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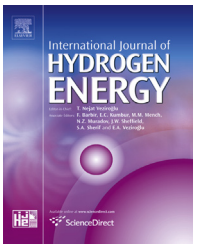

The synthesis of analcime zeolite nanoparticles using silica extracted from stem of sorghum Halepenesic ash and their application as support for electrooxidation of formaldehyde

Seyed Naser Azizi [a], *Shahram Ghasemi* [b,*], *Masoume Derakhshani-mansoorkuhi* [a]

[a] *Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran*
[b] *Faculty of Chemistry, University of Mazandaran, Babolsar, Iran*

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ABSTRACT

In this work, a free template method is used to synthesize nanostructured analcime (ANA) zeolite from natural source and the prepared zeolite is applied as substrate to fabricate a modified electrode. To this aim, ANA zeolite nanoparticles are synthesized by hydrothermal method using amorphous silica extracted from stem of sorghum ash (SSA) with approximately 92.34% purity in the absence of organic template. The effects of different parameters such as Si/Al ratio, heating time, temperature and stirring time on synthesis and crystallinity of zeolite are optimized. The synthesized zeolite is characterized using X-ray diffraction, Fourier-transform infrared and scanning electron microscopy (SEM) techniques. SEM shows that ANA zeolite nanoparticles appear as spherical particles contains some smaller nanoparticles which arranged in regular pattern to each other. Also, some fibers consist of nanoparticles in range of 30–48 nm are observed.

The modified carbon paste electrode (CPE) is prepared based on ANA modified with Ni species (Ni/ANACPE). The electrochemical oxidation of formaldehyde is studied at Ni/ANACPE in alkaline solution. From cyclic voltammetry studies, it is shown that Ni/ANACPE can facilitate the oxidation of formaldehyde compared to CPE. The effects of some parameters such as scan rate of potential, concentration of formaldehyde, amount of Ni-zeolite are investigated on the oxidation of formaldehyde. Also using chronoamperometry technique, the catalytic rate constant (k) for oxidation of formaldehyde is found to be 7.56×10^4 cm^3 mol^{-1} s^{-1}.

Introduction

Recently, much attention has been made to electrocatalytic oxidation of various compounds like methanol, formaldehyde and etc. using different modified electrodes due to their potential utilization as fuels in fuel cell systems. Fuel cells have high energy density [1–3] and can be used in various power applications. Although formaldehyde is a harmful substance to human health, it could be used as a small model molecule

* *Corresponding author*. Faculty of Chemistry, University of Mazandaran, P.O. Box: 4741695447, Babolsar, Iran.
E-mail addresses: sghasemimir@yahoo.com, sghasemi@umz.ac.ir (S. Ghasemi).

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for studies of the electrooxidation of large organic molecules [4]. The literature survey shows that significant interest has been focused in the electrochemical oxidation of formaldehyde for many years [5–15].

Zeolites are highly crystalline, porous, hydrated aluminosilicates contain tetrahedral units of $[SiO_4]_4$ and $[AlO_4]_5$ that join together by sharing of oxygen atoms and therefore make an infinitely extending three dimensional network [16]. These compounds are mainly used in the different fields of applications such as selective and strong adsorbents, selective ion exchangers and catalysis [17–20]. Analcime (ANA) is a type of zeolite with irregular channels, which is found in the nature. However many sources of the natural ANA are present in limited regions of the world but many attempts have been recently achieved to synthesize ANA with various sources of silica and alumina.

Sorghum halepense is a plant of grass family and is considered commonly as weed and is rich of silica. It is transformed into silica ash by burning in air. Using an easy procedure of alkaline extraction, pure silica can be obtained from stem of sorghum ash (SSA). Zeolites have been modified with some metals and metal ions such as Ag [21,22], Fe [23], Cu [24], Pb [25], Co [26], Pt–Ru [27] and Ni [28–30] for application as catalyst in catalytic process. The porous nature of zeolites makes them good candidates as support material to prepare modified electrodes (as a cheap and simple catalyst) and electrooxidation of fuels in fuel cells.

Zeolites have the ability of ion exchange and zeolite-modified electrodes (ZMEs) are based on this ability of zeolites [31–33].

Microporous (pores diameter <2 nm) and mesoporous (pore diameter between 2 and 50 nm) materials are usually used as substrates in catalytic purposes. The porosity of these materials plays the role of host for some guest materials such as metals, metal hydroxide and etc. which facilitate some catalytic reactions. Zeolites as microporous materials have small pores which limits their benefits. The preparation of nanozeolites with particle size dimensions in the nanometer range is one way to increase the surface area of zeolites. This is also most important for bulky ANA and P zeolite which most of their pores exist in the context of them and are not accessible during the catalytic process. To solve this problem, the size of zeolite nanoparticles should be reduced to nanometer dimension. The surface-to-volume ratio increases when the sizes of zeolite particles decrease to nanometer range. Therefore, any efforts to fabricate the nanostructured ANA makes it suitable substrate to prepare the new catalysts. In other hand, the idea of construction the porous materials in the absence of structure directing agents and templates such as amines and tri-block copolymers has been considered during the last years. There are a few reports which prepare ANA nanozeolites without using organic template. In this work, we reports a simple method for synthesis of ANA zeolite nanoparticles from stem surghom ash (SSA) as silica source using sol–gel and hydrothermal methods. ANA zeolite can be modified with Ni (II) ions (Ni/ANA) by dispersion in a nickel chloride solution. The modified carbon paste electrode (CPE) was prepared by incorporation of Ni (II) - zeolite in CPE (Ni/ANACPE). The electrochemical oxidation of formaldehyde was investigated at the surface of Ni/ANACPE in alkaline solution using cyclic voltammetry (CV) and chronoamperometry (CA) methods.

Experimental

Apparatus and chemicals

Sodium aluminate salt (>63% Al_2O_3, Fison Co.) was used as aluminum source. SiO_2 powder was extracted from SSA as silica source. Hydrochloric acid, nickel chloride, formaldehyde, sodium hydroxide (98%), and graphite powder (particle diameter: 0.15 mm) were purchased from Merck. High viscosity paraffin (Fluka, density of 0.88 g cm^{-3}) was used as pasting liquid for the preparation of CPE.

The structure of the products was examined by X-ray diffraction (XRD, SIEMENS D5000) using Cu K_α radiation. The diffractograms were recorded over the range of $5^\circ \leq 2\theta \leq 50^\circ$ with current of 40 mA and voltage of 40 kV. The chemical compositions of silica powder were identified by X-ray fluorescence (XRF: 8410 Rh 60 kV). Fourier-transform infrared (FT-IR) spectrum was recorded at room temperature using FT-IR spectrometer (Vector 22-Bruker) in the range of 400–4000 cm^{-1} using KBr pellet. Morphology and composition of modified zeolite was determined using a scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (SEM, VEGA TESCAN). All of the electrochemical examinations were performed in three electrode system by Dropsens, Bipotentiostat/Galvanostat (μSTAT 400). Ag|AgCl|KCl (3 M) and platinum wire electrodes were used as reference and auxiliary electrodes, respectively. Also, the prepared Ni/ANACPE was used as working electrode.

Preparation of pure silica powder from SSA

Stem of sorghum (SS) samples were provided from the region in the north of Iran (Neka, Mazandaran). They were washed with water to eliminate sticking soil and dust. Then SS samples was dried and burned in air to produce black SSA powder. An acid washing step was applied to remove small quantities of minerals prior to silica extraction. For this purpose, SSA samples were dispersed in 1 M HCl for 4 h. Then, mixture was filtered and residues were washed with distilled water several times until the filtrate was free of acid. After washing, the product was collected and dried at 100 °C overnight.

SSA was burned in furnace at 550 °C. The achieved product was characterized by XRF to determine the weight percent of components. Pure silica is obtained by dissolving the powder in 1 M NaOH under vigorous stirring followed by refluxing at 100 °C for 2 h to form sodium silicate solution. Then, the solution was filtered (solution 1). Also, the precipitate remained on filter paper was boiled with distilled water under the same condition and mixture was filtered. The obtained solution (solution 2) was mixed with solution 1 and allowed to cool to room temperature. Silica aqua-gel was precipitated from sodium silicate solution by acidification using HCl. The addition of the acid was done very slowly until a pH of 7 was reached.

The silica gel was aged for 18 h and then washed with deionized water to remove soluble salts. The gel was transferred into a beaker and dried at 80 °C overnight to produce

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