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Article

Encapsulation of a nickel Salen complex in nanozeolite LTA as a carbon paste electrode modifier for electrocatalytic oxidation of hydrazine

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A nickel salen complex was encapsulated in the supercages of nanozeolite NaA, LTA (linde type A) structure, using the flexible ligand method. The electrochemical behavior and electrocatalytic activity of a carbon paste electrode (CPE) modified with Ni(II)-Salen-A (Ni(II)-SalenA/CPE) for hydrazine oxidation in 0.1 mol/L NaOH solution were investigated by cyclic voltammetry, chronoamperometry, and chronocoulometry. First, organic-template-free synthesis of nanozeolite LTA was performed and the obtained material was characterized by various techniques. The average particle size of the LTA crystals was estimated to be 56.1 and 72 nm by X-ray diffraction and particle size analysis, respectively. The electron transfer coefficient was found to be 0.64 and the catalytic rate constant for oxidation of hydrazine at the redox sites of Ni(II)-SalenA/CPE was found to be 1.03 × 10^5 $cm^3/(mol\cdot s)$. Investigation of the electrocatalytic mechanism suggested that oxidation of hydrazine occurred through reaction with Ni^{3+}(Salen)O(OH) and also direct electrooxidation. The anodic peak currents revealed a linear dependence on the square root of the scan rate, indicating a diffusion-controlled process, and the diffusion coefficient of hydrazine was found to be 1.18 × 10^{-7} cm^2/s. The results indicated that Ni(II)-SalenA/CPE displays good electrocatalytic activity toward hydrazine oxidation owing to the porous structure of nanozeolite LTA and the Ni(II)-Salen complex. Finally, the general reaction mechanism for the electrooxidation of hydrazine on Ni(II)-SalenA/CPE in alkaline solution involves the transfer of four electrons, in which the first electron transfer reaction acts as the rate-limiting step followed by a three-electron process to generate environmentally friendly nitrogen and water as final products.

1. Introduction

Hydrazine (N_2H_4) is a small and reactive molecule with powerful reducing capabilities that can undergo diverse reactions in numerous applications. In addition, it is widely used in various fields, including fuel cells, catalysts, and industrial, agricultural, military, pharmacological, and aerospace applications [1,2]. Further, N_2H_4 is an important chemical of environmental and pharmaceutical interest, and reported to be a neurotoxin that produces carcinogenic and mutagenic effects [3]. Despite the wide application of N_2H_4 in various fields, it has been recognized to be unsafe for humans and therefore, sensitive and fast methods for the detection and determination of N_2H_4 in low concentrations in various media are becoming more significant [2,4]. N_2H_4 is an important high-performance fuel in aerospace propulsion applications, and also has promising potential applications in fuel cells. In fact, N_2H_4 may be an ideal fuel for direct fuel cell systems because the absence of

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carbon atoms in N_2H_4 leads to zero production of species that may poison the electrocatalyst and reduces the overall emission of CO_2 as a greenhouse gas [2]. The direct hydrazine fuel cell (DHFC) exhibits an electromotive force of 1.56 V vs. standard hydrogen electrode (SHE), which is higher than that for other fuel cells using hydrogen (1.24 V) or methanol (1.19 V) as a fuel [5]. In addition, the decomposition products of N_2H_4, nitrogen and water, are ecologically friendly.

The electrooxidation of N_2H_4 is connected with the technological development of DHFCs. Various materials have been investigated for the electrooxidation of N_2H_4, including Pt nanoparticles [1], Au-SH-SiO_2/MOF [2], Au electrodes [6], CuNPs-PANI-Nano-ZSM-5 [7], Pd modified multi-walled carbon nanotubes (MWCNTs) [8], nano-Ni-MWNTs-textile electrodes [9], nickel ternary alloys at graphite electrodes [10], nanoporous NiCuP amorphous alloys [11], NiO_x-Pt/C [12], CuO/NiO composite nanofibers [13], modified MWCNTs [14], and modified carbon paste electrodes (CPEs) [15–17].

Zeolites are crystalline aluminosilicate composites of Si, Al, and O with a structure of linked tetrahedra, each consisting of four O atoms surrounding a cation; the structure contains a network of channels and cages [18]. One of the most representative artificial aluminosilicate zeolites, zeolite NaA (LTA), was first synthesized by a hydrothermal crystallization method and has been utilized industrially in catalysts, adsorbents, ion exchangers, and zeolite membranes [19,20]. This material is a microporous crystalline aluminosilicate zeolite that has a channel opening size of 0.4 nm and a cubic structure of three-dimensional pores [19,21]. The preparation of zeolite-modified electrodes (ZMEs) is fast, easy, and cheap [22]. The next challenge is to prepare ZMEs on a carbon substrate for cyclic voltammetry (CV) because the prepared catalysts have to be loaded on a substrate to act as a stable solid electrode [22].

It is important to develop a novel electrode that has high sensitivity and stability for the electrooxidation of N_2H_4. Some studies have been performed on the synthesis of metal Salen (*N*,*N*′-bis(salicylidene)ethylenediamine) complexes immobilized on zeolites as active catalysts for organic reactions [23,24]. Most studies have focused on the encapsulation of metal salen complexes in zeolitic hosts for the electrocatalytic oxidation of methanol in alkaline solution [25–28]. There are no literature reports on the application of CPEs modified with nickel(II) salen complexes encapsulated in nanozeolite LTA for the electrocatalytic oxidation of N_2H_4. Hence, the synthesis of nanozeolite LTA without an organic template was performed and the obtained material was characterized by various techniques. Then, a CPE was modified with a nanozeolite LTA-encapsulated Ni(II)Salen complex (Ni(II)-SalenA/CPE) and its electrocatalytic performance for N_2H_4 oxidation was evaluated in alkaline solution. The reaction mechanism of N_2H_4 oxidation on the modified electrode was further considered using CV, chronoamperometry, and chronocoulometry.

2. Experimental

2.1. Reagents and materials

All chemicals were analytical grade and used without any further purification. NaOH, tetraethyl orthosilicate (TEOS), N_2H_4, $Ni(CH_3COO)_2$, ethylenediamine, salicylaldehyde, KCl, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ were purchased from Merck. Diethyl ether (99 wt%) and sodium aluminate were purchased from Daejung Company. Graphite powder and paraffin oil (d = 0.88 g/cm^3) as the binding agent (both from Daejung Company) were used for preparing the pastes. Deionized water was used throughout the experiments.

2.2. Synthesis of organic-template-free nanozeolite NaA

The synthesis procedure for nanometer-sized zeolite NaA has been described elsewhere [29]. Aluminosilicate gel was prepared by mixing a freshly prepared aluminate solution with a silicate solution at a molar ratio of 1.0 Al_2O_3:4.0 SiO_2:5.5 Na_2O:190 H_2O. First, a 300 mL plastic bottle containing a freshly prepared sodium aluminate solution (17.46 g of NaOH, 180 mL of H_2O, and 10.52 g of $NaAlO_2$) and a stirring bar was immersed in an ice-water bath. The mixture was cooled for 1 h with stirring and then 47.13 mL of TEOS was added. The hydrolysis of TEOS was controlled at 0 °C in order to obtain a nanometer-sized aluminosilicate gel. Stirring was continued at 0 °C for 6 h and then at room temperature for another 24 h. Hydrothermal crystallization was performed at 60 °C for 48 h in a shaker with a rotation rate of 250 r/min. The powdered products were recovered by repeated high-speed centrifugation at 12000 r/min and washing with deionized water until pH < 8, followed by drying at room temperature for 24 h.

2.3. Preparation and characterization of the Ni(II)-SalenA

To prepare Ni(II)A using the ion-exchange method, 2 g of nanozeolite NaA was suspended in 50 mL of $Ni(CH_3COO)_2$ aqueous solution (0.01 mol/L), and the mixture was stirred for 24 h at ambient temperature. Then, the solid fraction was filtered, washed three times with deionized water, and dried at 100 °C for 12 h to obtain Ni(II)A [30]. The metal complex was encapsulated in the structure of nanozeolite NaA by using the flexible ligand method [31]. First, Ni(II)A was mixed with excessive amounts of H_2Salen (n_{ligand}/n_{metal} = 3) in a crucible with a cover. The complexation was performed at 170 °C for 24 h under high vacuum conditions. The molten slurry was cooled to room temperature and extracted with acetone by Soxhlet extraction until the solvent was colorless in order to remove uncomplexed ligands and complex molecules adsorbed on the exterior surface. The extracted sample was then ion-exchanged with a NaCl aqueous solution (0.1 mol/L) to remove uncoordinated Ni^{2+}, followed by washing with deionized water until no chloride ions were detected with a $AgNO_3$ aqueous solution to obtain Ni(II)-SalenA.

2.4. Apparatus and characterization

Powder X-ray diffraction (XRD) patterns were recorded using a X-ray diffractometer (MPD 3000 Instrument) with Be-filtered Cu K_α radiation (λ = 1.5418 Å) operating at 35.4 kV