

Novel nano-zeolite modified carbon paste electrode for electrocatalytic oxidation of methanol

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Abstract Methanol is used as a fuel in the direct methanol fuel cell. Direct oxidation of methanol encounters large overvoltages at most unmodified electrode surfaces. The development of new procedures for electrocatalytic oxidation of methanol to decrease this overvoltage is therefore very desirable. In this paper, we report a new zeolite-modified carbon paste electrode based on Ni-ZSM-5 for methanol electrooxidation. Nanocrystallites of ZSM-5 (Si/Al of 50) with average particle size of 58 nm were synthesized using clear solutions at low temperature (90 °C) under atmospheric pressure. Ni(II) ions were incorporated into the zeolite by immersion of the modified carbon paste electrode with synthesized zeolite in a 1.0 M nickel chloride solution. Cyclic voltammetry showed that by using nano-sized zeolite, the oxidation current increased compared with that of micron-sized zeolite crystallites.

Keywords Zeolite modified electrode · Nanocrystal · Cyclic voltammetry · Electrooxidation

Introduction

Direct fuel cells as a novel energy conversion device are attractive for use in portable power generator applications owing to their convenient transportation and storage,

simplified systems, high energy density, etc. [1–3]. In the direct methanol fuel cell (DMFC), methanol is used as a fuel, and it is important to develop a new procedure for electrocatalytic oxidation of methanol in order to decrease the large overvoltages encountered in its direct oxidation at most unmodified electrode surfaces. The selection of possible materials and efficiency of the fuel cell increase in alkaline solutions [4, 5] and considerable efforts have been directed towards the study of electrooxidation of methanol in alkaline solution. The mechanism and kinetics of methanol oxidation have been studied under various conditions using different electrodes including Pt [6], modified electrodes [7, 8], nanocomposites [9, 10], and nickel [11–13]. Studies show that nickel-based electrodes exhibit high stability in alkaline solution together with excellent catalytic efficiency for oxidation of various organic materials [11–14].

Microporous zeolite materials exhibit interesting physical and chemical properties such as sorption, ion exchange capacity, and catalytic activity in various reactions [15–18]. Zeolites with particle sizes of less than 100 nm are referred to as nano-sized zeolites. Zeolite nanoparticles are more efficient catalysts and adsorbent materials because of their higher surface areas compared with the conventional micron-sized zeolites. Reducing the particle size decreases the diffusion path lengths and makes active sites more readily accessible [19–22]. Among all zeolite types, ZSM-5 is important both from industrial and academic points of view owing to its unique shape selectivity, acidity, thermal stability, and applications in the petrochemical industry, oil refinery, and environmental catalysis [23–27].

This paper introduces a novel zeolite modified electrode based on Ni modified ZSM-5 nanocrystallites for electrocatalytic oxidation of methanol. Nano-sized crystallites of ZSM-5 zeolite were synthesized at low temperature and characterized by means of XRD, FT-IR, and SEM

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analytical techniques. The carbon past electrode was manufactured by adding as-synthesized nanocrystallites and modified by Ni(II) ions. We show that Ni(II) ions incorporated into the ZSM-5 carbon paste modified electrode (MCPE) can be used for effective electrocatalytic oxidation of methanol in alkaline solution.

Results and discussion

Characterization of synthesized nanocrystalline ZSM-5 zeolite

The XRD pattern of the synthesized sample is illustrated in Fig. 1. By comparison of the main peaks at $2\theta = 7.9, 8.9, 23.3,$ and 24.05° with those of the reference sample [16–22] the crystallization of almost pure nano-MFI phase was ascertained.

The infrared spectrum of the synthesized sample is shown in Fig. 2. IR bands at 451, 544, and a broad band at $1,222\text{ cm}^{-1}$, which is assigned to a ZSM-5 structural vibration [16, 26], provide further evidence of the successful synthesis of ZSM-5. A SEM image of the sample is illustrated in Fig. 3. Synthesis of spherical crystallites with average particle size of $\sim 58\text{ nm}$ can be ascertained.

Electrocatalytic oxidation of methanol on the modified electrode

Typical results obtained for a potential scan from 0.0 to 0.8 V versus Ag|AgCl|KCl (3 M) are shown in Fig. 4. The electrochemical responses of ZSM-5/MCPE in the absence and presence of 0.1 M methanol in the alkaline solution are shown in Fig. 4a, b, respectively. From this figure one can see no effect on the electrochemical response of the ZSM-5/MCPE. The electrochemical response of Ni-ZSM-5/MCPE in 0.1 M NaOH solution exhibits well-defined anodic and cathodic peaks (Fig. 4c) associated with the

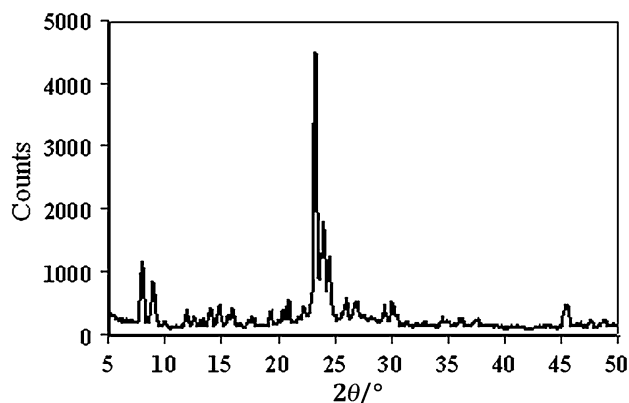


Fig. 1 XRD pattern of synthesized nanocrystalline ZSM-5 zeolite

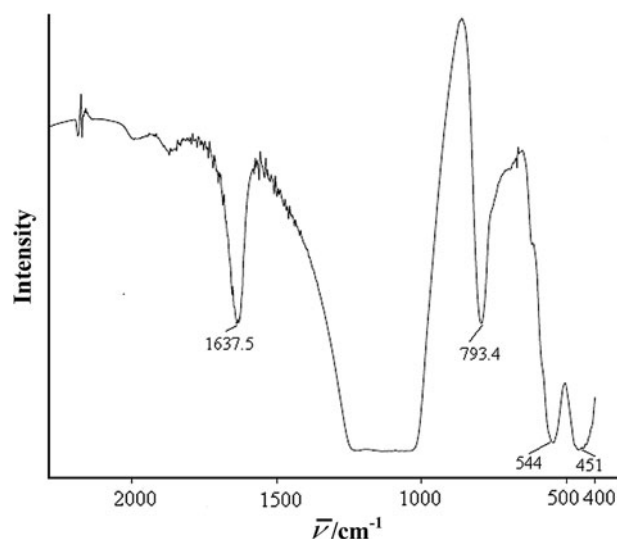


Fig. 2 FT-IR spectrum of synthesized nanocrystalline ZSM-5 zeolite

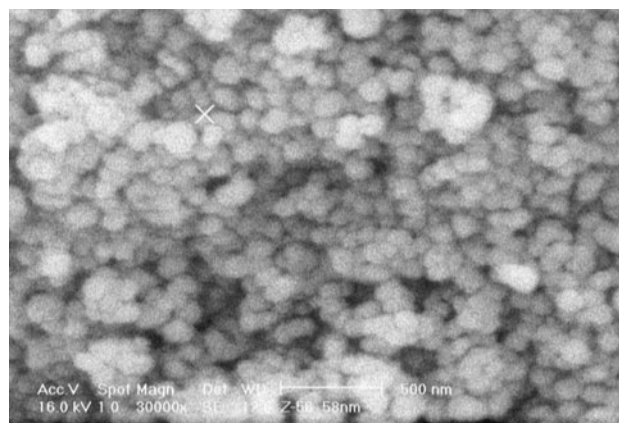


Fig. 3 SEM image of synthesized nano-sized ZSM-5 zeolite

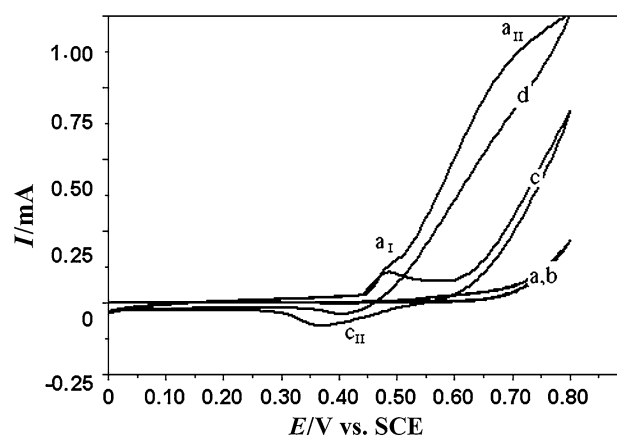
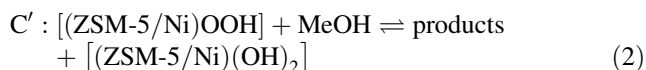


Fig. 4 Electrochemical responses of ZSM-5/MCPE in 0.1 M NaOH in a absence and b presence of 0.1 M MeOH and Ni/ZSM-5/MCPE in c absence and d presence of 0.1 M MeOH at scan rate of 20 mV s^{-1}

Ni(II)/Ni(III) redox couple and oxygen evolution reaction at about 0.7 V. Electrooxidation of a 0.1 M solution of methanol over the prepared modified electrode at a scan rate of 10 mV s^{-1} is shown in Fig. 4d. The main effects observed upon the addition of methanol to the electrochemical cell are an increment in the anodic peak (P_{a1}) followed by the new anodic peak (P_{an}) at a more positive potential and a clear decrease of the cathodic peak current (P_{c1}) during the reverse scan. We believe that the added modifier of Ni-ZSM-5 [i.e., $(\text{Ni-ZSM-5})(\text{OH})_2$] as the active component promotes the electrooxidation of methanol in NaOH solution. Methanol oxidations occur in two regions, the first of which is attributed to where Ni(III) species begin to be produced. At the applied potential, increasing of P_{a1} along with a decrease in cathodic peak current in the negative sweep can be considered as evidence of oxidation of methanol (an EC' mechanism). The remarkable decrease of the cathodic peak height in the presence of methanol is attributed to partial consumption of nickel oxy-hydroxide species for the oxidation of methanol through the formation of nickel hydroxide according to the following reactions:



This indicates that the electrocatalytic oxidation of methanol was carried out directly with the applied modifier. In the second region of the potential, where only Ni(III) species exist, a sharp anodic peak (P_{an}) with a large peak current appears. This anodic peak P_{an} at more positive potentials leads us to the conclude that the oxidation of methanol takes place after the oxidation of Ni(II)/Ni(III), as was reported by Taraszewska and Roslonek [28]. In this way, there is a separation of the Ni(II)/Ni(III) oxidation peak from that of methanol oxidation. Higher catalytic efficiency of the synthesized zeolite nanoparticles toward electrooxidation of methanol was ascertained in comparison with a synthesized micron-sized ZSM-5. The oxidation current achieved by using nanocrystalline zeolite increased by a factor of 1,000 in comparison with the electrode modified by using micron-sized zeolite crystals (Fig. 5). This efficient result can be attributed to the larger surface areas of nanocrystalline ZSM-5 which reduced the diffusion path lengths in comparison with those of common micron-sized ZSM-5 zeolite. Furthermore, these nano-sized crystallites can adsorb more Ni ions into their surfaces, cavities, and channels and, therefore, more catalytically active sites will be available for oxidation of methanol.

In conclusion nano-sized crystallites of ZSM-5 zeolite with average particle size of 58 nm were successfully

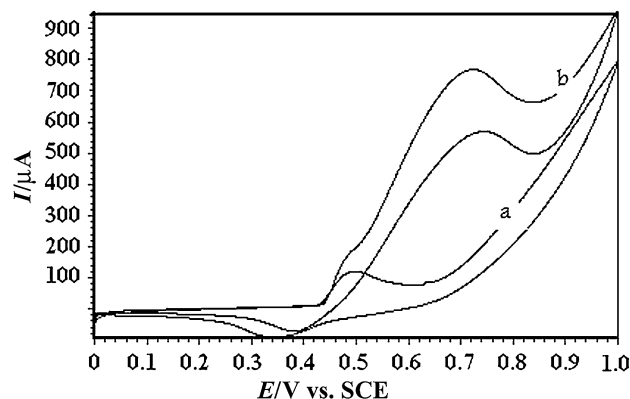


Fig. 5 Electrochemical responses of the Ni/ZSM-5/MCPE in 0.1 M NaOH in *a* absence and *b* presence of 0.1 M MeOH at scan rate of 20 mV s^{-1}

synthesized under mild conditions at 90°C . These crystallites were used for preparation of a novel nano-zeolite modified carbon paste electrode (ZMCPE) for effective electrocatalytic oxidation of methanol in alkaline solution. The novel ZMCPE impregnated with nickel ions has been described herein. The oxidation current achieved by using nano-crystalline zeolite increased compared with that of the electrode modified by using micron-sized zeolite crystals.

Experimental

Materials

The used silicon source was tetraethyl orthosilicate (TEOS) (>98%, GC, Merck) and the aluminum source was aluminum isopropoxide (Sigma-Aldrich). Tetrapropylammonium hydroxide (TPAOH, 20 wt% aqueous solution, Merck), as an organic template, was utilized to synthesize the zeolite. Sodium hydroxide and methanol were analytical grade (Merck). High viscosity paraffin (density 0.88 g cm^{-3} , Fluka) was used as the pasting liquid for the CPE. Graphite powder (particle diameter 0.10 mm, Merck) was used as the working electrode (WE) substrate.

Nanocrystalline ZSM-5 synthesis

ZSM-5 was synthesized hydrothermally by using a clear solutions approach described by Van Grieken and co-workers [24]. The molar composition of the prepared clear TPAOH/ Al_2O_3 / SiO_2 / H_2O / EtOH / Na_2O solution was 5:0.25:25:480:100:0.1. Appropriate amounts of H_2O , NaOH, TPAOH, and aluminum isopropoxide were mixed and agitated at 0°C for 4 h to achieve a clear solution. TEOS was then added dropwise and agitated at room temperature

for several hours to achieve complete hydrolysis of TEOS. The achieved sol was heated in an oil bath at 90 °C under atmospheric pressure (reflux) for 48 h. The product was then recovered by centrifugation at 12,000 rpm for 30 min, washed with deionized water, and dried at 120 °C for 10 h. The ZSM-5 crystals were calcined at 550 °C under air flow to remove the template.

Instrumentation

The X-ray diffractogram of nanocrystalline ZSM-5 was measured by using an X-ray diffractometer (GBC MMA instrument) with Be-filtered Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) at 35.4 kV and 28 mA with a scanning speed of $2\theta = 10^\circ \text{ min}^{-1}$. For phase identification purposes, automatic JCPDS library search and match were used. The FT-IR spectrum was recorded at room temperature using an FT-IR spectrometer (Vector 22-Bruker), in the range of 450–2,000 cm^{-1} with a resolution of 2 cm^{-1} as a KBr pellet. Morphology and particle size of the synthesized zeolite were determined using a JEOL JXA-840 scanning electron microscope.

Electrochemical experiments were performed on a Metrohm 746VA trace analyzer potentiostat with a Metrohm voltammetry cell in a three-electrode configuration. A saturated calomel electrode (SCE) was used as the reference electrode, a platinum wire as the auxiliary electrode, and a homemade carbon paste electrode (ca. 3.4 mm internal diameter) as the working electrode.

Electrode preparation and electrochemical experiments

A mixture of 0.1 g of nano-sized ZSM-5, 0.4 g of graphite powder, and paraffin was blended by hand mixing with a mortar and pestle for preparation of the zeolite modified carbon paste (ZSM-5/MCP). The resulting paste was then inserted in a glass tube. The electrical connection was implemented by a copper wire lead fitted into the glass tube. In order to incorporate Ni(II) ions into the zeolite modified carbon paste electrode (ZSM-5/MCPE), the zeolite modified electrode was placed at open circuit in a well-stirred aqueous solution of 1.0 M NiCl₂. Accumulation of nickel ions was carried out by ion exchange between Ni(II) ions with Na⁺ present in the channel and cavities of zeolite framework for 10 min (accumulation time). The oxidation of methanol was first studied at ZSM-5/MCPE (without the

incorporation of nickel ions) by cyclic voltammetry in 0.1 M NaOH solution. The obtained results for ZSM-5/MCPE were compared with those of Ni-ZSM-5/MCPE.

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