxygen evolution at potentials >1.1 V. The vertical shift between the curves corresponding to opposite polarization directions was very pronounced. Such behavior is characteristic for electrodes with high surface area that gives rise to interfacial capacitance (Mentus et al., 2004). Therefore, low polarization rates were used to minimize the capacitance current. The Al,Co-PILC electrode showed only a capacitive current, while in Na-B, Al-PILC, Al,Cu-PILC and Al,Fe-PILC voltammograms certain waves appeared. These four voltammograms had pairs of peaks at around 0.5 V corresponding to Fe^{3+}/Fe^{2+} oxidation/reduction process (Amonette, 2002). Peak currents showed a linear dependence on the square root of the polarization rate while the peak potential shifted toward more positive values with increased polarization rate. Althought this behavior is typical for diffusion controlled processes, it can be assumed that these peaks corresponded to structural iron ions. According to Amonette (2002) the reduction potential is lower for structural Fe^{3+} than for solution Fe^{3+}. Having in mind the high content of iron in Na-B (Table 1) it is expected that this oxidation/reduction process occurred in all synthesized pillared bentonites. This peak is not distinguished in the presented cyclic voltammogram (CV) for the Al,Co-PILC electrode, probably due to the high capacitive current.

The voltammogram obtained for the Al,Cu-PILC electrode showed an anodic peak at a potential of 70 mV vs. Ag/AgCl and its corresponding cathodic peak at potential of – 40 mV. The height of this pair of peaks was almost independent on the rotation speed. Since the reduction of peak heights with rotation speed would indicate formation of some soluble species (Benedetti et al., 1995), it can be concluded that no copper soluble species were released. Peak currents showed deviation from linear dependence on the square root of

Table 2
Selected textural properties of investigated samples.

Sample	S_{BET} [m^2/g]	$V_{0.98}$ [cm^3/g]	V_{mic} [cm^3/g]	D_{max} [nm]	D_{med} [nm]
Na-B	99	0.094	0.041	3.9	3.9
Al-PILC	179	0.160	0.088	3.9	4.8
Al,Co-PILC	142	0.142	0.057	3.9	6.4
Al,Cu-PILC	153	0.154	0.063	4.0	5.2
Al,Fe-PILC	172	0.229	0.072	5.3	7.3

Where: S_{BET} - specific surface area; $V_{0.98}$ - total pore volume, V_{mic} - micropore volume, D_{max} - the pore diameter where the maximum of derivative cumulative volume curves is reached; D_{med} - median value of pore diameter.