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Synthesis and characterization of nano-ZSM-5 zeolite and its application for electrocatalytic oxidation of formaldehyde over modified carbon paste electrode with ion exchanged synthesized zeolite in alkaline media

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Dedicated to Prof. Carmine Colella on the occasion of his 70th birthday.

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ABSTRACT

This study reports the synthesis and characterization of template free nano sized ZSM-5 zeolite. The Synthesized ZSM-5 zeolite with an average particle size of 60 nm was synthesized using clear solution at 180 °C under autogenously pressure. The synthesized zeolite was characterized using X-ray diffraction, FT-IR and scanning electron microscopy techniques. Then it was used to prepare a new zeolite-modified carbon paste electrode (ZMCPE) based on the Ni-MFI type zeolite for formaldehyde electrocatalytic oxidation. The incorporation of Ni (II) ions into the zeolite framework was done by the immersion of synthesized zeolite in a 0.5 M nickel chloride solution for 5 h. After the preparation of modified carbon paste electrode using the synthesized zeolite, the electrocatalytic oxidation of formaldehyde in alkaline solution was investigated using the cyclic voltametry method. Transfer coefficient ($\alpha = 0.51$) as a kinetic parameter was calculated.

1. Introduction

Fuel cells are being considered as an important technology that can be used for various power applications. Recently, much attention has been paid to the electrooxidation of small organic molecules which are regarded as promising future power sources for mobile and portable applications [1,2]. Formaldehyde, has prompted its use as a model to gain insight into the processes of the electro-oxidation of small molecules, a subject of long-term interest in the development of the fuel cell technology [3]. The mechanism of formaldehyde oxidation has been studied under a wide range of conditions and over various electrodes including binary and ternary alloys [4], pt and polymeric modified electrodes [5,6]. The use of zeolites as supported electrodes represents a good feature for preparation of modified electrodes for fast, easy and cheap for electrooxidation of fuels in fuel cells. The zeolite nano particles are more efficient catalysts and adsorbent materials because of their higher surface areas compared to the conventional micron size zeolites. By reducing the particle size, the diffusion path lengths will decrease and active sites will be accessible readily [7–13]. Among all zeolite types, ZSM-5 is important both from industrial and academic point of view due to its unique shape selectivity property, acidity, thermal stability and application in petro-chemical industry, oil refinery and environmental catalysis [14–17]. The current study intends to introduce a novel zeolite modified carbon paste electrode based on Ni modified template free synthesized nano ZSM-5 crystallites for the electrocatalytic oxidation of formaldehyde. The electrocatalytic oxidation of formaldehyde on the mentioned home-made electrode was investigated using the cyclic voltametery technique.

2. Experimental

2.1. Materials

The used aluminum source was sodium aluminate salt (>63% Al_2O_3, Fison Co.) and the silicon source was silica sol (Sigma–Aldrich). Sodium hydroxide and formaldehyde were the analytical grade of Merck origin. High viscosity paraffin (density: 0.88 g cm^{-3}, Fluka) was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter: 0.10 mm, Merck) was used as the working electrode (WE) substrate.

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2.2. Template free synthesis of nano-zsm-5 zeolite

A mixture of 0.35 g NaOH and 0.147 g sodium aluminate salt in H_2O was aged for 5 h. Then 6.6 g silica sol was added dropwise and the resulting mixture was stirred at room temperature for 1 day. After that, the homogenous mixture was heated for 24 h at 180 °C under autogenously pressure. The solid product was centrifuged and washed with dionized water until its pH reached 8. After drying the synthesized nano crystalline zeolite, an appropriate amount of it was immersed to 0.5 M $NiCl_2$ solution to obtain Ni ion doped ZSM-5 solid.

2.3. Instrumentation

The X-ray diffractogram of nanocrystalline ZSM-5 was measured by using an X-ray diffractometer (XRD, GBC MMA Instrument) with Ni filtered Cu K_α radiation (λ = 1.5418 Angestroem) at 35.4 kV and 28 mA with a scanning speed of $2\theta = 10^\circ$ min^{-1}. For phase identification purposes, automatic JCPDS library search and match were used. FT-IR spectrum was recorded at room temperature using FT-IR spectrometer (Vector 22-Bruker), in the range of 450–1500 cm^{-1} with a resolution of 2 cm^{-1} on KBr pellet. Morphology and particle size of the synthesized zeolite was determined using a JEOL JXA-840 scanning electron microscope.

The electrochemical experiments were performed on a potentiostat/galvanostat (sama 500-c Electrochemical Analysis system, sama, Iran). SCE was used as the reference electrode, a platinum wire as the auxiliary electrode, and a home-made carbon paste electrode (ca. 3.4 mm internal diameters) as the working electrode.

2.4. Electrode preparation

A mixture of 30% of nanosized NiZSM-5, 70% of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for the preparation of zeolite modified carbon paste [ZMCP]. 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 more Ni (II) ions into the zeolite modified carbon paste electrode [ZMCPE], the zeolitic modified electrode was placed at an open circuit in a well-stirred aqueous solution of 0.5 M $NiCl_2$ for 5 min. The carbone paste electrode (CPE) used for comparison was prepared in the same way but omitting the zeolite addition step. The oxidation of Formaldehyde was studied at CPE and NiZSM-5/CPE by cyclic voltametric experiment in a 0.1 M NaOH solution; then the obtained results were compared with each other.

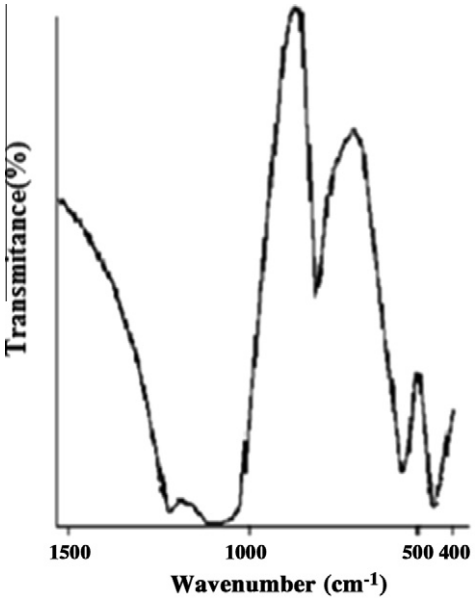

Fig. 1. FT-IR spectrum of synthesized nano crystalline ZSM-5 zeolite.

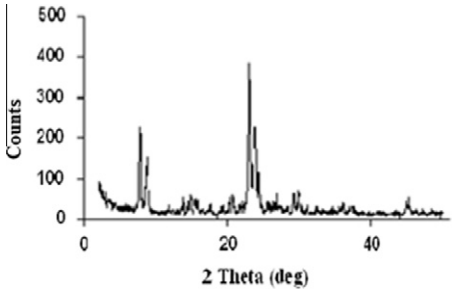

Fig. 2. X-ray difractogram of synthesized nano crystalline ZSM-5 zeolite.

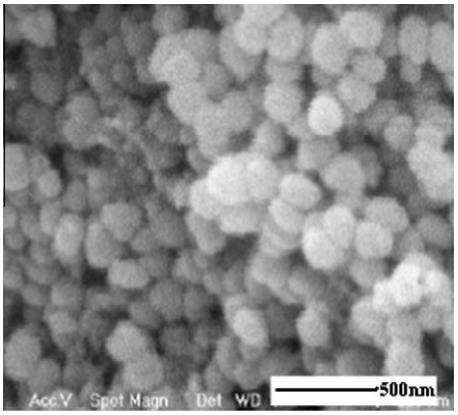

Fig. 3. SEM image of synthesized nano crystalline ZSM-5 zeolite.

3. Results and discussion

3.1. Characterization of the synthesized nano-ZSM-5 zeolite

The FT-IR spectrum of the synthesized sample is shown in Fig. 1. The bands around 790, 1080 and1200 cm^{-1} are characteristics of TO_4(T = Si, Al)tetrahedron units. The band near 790 cm^{-1} is assigned to the symmetric stretching of external linkages and the one near 542 cm^{-1} is attributed to a structure-sensitive vibration caused by the double five-member rings of the external linkages

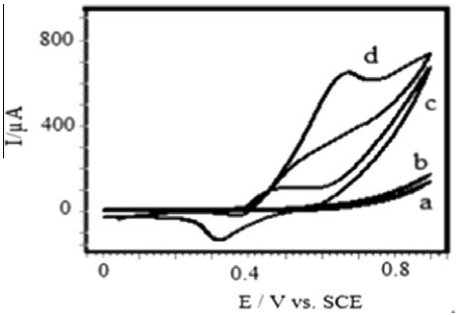

Fig. 4. Cyclic voltamogram of carbon paste electrode (CPE) in the (a) absence and (b) presence of 5 mM formaldehyde and zeolite modified electrode (Ni/NZMCP) in the (c) absence and (d) presence of 5 mM formaldehyde in 0.1 M NaOH at scan rate of 20 mV s^{-1}.