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Review

Performance of sol–gel Titanium Mixed Metal Oxide electrodes for electro-catalytic oxidation of phenol

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ABSTRACT

Mixed metal oxides SnO_2–RuO_2–IrO_2, Ta_2O_5–IrO_2 and RhO_2–IrO_2 were immobilised on a Ti substrate using sol–gel techniques. The Ti mixed metal oxides were characterized in terms of morphology using scanning electron microscopy. Cyclic voltammetric responses of phenol at Ti/SnO_2–RuO_2–IrO_2, Ti/Ta_2O_5–IrO_2 and Ti/RhO_2–IrO_2 electrodes were evaluated and showed significantly low potentials for Ti/Ta_2O_5–IrO_2 (+100 mV), Ti/SnO_2–RuO_2–IrO_2 (+200 mV) and Ti/RhO_2–IrO_2 (−100 mV). The degradation of phenol in aqueous solution and its intermediates were investigated by bulk electrolysis and quantitatively assessed by HPLC analysis to elucidate the decomposition pathways and to develop a kinetic model for the electro-catalytic oxidation of phenol over Ti mixed metal oxides. Ring compounds, benzoquinone/hydroquinone, catechol, and short chain organics, carboxylic acids, have been identified as intermediate products for the electro-catalytic oxidation of phenol. Fundamental kinetic data were obtained for the conversion of phenol at these electrodes and was found to proceed in accordance with the pseudo-first-order kinetics with respect to the phenol concentration.

Contents

1. Introduction

Widespread contamination of water by phenol has been recognized as an issue of growing importance in recent years. It has attracted more attention for research because of its toxicity

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and the frequency of industrial processes producing waters contaminated by phenol [1–4]. Phenol is carcinogenic and is a considerable health concern, even at low concentration. The main sources of phenolic wastewater are industries such as petrochemicals, coal gasification, pesticides manufacture, electroplating and metallurgical operations [5–8]. In addition, phenol is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic hydrocarbons, thus it is often used as a model compound for advanced wastewater treatments [1,3,5].

Many technologies have been investigated for removing and degradation of phenolic compounds in wastewater. They include photocatalytic oxidation [5], wet oxidation [6], supercritical water oxidation [8], adsorption [9] and biological treatment [10]. Several researchers [1,3,4,11–15] have worked on the electrochemical destruction of phenolic wastes, but to date it has not been considered to be commercially viable because of a low phenol reaction rate and/or low removal and destruction efficiency.

Thus far, oxidation technology has shown its potential to destroy phenol completely in wastewater. Although this process (phenol oxidation) was demonstrated before [14–24], there is still considerable controversy about the reaction mechanism of this anodic oxidation process [25]. The mechanism of electrochemical oxidation of phenol has been studied by various researchers [1,3,6,11,13,20,25]. It is generally considered that phenol oxidation starts with a one electron transfer, leading to a phenoxy radical reaction. It is further considered that some possible reactions of phenoxy radical relate to radial–radial coupling, radial disproportionation, radial elimination or radial oxidation to cation, and then followed by benzoquinone formation [18,26–31]. It is possible that intermediate species in aqueous phenol solution are formed before the detection of benzoquinone and are not detected because of their instability.

Most researchers believe that benzoquinone/hydroquinone is an important intermediate, and that the benzoquinone degrades to form various carboxylic acids [22,23,32,33]. Different researchers have proposed the formation of various carboxylic acids under various experimental conditions [1,18,23,33]. The process of carboxylic acid degradation was more complicated than benzoquinone formation. There are several suggested mechanisms for benzoquinone degradation. If benzoquinone is absorbed onto the electrode surface and gives an electron, an adsorbed OH radical will attack the benzoquinone. When this process repeats itself at the para position, the aromatic ring could be opened, resulting in the formation of malic or maleic acid and other small organic acids, such as oxalic and malonic acids.

Phenol has been oxidized at electrodes such as graphite [16], platinum [17], bismuth-doped lead dioxide [18] and SnO_2–Sb_2O_5 [14]. The encountered problems of electrode fouling, which reduces the efficiency of the process and hinders it from practical implementation has been a draw-back [14,19].

Furthermore, the development of non-toxic anode materials, as well as anodes exhibiting good efficiencies for the oxidation of organic compounds down to low concentration, is needed. Currently, promising materials are doped tin oxide and doped lead oxide as thin films on titanium, which seem to allow complete oxidation of many organics [14,26]. They are however, prone to fouling due to the intermediate degradation products. Stability of these electrodes over a long period also has not been proven conclusively.

In this work the measure of the effect of different mixed metal oxides on a Ti substrate towards the oxidation of phenol were studied under neutral, alkaline and acidic conditions. The effects of pH on the phenol decomposition, intermediates and kinetics will also be investigated.

2. Experimental

2.1. Reagents

Reagents $TaCl_5$, $RuCl_3$, $SnCl_2$, $RhCl_3$, $IrCl_3$, Na_2HPO_4, Ti foil and C_6H_5OH were obtained from Aldrich (Germany). Merck's absolute ethanol, methanol, potassium chloride and hydrochloric acid were used in the experiments. All reagents were of analytical grade, were used without further purification and were purchased in Cape Town (South Africa).

2.2. Sol–gel and thin film preparation

The metal oxides were prepared by dissolving hydrated chloride precursors in absolute ethanol using a sol–gel technique. The sol–gel synthesis for the metal oxides titanium materials were based on synthesis procedures modified from literature [27,28]. The starting materials were placed in a round-bottomed flask fitted with a thermometer, and the solutions were well stirred and refluxed for 1 h, before being left to age at room temperature for at least 24 h to ensure ageing of the gel. For the purpose of producing the thin films, the gels were retained in the liquid form. The titanium substrates were cut to size (1 cm × 1 cm), sandblasted and etched in HCl (11.5 M) for 5 min, rinsed with copious amounts of UHQ water and finally rinsed with absolute ethanol and dried with air.

The Ti substrates were dipped into the gel solution and then slowly withdrawn at a rate of $80\,\mathrm{mm\,min^{-1}}$. The titanium substrates onto which thin metal oxides films were coated were affixed to the rotating disk surface and rotated at full speed (~1000 rpm) for 10 s to give reproducible thin films. The thin films were then annealed in an oxygen-rich atmosphere in a quartz tube furnace at a slow heating rate (1 °C/min) up to 700 °C and then allowed to cool to room temperature, under ambient conditions.

2.3. Electrodes preparation

The electrical connection was made through a Cu wire welded to the metal oxides titanium substrate by means of silver epoxy. The back of the electrode and the copper contact was isolated with an inert-conductive polymer resin to base the results exclusively on the active surface. The composition ratio of the conducting metal oxides was varied to investigate the electro-catalytic activity using cyclic voltammetry (CV).

3. Analytical methods

3.1. Scanning electron microscopy (SEM)

The surface morphologies of the electrodes were analyzed by SEM. An ABT60 Scanning Electron Microscope was used for the experiments. The SEM pictures were taken at a working distance of 7 mm and an accelerating voltage of 7 kV. The samples were placed horizontally on the stubs and they were not coated for viewing. For the X-ray analysis, the working distance was 12 mm and the accelerating voltage was 25 kV. The samples were tilted at 30°. The SEM cross-sections of the thin films were obtain as follows: the samples were left in a resin for 24 h in an oven at 60 °C, cut and polished into small pieces and mounted vertically on the stubs.

3.2. Electrochemical measurements

The surfaces of the modified electrodes were characterized by means of cyclic voltammetric curves to evaluate the catalytic response of the electrode surfaces. All electrochemical experi-