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Fabrication of novel nanozeolite-supported bimetallic Pt–Cu nanoparticles modified carbon paste electrode for electrocatalytic oxidation of formaldehyde

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ABSTRACT

In this work, a highly active X nanozeolite-supported bimetallic Pt–Cu nanoparticles modified carbon paste electrode (Pt–Cu-XNZ/CPE) was fabricated for the first time and its electrocatalytic activity toward formaldehyde oxidation was investigated. To do this, the NaX nanozeolite/CPE (NXNZ/CPE) was firstly prepared and then Cu²⁺ ions were introduced into nanozeolite structure by ion exchange followed by electrochemical reduction to Cu⁰. Then the partial replacement of Cu species by Pt species was achieved. The characterization of the proposed electrode was performed by energy dispersive X-ray analysis and scanning electron microscopy. Also, the performance of the as-prepared electrode toward formaldehyde electrooxidation was studied by the cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometric techniques. Furthermore, the effects of various parameters including times of ion exchange (t_{ex}) and replacement (t_r) as well as long-term stability of the prepared electrode were investigated on the formaldehyde oxidation. The obtained results show that the as-prepared Pt–Cu-XNZ/CPE indicates good electrocatalytic performance including high current and low overpotential for formaldehyde oxidation. It can be attributed to the presence of zeolites as nanoporous material on the electrode surface which provides the porous structure for bimetallic Pt–Cu nanoparticles formation and active sites for formaldehyde oxidation.

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Introduction

Fuel cells have been considered as an attractive electricity generation technology, which supply very effective and direct conversion of chemical energy into electricity [1–5]. To develop fuel cells, the improvement of anodic catalyst have

been an important challenge. Therefore, some research fields have been dealing with the challenges to synthesis of cost effective and highly active catalyst for oxidation process of fuel in the fuel cells [6–8].

Formaldehyde fuel cells have been considered because formaldehyde is an intermediate in the methanol oxidation [9]. Pt-based electrocatalysts are regarded as ideal catalyst for

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formaldehyde oxidation due to their prominent properties in the catalytic processes. The oxidation process on the Pt-based electrocatalysts surface can be occurred through the 'dual path' mechanism, including the 'direct path' and 'indirect path', in which the indirect path involves the formation of CO as the reaction intermediate [10]. However, Pt is one of the noble metals and high cost of noble metals can restrict their wide applications. Therefore, it is worthwhile to decrease the required amount of Pt in the electrocatalysts. The addition of a secondary element, in oxidized form or metallic form, into Pt catalyst is an effective way to reduce the amount of Pt. Also, bimetallic catalysts can improve the activity and stability of Pt-based catalysts due to change of Pt–Pt bond distance, d-band center shift, and Pt skin effect which result into lattice shrinking or lattice strain [11]. In fact, the synergistic effect of the elements in the bimetallic catalyst makes them better than monometallic ones [12,13]. However, in the bimetallic systems, the catalytic efficiency and oxidation kinetic are strongly rely on various parameters including second metal content, degree of its alloying with Pt and electrode pretreatment [14].

Bimetallic systems can be prepared by several methods including microemulsion method [15], impregnation of high surface area carbons by the metal ions followed by chemical reduction in a hydrogen atmosphere at elevated temperatures or in solutions of appropriate reducing agents [16] and galvanic replacement [17]. Galvanic replacement or transmetalation is an industrially-relevant method that is based on the spontaneous replacement of a non-noble or less noble metal by a second (more noble) one. The key feature of this method is simplicity and very low consumption of noble metal [18]. This method was first established by Adzic et al. [19–21] for replacement of Cu underpotential deposition (UPD) monolayers by Pt, Pd or Ag and then by a series of noble metals or their mixtures. Sotiropoulos et al. [22–24] reported the preparation of several bimetallic systems including Pt–Ni, Pt–Fe, Pt–Cu, Pt–Co, and Pt–Pb by the galvanic replacement reaction. In the bimetallic systems like monometallic systems, the use of supporting material such as zeolite has various advantages such as stabilizing the nanoparticles against aggregation and achieving the highest possible electrode surface area which results in remarkable catalytic activity and efficiency [25,26]. Zeolites, as microporous aluminosilicate crystallites, are suitable supporting materials for fuel cell applications due to their interesting properties such as ion exchange capacity, large accessible surface area, high thermal and chemical stability and size selectivity [27]. Moreover, nanozeolites are zeolites with dimensions less than 100 nm that have larger surface area and higher catalytic activity than zeolites with larger size. Zeolite-supported electrodes combine the noticeable properties of zeolites with the high sensitivity of modern electrochemical techniques which leads to significant improvements in their catalytic activity compared to the other supported electrodes. Up to now, zeolite-supported bimetallic electrodes such as Pt–Ru(HY) [28] and NiCosalen A [29] have been used in methanol electrooxidation.

Previously, in our research group, template-free NaX nanozeolite was first synthesized from stem sweep as a low cost silica source and its electrocatalytic activity for H₂O₂ reduction was investigated [30]. Zeolite NaX is one of the

aluminosilicate zeolites with well-defined structure, large pore volume, and appropriate ion exchange capability that have been utilized as ion-exchanger, absorbent and catalyst [31]. It is necessary to mention that other zeolite such as NaY or NaA can be also used due to their appropriate pore size and ion-exchange capacity. However, the purpose of this work is the feasibility of preparation of bimetallic Pt–Cu on NaX zeolite nanoparticles as paradigm and investigation of its performance toward formaldehyde oxidation. Anyway, preparation of bimetallic Pt–Cu on other type of zeolite as supporting material would be investigated in another work. Therefore, due to appropriate properties of NaX zeolite, we choice NaX and apply it for the preparation of proposed electrode. In this work, we synthesized NaX nanozeolite according to method proposed in our previous work and used it for the first time for preparation of X nanozeolite-supported bimetallic Pt–Cu nanoparticles modified carbon paste electrode (Pt–Cu-XNZ/CPE). After modification of CPE with nanozeolite, Cu²⁺ ions were introduce into nanozeolite structure by ion exchange method and then electrochemically reduced to Cu⁰. Then Cu was galvanically replaced and Pt–Cu-XNZ/CPE was prepared. To our best knowledge, there is no reported literature about fabrication of bimetallic Pt–Cu on the synthesized NaX nanozeolite prepared from stem sweep as a supporting material for electrocatalytic oxidation of formaldehyde.

Experimental

Chemicals and apparatuses

H₂SO₄ (sulfuric acid, 98%), K₃Fe(CN)₆ (potassium hexacyanoferrate (III)), K₄Fe(CN)₆ (potassium hexacyanoferrate (II)), KCl (potassium chloride, >99%), K₂PtCl₆ (potassium hexachloroplatinate (IV)), CuSO₄ · 5H₂O (copper(II) sulfate pentahydrate, 99%) and HCHO (formaldehyde, 37%) were all supplied from Merck. Graphite powder and paraffin were also purchased from Fluka. Also, all solutions were prepared with double distilled water.

In order to synthesize of NaX nanozeolite, nanosilica was first extracted from stem sweep ash according to method proposed in our previous work [30]. Then 1.07 g of extracted nanosilica and 0.6 g of sodium aluminate were singly dissolved in NaOH solution and then prepared solutions were mixed together with vigorous stirring. Afterward, the mixture was transferred into Teflon-lined stainless steel autoclave and heated at 60 °C for 72 h. After this time, the product was filtered, washed and dried.

All cyclic voltammetry (CV) and chronoamperometry measurements were performed by a Dropsens, Bipotentiostat/Galvanostat (μSTAT 400) with DropView software in conventional three-electrode cell at room temperature. The prepared Pt–Cu-XNZ/CPE, platinum wire and Ag|AgCl (KCl 3 M) were used as working, counter and reference electrodes, respectively. The electrochemical impedance spectroscopy (EIS) was investigated in the frequency range from 2 × 10⁴ Hz to 10⁻² Hz with an ac amplitude of 10 mV using a potentiostat galvanostat Palmsense (PS Trace software version 4.2.2, Netherlands). The microstructures, morphology and texturing

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