Catalysis Communications 67 (2015) 49–53

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Electrocatalytic degradation of aspen lignin over Pb/PbO_2 electrode in alkali solution

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ARTICLE INFO

Article history:
Received 5 January 2015
Received in revised form 7 March 2015
Accepted 24 March 2015
Available online 28 March 2015

Keywords:
Aspen lignin
Electrocatalytic degradation
4-Methylanisole
Pb/PbO_2 electrodes
Alkaline water electrolysis

ABSTRACT

A novel procedure about electrochemical catalysis degradation of aspen lignin with Pb/PbO_2 anode in the three-dimensional electrode (TDE) reactor was investigated. SEM, XRD and cyclic voltammogram tests were employed to study the surface morphology, composition and the electrochemical redox performance of the fabricated Pb/PbO_2 electrode. The lignin was cracked by $^{\bullet}OH$ and hydrogenated by [H] atom generated from alkaline water electrolysis, leading to the production of 4-methylanisole and other products. Raw material lignin concentration, current density, temperature and time were optimized. The pathway of electrocatalytic degradation and hydrogenation process of lignin in alkaline solution was also discussed.

1. Introduction

As a kind of renewable resource of organic carbon, lignin accounts for about a quarter in woody plants. Lignin is considered to be, after cellulose, the second most abundant natural polymer. However, lignin has been regarded as a waste byproduct of the lignocellulosic biomass conversion processes despite that it is composed of valuable aromatic monomers [1]. For exploring the specific structure of lignin and getting valuable refine chemical, many efforts have been paid to degrade lignin such as fast pyrolysis, hydrothermal degradation, photodegradation and electrochemical degradation.

In recent years, owing to its ease of operation and environmental friendliness, electrocatalytic oxidation has been employed for the degradation of lignin [2]. The variety and yields of products obtained from lignin oxidation varied according to the nature of the anode. B. Mahdavi [3] studied the degradation of lignin model compounds in aqueous ethanol at Raney nickel electrodes, showing the efficiency of hydrogenolysis of the C–O bond can be optimized to 100% at proper condition.

We had previously reported the degradation of lignin to BHT by electrocatalytic reaction in 2D electrode system [4], however there was a problem of the electrochemical impedance as the case for the strong adsorption of hydroxyl group in lignin. The TDE reactor based on electrochemical catalysis has been employed in this research work. Because there are a large number of the particle electrode materials placed into the TDE reactor to form charged microelectrodes and increase its large specific surface areas in connection with the reactant. The reactivity of electrochemical oxidation in TDE reactor can be improved. By contrast with 2D electrode, the addition of granular activated carbon may enhance the conductivity and mass transfer or the adsorption of reactant [5], 3D electrode has greater advantage in degrading organics [6,7].

4-Methylanisole, also known as 1-methoxy-4-methyl benzene, belongs to methoxybenzene derivatives. It mainly applies in food flavor, inedible essence, and pharmaceutical intermediate. 4-Methylanisole is an edible spice (as seen in FDA104-93-8), especially in the preparation of walnut, hazelnut and other nut essence. It had been achieved by upgrading of bio-oil in a catalytic pulsed dielectric barrier discharge plasma reactor [8].

2. Materials and experimental methods

2.1. Materials

Aspen lignin was supplied by Luohe Huadong Lignin Company, Henan Province, China. Elemental analysis (C, H, N) of aspen lignin was conducted using a FlashEA 1112 Series element (Thermo Electron Corporation). The contents of carbon and hydrogen in aspen lignin were 59.7% and 5.94%, respectively. Lead chips and stainless steel wire mesh (purity ≥ 99.99%) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. The granular activated carbon with particle sizes in range of 1.40–3.35 mm provided by Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd, China. All of the solutions were prepared using deionized water.

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http://dx.doi.org/10.1016/j.catcom.2015.03.033
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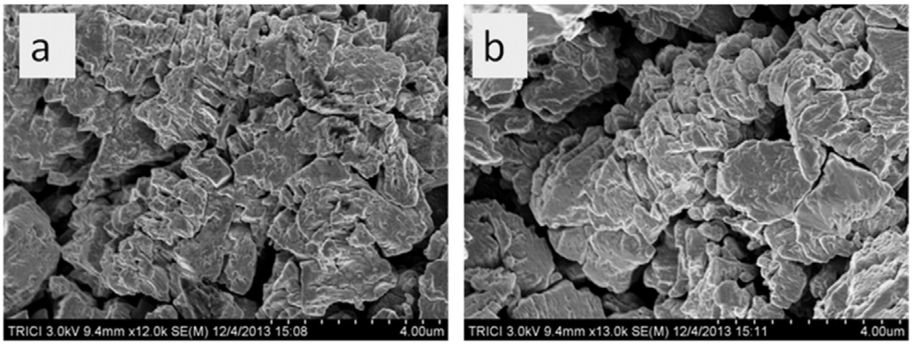

Fig. 1. SEM images of the Pb/PbO_2 electrode before (a) and after (b) electrolysis in 1 mol/L NaOH solution.

2.2. Preparation of the Pb/PbO_2 electrode by electrodeposition

The Pb/PbO_2 electrode was prepared by electrodeposition [9]. The pretreatment of lead sheet included following steps: burnish the surface of lead sheet with sandpaper (P 120), impregnate into acetone, clean by mixture solution (Na_2CO_3 20 g/L, Na_3PO_4 20 g/L, NaOH 50 g/L), acidic clean by mixed acid solution (HNO_3 400 g/L, HF 5 g/L) for 2 min and boil for 5 min in oxalic acid solution (100 g/L). The pure lead sheet, about 12 (2×6) cm^2, was sited in an electrolytic cell which composed of anode, copper sheet of the same size used as cathode and 0.86 mol/L H_2SO_4 electrolyte solution. The electrodeposition was performed with 50 mA/cm^2 controlled by a DC regulated power supply (ss1792c, Shijiazhuang KeHeng Electronic Company, China) at room temperature for duration 1 h. Then the Pb/PbO_2 electrode was obtained.

2.3. Electrocatalytic degradation of aspen lignin to chemicals based on three-dimensional electrodes

The experiments were carried out in three-dimensional electrode reactor [10]. Particle electrode was filled between Pb/PbO_2 electrode (anode) and stainless steel wire mesh ($5 * 5$) electrode (cathode). Sodium hydroxide (1 mol/L) solution was used to dissolve lignin and gave the concentrations of lignin solution of 40 g/L in the electrolytic cell. The DC regulated power supply provided current 20–90 mA/cm^2 for the electrocatalytic degradation of lignin. The lignin alkali solution was stirring by magnetic stirring for mass transfer uniform. The reaction temperature and time were controlled within 30–90 °C and 0–8 h, respectively.

2.4. The analysis and separation of the degradation products

The degradation liquid of lignin was extracted with the same volume ethyl acetate and acidified to pH 2–3 by 0.86 mol/L H_2SO_4 solution to precipitate unreacted lignin residua simultaneously. The mixed liquor of organic solvent and water phase was sufficiently stirred until the lignin residue flocculation. The extract liquor and unreacted lignin residue were separated by the vacuum filter. The filter cake was dried to calculate the lignin degradation rate and the filtrate was separated by separatory funnel into water and extractive phase.

The crude products of lignin degradation were got by reduced pressure distillation to evaporate and recover the solvent. The separation and purification of products depended on thin layer chromatography and column chromatography separation (silica 200–300 mesh, eluent, n-hexane: ethyl acetate = 6:1, v/v). The main product was 4-methylanisole and its chemical structure was confirmed by GC–MS, NMR spectra. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.789 (s, 1H, CH), δ 6.81 (s, 1H, CH), δ 7.069 (s, 1H, CH), δ 7.090 (s, 1H, CH), δ 2.97 (s, 3H, CH_3), δ 3.769 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 157.45, 129.877, 129.808, 113.672, 55.249, 20.442; MS: 123(7), 121(46), 107(30), 79(20), 77(34), 51(9), 50(4). The other degradation products such as acetovanillone, toluene, vanillin, syringaldehyde, 2,6-dimethoxyphenol and styrene were confirmed by GC with internal standard methods.

The products were qualitatively and quantitatively measured by internal standard method on the gas chromatography (GC) instrument (SHIMADIU, GC-2010) equipped with a FID detector and an Agilent J&W GC column (DB-FFAP, length 30 m, diameter 0.32 mm, film 0.25 μm). The temperature of injection inlet, column and detector was 240 °C, programming 50 °C–220 °C and 280 °C respectively. The flow rate of carrier gas, high purity nitrogen (purity of 99.99%), was controlled with 38.7 $mL \cdot min^{-1}$ and injecting volume of sample solution was 1 μL for split sampling program of split ratio 20.0.

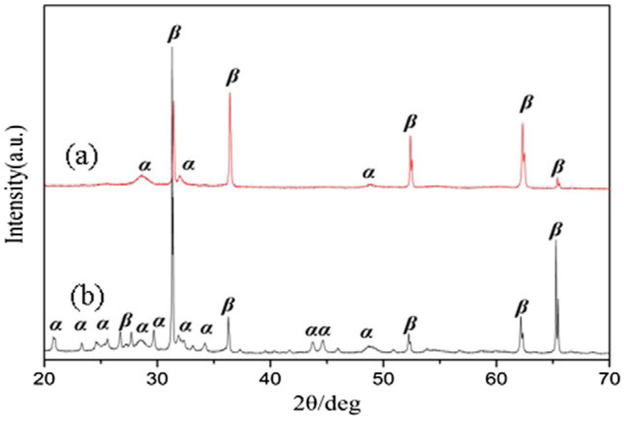

Fig. 2. XRD patterns of Pb/PbO_2 before and after electrolysis in 1 mol/L NaOH solution.

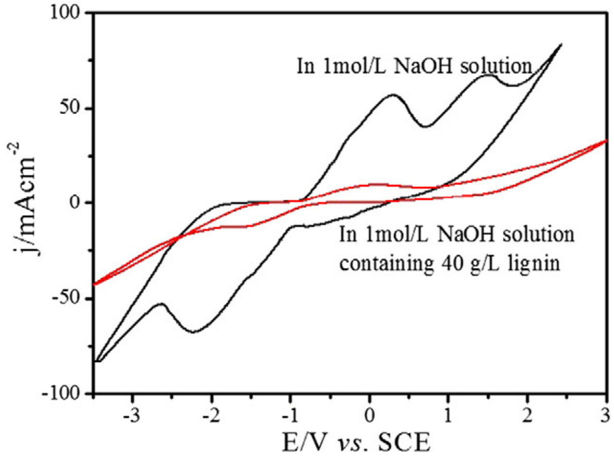

Fig. 3. CV curve recorded for the Pb/PbO_2 electrode without and with lignin in the three-dimensional electrochemical reactor.