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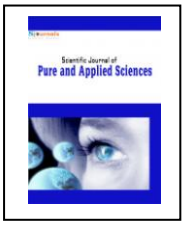

Original article

Electrocatalytic behavior of modified carbon paste electrode with Ni(ii)-zeolite for oxidation of methanol in a basic solution

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ABSTRACT

In this research, the electrochemical behavior of Ni-zeolite modified carbon paste electrode in the form of Ni/NiZSM-5/CPE and unmodified carbon paste electrode were studied using cyclic voltammetry and chronoamperometric techniques. It was found that methanol was oxidized by NiOOH generated with further electrooxidation of Ni ions which were doped in modified electrode during the anodic sweep. Also, the rate constant for the catalytic reaction (K) of methanol was calculated 2.64* $10^5 cm^3 s^{-1} mol^{-1}$ via Cottrell equation.

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1. Introduction

Electrocatalysts oxidation of methanol has been receiving great attention over the last two decades due to the possible application in direct methanol fuel cell (DMFCs), which show great potential as high-efficiency, low-emission future power source (Wang et al., 2011; Raoof et al., 2011; Abrishamkar et al., 2012; Danaee et al., 2010). Recently Pt-based electrocatalysts for methanol electro-oxidation in acid solution has been widely studied in (Bensebaa et al., 2005; Fjigu et al., 2012; He et al., 2011). However, high cost and limited resource do not allow using Pt at commercial level (Feng et al., 2012; Ma et al., 2010; Maialagan and Nawaz 2009). The zeolite modified electrodes find applications in sensors, batteries and electrocatalysis, the electron transfer process of the electroactive species at the zeolite modified electrode is an important phenomena and understanding for various applications. Three types of mechanisms are anticipated for the electrodic process: extrazeolitic, intrazeolitic and

surface mediated electron transfer reaction. The electrochemical behaviour of zeolite modified electrodes using metal complexes, counter ions and organic molecules is known to be influenced by various parameters such as charge balancing cations, supporting electrolyte and immersion time of the electrode in to the solution among others (Abrishamkar and Bagherfard, 2013; Abrishamkar and Izadi, 2013; Ojani et al., 2012; Rohani and Taher 2009). In the present work, was introduced a novel zeolite modified electrode based on Ni doped ZSM-5 zeolite for electrooxidation of methanol. We show that Ni-ZSM-5 modified carbon paste electrode can be used for effective electrocatalytic oxidation of methanol in alkaline medium.

2. Materials and methods

2.1. Apparatus and chemicals

The ZSM-5 zeolite was synthesized by a literature method(Abrishamkar et al., 2012). Graphite powder and nickel chloride were from Fluka. Ethanol and sodium hydroxide used in this work were also purchased from Merck. Electrochemical experiments were carried out using a potentiostat/galvanostat (sama 500-c Electrochemical Analysis system, sama, Iran). An $Hg|Hg_2Cl_2|KCl$ (4.6M) electrode as reference electrode, a platinum wire as the auxiliary electrode and carbon paste electrode modified with zeolite as the working electrode were used.

2.2. Preparation of working electrode

To prepare the modified ZSM-5 zeolite with Ni ions (NiZSM-5), 0.5 g of synthesized zeolite was immersed to 10 ml of 1 M $NiCL_2$ solution for 5 h. Then, the ion exchanged zeolite was dried in oven at 350 K for 8 h. Carbon paste electrode containing NiZSM-5 was obtained by homogeneously mixing of graphite particles and NiZSM-5 in 3:1 mass raito and then paraffin oil was added drop-wise unitl a uniformly wetted paste was obtained. A portion of prepared paste was packed in to the end of a glass tube and the electrical connection was implemented with a copper wire lead fitted in to the glass tube. In order to incorporate more Ni(II) ions in to the zeolite modified carbon paste electrode the modified electrode was immersed in 1 M Ni solution for 20 min. The CPE, used for comparison, was prepared in the same was but omitting the zeolite addition step.

3. Results and discussion

3.1. Electrocatalytic oxidation of methanol at the surface of Ni/NiZSM-5/CPE

In order to further clarify the electrochemical oxidation mechanism of methanol on the surface of proposed electrode, the effect of methanol concentrations on the cyclic voltammetric responses of this electrode was investigated (Fig 1A). As shown at Fig.1B, in low concentration of methanol, there are two anodic peak; a_1 (assigned to the couple α-$Ni(OH)_2$ /NiOOH) and a_2 (assigned to the couple β-$Ni(OH)_2$ /NiOOH). The catalytic peak a_2 results from the anodic oxidation of $Ni(OH)_2$ formed from reaction (1).

$$NiOOH + methanol \leftrightarrow Ni(OH)_2 + products \quad (1)$$

$Ni(OH)_2$ have two different crystallographic forms, α-$Ni(OH)_2$ and β-$Ni(OH)_2$. The α-$Ni(OH)_2$ is firstly oxidized to NiOOH (anodic peak a_1) through the electrode reaction (2).

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad (2)$$

In an alkaline medium; then the generated NiOOH is reduced to β-$Ni(OH)_2$ by methanol through the chemical oxidation- reduction reaction (1). Subsequently, this β-$Ni(OH)_2$ is converted to NiOOH at higher potentials, leading to the appearance of a new anodic peak (a_2). Therefore corresponding electrode reaction involved in the anodic peak a_2 might be:

$$\beta\text{-}Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad (3)$$

Fig. 1B shown that when methanol concentration increases, the current density of the peak a_2 increases significantly, while the peake a_1 decreases and even disappears. Increasing of methanol concentration makes more NiOOH to be consumed through the reaction (1). Therefore reaction (3) will proceed at higer current densities, because more β-$Ni(OH)_2$ is to be oxidized.

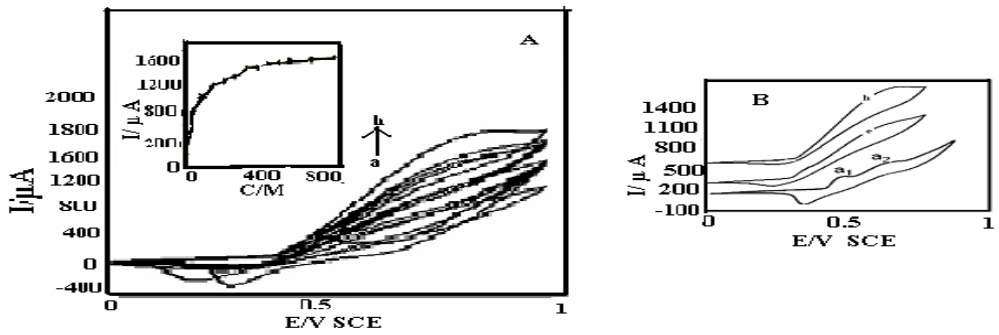

Fig. 1. (A) cyclic voltammograms of Ni/NiZSM-5/CPE in the presence of various concentration of methanol (a) 0.0, (b) 0.02, (c) 0.05, (d) 0.073, (e) 0.123, (f) 0.172, (g) 0.221, (h) 0.293 M, in 0.1 NaOH solution at scan rate 20 mvs^{-1}, (B) zoomed voltammograms of (b(, (c), (h) from main panel A.

3.2. Chronoamperometric study

The chronoamperometriy as well as the other electrochemical methods was used for the examination of electrode processes at proposed modified electrodes. Fig. 2, shows chronoamperograms of methanol at Ni/NiZSM-5/CPE. This figure represents the current-time profiles obtained by setting the working electrode potential at 0.7 V (in first step) and 0.35 V (in second step) vs SCE in the 0.1M NaOH solution for various concentrations of methanol. The forward and backward potential step chronoamperometry of the modified electrode in the blank solution that showed an almost symmetrical chronoamperogram with almost equal charges consumed for the oxidation and reduction of the surface confined Ni(II)/Ni(III) sites (fig 2A(curve a′)). However, in the presence of methanol, the charge value associated with the forward chronoamperomtry, Q is greater than that observed for the backward chronoamperometry (fig. 2A(curve c′)).The rate constant for the chemical reaction between the redox site on the modified electrode and methanol can be calculated via Cottrel equation as below:

$$I_C/I_L = \gamma^{1/2}\,[\pi^{1/2}\,\mathrm{erf}\,(\gamma^{1/2}) + \exp(-\gamma)\,\gamma^{1/2}/ \qquad (1)$$

Where I_C is the catalytic current of the Ni/NiZSM-5/CPE in the presence of methanol, IL is the limiting current in the absence of methanol and C_0t ($\gamma = K C_0$ is the bulk concentration of methanol) is the argument of the error function. In cases where γ exceeds 1.5, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_C/IL = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kC_0t)^{1/2} \qquad (2)$$

Where K, C_0 and t are the catalytic rate constant ($cm^3.s^{-1}.mol^{-1}$), methanol concentration (mol cm^{-3}) and time elapsed (s), respectively. We can simply calculate the value of K for a given concentration of substrate from the slop of the I_C/I_L vs $t^{1/2}$ plot. The inset (B) of fig.2 shows one such plot, constructed from the chronoamperogram of the Ni/NiZSM-5/CPE in the absence and presence of 0.1M methanol. The mean value for K found to be 2.64* $10^5 cm^3 s^{-1} mol^{-1}$.

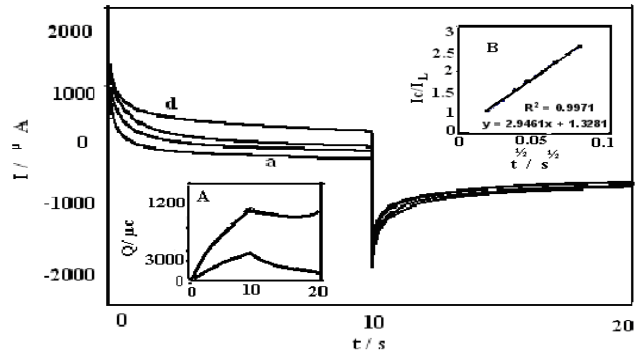

Fig. 2. choronoamperograms obtained at the Ni/NiZSM-5/CPE in the absence(a) and presence of (b) 0.06, (c) 0.014 (b) 0.005 M of MeOH in 0.1M NaOH solution. First and second potential steps were 0.7 and 0.35V vs reference electrode. inset (A) dependence of charge (μC) verses t , (a′) and (c′), derived from the data of chronoamperograms of (a) and (c), receptivity. Inset (B) dependence of I_C/I_L on t½, derived from the data of choronoamperograms of (a) and (c).

4. conclusion

Current study was reported the applications of synthesizes ZSM-5 zeolite to prepare zeolite modified electrode for electrocatalytic oxidation of methanol. The results were show that zeolite modified carbon paste electrode was suitable for the electrocatalytic oxidation of methanol. Also, the catalytic rate constant (K) value for electrochemical reaction between NiOOH and methanol was obtained from the chronoamprometric method. Which indicates the modifiled electrode can overcome the kinietic limitation by catalytic process and can decrease the overpotential of electrooxidation of methano in an alkaline medium.

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