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Electrochemical oxidation of aniline at mono and bimetallic electrocatalysts supported on carbon nanotubes

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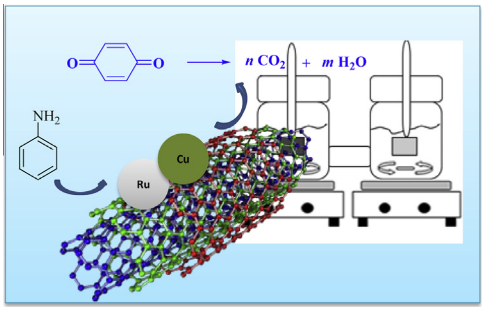
HIGHLIGHTS

- Oxidation of aniline was investigated on carbon nanotubes supported metal catalysts.
- Kinetic parameters of the redox reactions were determined using cyclic voltammetry.
- Membrane separated electrochemical cell was used for the mineralization of aniline.
- The highest conversions were obtained with the Ru-Cu/CNT/CT modified electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrochemical mineralization of aniline, a compound that causes serious environmental problems, was investigated at Pt, Pd and Ru–Cu catalysts supported on multiwalled carbon nanotubes (CNTs). The modified electrodes, based on commercial CNT samples, were prepared and dispersed onto Toray carbon (CT) using a Nafion/water solution. The electroreactivity of aniline at the electrocatalysts based on CNTs, and the kinetic parameters of the redox reactions, were determined using cyclic voltammetry. In order to determine the conditions that allow an efficient mineralization, the electrochemical oxidation of aniline was carried out in a membrane separated electrochemical cell. The reaction products were identified and quantified using chromatographic methods in order to evaluate the mineralization efficiency. The highest conversions were obtained with the Ru–Cu/CNT/CT modified electrode.

1. Introduction

The increasing demand for clean natural sources of water encourages the development of new emerging technologies and processes for water remediation. The increase of organic pollutant concentrations in natural water sources can bring serious consequences, such as high risks to public health and the environment. Aniline and its derivatives are used as intermediates for the manufacturing of various synthetic compounds such as dyes, pharmaceutical products and synthetic resins. Aniline, which is known as carcinogenic, can also transform the hemoglobin into metahemoglobina causing anoxia, erythrocyte damage and spleen effect [1]. Several treatments methods for the removal of aniline from contaminated waters, including ozonation [2], biodegradation [3], catalytic oxidation [4–6], electrochemical oxidation [7–10], separation using membranes [11], Electro-Fenton [12] and photo-electron-Fenton processes [13], have been developed. However

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the mineralization of this compound at high rates, in relatively mild conditions, continues to be a challenge. Catalysts using nanomaterials consist of a recent offer on oxidation of organic compounds, with special focus on environmental protection [14–17]. Recently, the use of carbon nanotubes (CNTs) as a catalyst or support has attracted growing attention for environmental applications, including the oxidation of organic compounds present in polluted water by catalytic wet oxidation or electro-oxidation [18–20]. Among various technologies, electrochemical oxidation appears as one of the most promising technologies for the treatment of wastewater containing organic pollutants, considering its environmental compatibility, low temperature and pressure requirements [21–25]. CNT-modified electrodes allow lower overpotentials and higher peak current intensities providing higher sensitivity and selectivity in comparison with smooth support electrodes. The results presented in a previous paper [26] show that the oxidation of oxalic and oxamic acids, refractory pollutants, occurs at lower potentials on CNT than those find for conventional electrodes.

Thus the present work reports the study of the mineralization of aniline at mono and bimetallic electrocatalysts based on carbon nanotubes. The electro-reactivity of aniline in aqueous medium on CNT-supported metal modified electrodes was investigated by cyclic voltammetry. The modified electrodes were prepared by deposition of the Metals/CNT on Toray carbon surface using a Nafion/water solution. The kinetic parameters of the redox reactions were also investigated. Exhaustive electrochemical oxidation of aniline at mono and bimetallic electrodes was carried out in order to determine the effect of some experimental conditions on product distribution.

2. Experimental section

2.1. Materials and reagents

A commercial multiwalled carbon nanotube sample Nanocyl-3100 (sample CNT) was obtained from Nanocyl S.A. The metal salts ($PdCl_2$, $Cu(NO_3)_2$, $RuCl_3$ and H_2PtCl_6) for the preparation of the electrocatalysts were purchased from Alfa Aeser and Aldrich, respectively, and used as received. The supporting electrolytes were prepared with ultrapure water (18 MΩ cm, Barnstead E-pure system) and sodium hydroxide (Panreac, 98%). Toray carbon (TC) was obtained from Quintech. Aniline and HPLC standards were reagent grade and purchased from Sigma–Aldrich.

2.2. Preparation of the bimetallic electrocatalysts based on CNT

The active metals were supported on CNT samples by incipient wetness co-impregnation, from aqueous solutions of the metal salts ($PdCl_2$, $Cu(NO_3)_2$, $RuCl_3$ and H_2PtCl_6). The samples were dried at 100 °C for 24 h, calcined under a nitrogen flow at 200 °C for 1 h, and finally reduced at 200 °C in hydrogen flow for 3 h. The amounts of noble metal and copper were maintained constant at 1% wt each. The samples were characterized using different techniques: temperature programmed reduction (TPR), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) and these results have been reported elsewhere [27].

2.3. Preparation of the mono and bimetallic modified electrodes based on CNT/CT

For the preparation of modified electrodes, 2.0 mg of M/CNT or M-Cu/CNT, was dispersed in a Nafion/water solution (180 μL Nafion/180 μL ultra-pure water). The resulting suspensions were homogenized using an ultrasound bath and deposited on a Toray carbon paper with an area of 2.5×2.5 cm^2. Finally the Toray carbon paper was glued to the platinum wire using conductive carbon cement (Quintech) and was dried at room temperature during 24 h [26].

2.4. Electrochemical studies

The voltammetric study was performed in a thermostated three-electrode glass cell and a two-compartment glass cell separated by an ion exchange membrane (Nafion 117). A tap was introduced into the Luggin bridge in order to establish the contact between the reference and the electrolyte solutions without any contamination of the later by the ions of the reference electrode solution. A saturated calomel electrode and a platinum foil (99.95%) were used as reference and counter electrode, respectively. Before each experiment, the solutions were deaerated with ultra-pure nitrogen (U Quality from Air Liquide) and the nitrogen stream was maintained over the solution during the measurements. The electrochemical instrumentation consists of a potentiostat/galvanostat from Amel Instruments coupled to a microcomputer by an AD/DA converter. The Labview software (National Instruments) and a PCI-MIO-16E-4 I/O module were used for generating and applying the potential program as well as acquiring data, such as current intensities.

2.5. Product analysis

In order to check for the absence of significant interferences, the quantitative analysis of reaction products was performed using two chromatographic set-ups: a high performance liquid chromatograph (HPLC) using an isocratic pump and a double on line detection including an UV–Vis detector and refractometer, and an ionic chromatograph (IC, Dionex) using a conductivity detector. The product partition was carried out in two different analytical columns: Aminex HPX-87 H from Biorad for HPLC and AS11-HC from Dionex for IC. The gaseous products of the reactions were detected by a Dual cell microvolume thermal conductivity detector (Vici, Valco Instruments Co. Inc.). The product separation, in this case, was carried out by a packed GC column: Chromosorb 104 (1.8 m × 1/8 in. × 2.1 mm).

3. Results and discussion

3.1. Voltammetric study of aniline at mono and bimetallic electrocatalysts based on CNT/CT

The electroreactivity of aniline at different mono and bimetallic electrocatalysts, in NaCl 0.10 M medium was studied by cyclic voltammetry. The voltammograms of Pt/CNT, Pd/CNT and Ru–Cu/CNT modified electrodes in NaCl 0.10 M medium, in presence of aniline 0.01 M, are given in Fig. 1.

High anodic and cathodic current densities were noticed in presence of aniline. During voltammetric study an increase of the maximum current densities for successive cycles was also observed. For each measurement successive voltammograms were registered in order to check the absence or presence of fast polymerization on electrode surface but only the first one is presented for clarity. The increase of anodic and cathodic limits after the addition of aniline can be explained by an important decrease of the active sites for both OH^- and H^+ adsorption due to the coverage of the electrode surface by strongly adsorbed species. These results suggest the formation of an electroactive polymeric film on the electrode surface considering that the oxidation of the dimerization products of aniline could be easier than the initial substrate. The fast polymerization reaction on the electrode surface in this