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Electrochemical detection of thiocyanate using phosphate-modified zeolite carbon paste electrodes

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ABSTRACT

Mordenite zeolite with an average size of 17 μm was synthesized hydrothermally from the gel composition of 9.4 Na_2O : Al_2O_3 :40 SiO_2 :1040 H_2O in the absence of organic structure directing agent (OSDA) and without seed addition. The crystallinity, elemental composition, and morphology of the mordenite crystals were confirmed by XRD, EDS and FE-SEM, respectively. The impregnation with phosphate of the synthesized mordenite was achieved by suspending it in aqueous solution of 5 wt.% H_3PO_4 . The effect of the phosphorus impregnation was studied using solid-state NMR. The electrochemical behavior of phosphate mordenite zeolite was investigated in carbon paste via cyclic voltammetry. The optimized composite electrode was used for detection of thiocyanate ions.

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1. Introduction

Zeolites, particularly aluminosilicates, are well known for their industrial application especially in oil refining, petrochemicals and fine chemicals production owing to their large surface area, pore volume, acidity, uniform microporous channel and excellent hydrothermal and chemical stabilities [1]. Mordenite is a high-silica, hydrophobic and 1-dimensional zeolite with the typical composition $\text{Na}_8 \text{Al}_8 \text{Si}_{40} \text{O}_{96} (\text{H}_2\text{O})_{24}$ as first discovered and reported by Meier [2]. The siliceous (high silica content) material, is normally an assembly of channels which were enclosed by 8 and 12-membered rings of SiO_4 and AlO_4 with a unit cell parameters $a = 18.1 \text{ \AA}$, $b = 20.5 \text{ \AA}$ & $c = 7.5 \text{ \AA}$, while the void volume is 0.14 ccg^{-1} (cubic centimeter per gram) and framework density of $17.2 \text{ T atoms} / 1000 \text{ \AA}^3$ (where T is tetrahedral Si or Al) [3,4]. Mordenite has orthorhombic symmetry and belongs to the *cmcm* space group. The framework in the (001) direction contains elliptical micropore ($6.7 \times 7.0 \text{ \AA}$) channels parallel to *c*-axis and ($2.6 \times 5.7 \text{ \AA}$) channels parallel to the *b*-axis leading to the one-dimensional nature as a result of difficulty to sorption of most molecules due to the tightness of the later channels of mordenite [3,5].

The introduction of phosphorus into zeolites has been proven to facilitate the adjustment of acid sites and more effective con-

trol of hydrogen transfer reaction [6–8]. Most of the effort invested on phosphorus modification has been invested to increased para-selectivity during the isomerization of xylene or disproportionation of toluene [6]. In recent years, phosphorus modification of zeolites has been used to enhance the selectivity of lighter olefins [8–15].

Owing to the negative charge in the zeolites framework, potential selectivity should be observed based on the charge on a molecule. Xu et al reported that the absorbed molecules-zeolite interaction, hydrophobicity or hydrophilicity, and ion-exchanged capacity of zeolite can all be altered by changing the framework Si/Al molar ratio [16]. In gas sensors applications, compounds with the desirable sensing property are assembled into the zeolite cages or channels to enhance and modify the intrinsic zeolite property [16]. These intrinsic properties may be coupled with an electrochemical reaction of interest to generate a new responsive electrochemical surface which can be categorized in the so-called chemically modified electrodes (zeolites modified electrodes). The composition, response time, ionic strength, thermal stability, and pH range of the material surface can be electrochemically investigated [17]. The first use of zeolite as a membrane electrode in potentiometric technique led to the eventual advances in zeolite modified electrodes (ZMEs) [18]. Zeolite-modified electrodes received great interest in the late 1980s due to their high stability, low cost, and potential industrial applications [17].

Manea et al successfully established the composition of Ag-doped zeolite expanded graphite-epoxy electrode using cyclic voltammetry (CV). The electrode showed a linear dependence of

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current against the two analytes during the simultaneous determination of nitrites and nitrates in aqueous solution using Multiple-pulse Amperometry [19]. It was investigated and reported elsewhere that the peak current depends on the electroactive surface area from cyclic voltammetry data [20]. The electrochemical mechanism in mordenite zeolite catalytic process in mordenite-poly(ethylene oxide) oligomer electrode was investigated using cyclic voltammetry, the mordenite framework Al-O bond was found to be prone to destruction at high positive potential, owing to the negative charge of the framework aluminum [21–25].

Thiocyanate commonly exists as potassium thiocyanate or sodium thiocyanate. It is a conjugate base of thiocyanic acid. The anion is oxidized to sulfate and cyanide during metabolism in acidic medium by peroxidase [26]. Discrimination of tobacco smokers can, therefore, be made by thiocyanate measurement for its high production due to tobacco smoke degradation [27]. Higher concentration of thiocyanate might lead to coma condition as it affects the process of dialysis of the protein [28]. Moreover, thiocyanate as part of industrial effluents might present significant toxicity to aquatic lives and hence its detection is a highly important research pursuits. Although spectroscopic and chromatographic approaches have been employed in this experimentation, the ease of preparation, stability, selectivity, and sensitivity of the so-called chemically modified electrode might be advantageous. The electrochemical technique employed for thiocyanate detection depend mainly on the construction of potentiometric sensors. The used of superconducting material based on copper oxide for the oxidation of thiocyanate was reported by Badri and Pouladsaz [28]. However, cyclic voltammetry was used which is less sensitive technique compared to the square wave voltammetry.

The aim of this work was to investigate the behavior of a novel phosphate mordenite carbon paste electrode (PMCPE). The synthesized mordenite was converted into the proton form by ion-exchange using ammonium nitrate solution, afterward, synthesis phosphorus impregnation was carried out. A novel mordenite carbon paste electrode (MCPE) was constructed from the phosphate mordenite. Cyclic voltammetry was used to further investigate the electrode properties. The best new composite electrode was employed in the electrochemical detection of thiocyanate ion via square wave voltammetry.

2. Experimental

2.1. Materials

PTFE-lined autoclave was used in the zeolite synthesis. Silica gel (Sigma-Aldrich grade 7734 pore size 60 Å, 70–230 mesh) was used as a silica source, Sodium aluminate 13404 Sigma-Aldrich was used as an aluminium source. Sodium hydroxide pellets (PRS-CODEX 98%) was used to control pH of the gel. Orthophosphoric acid (Sigma-Aldrich 85%) was used for the post-synthesis impregnation. For the electrochemical characterization, potassium ferrocyanide $K_4Fe(CN)_6$ (BDH chemicals) was used as the analyte in characterizing the electrodes and KCl (anhydrous, Sigma-Aldrich) was used as supporting electrolyte. Sodium phosphate monobasic (anhydrous, Sigma-Aldrich) and sodium phosphate dibasic (anhydrous, Sigma-Aldrich) were used as received. Potassium thiocyanate (Sigma-Aldrich) was used to study the efficacy of the electrode in the electrocatalytic oxidation of thiocyanate. Low viscosity paraffin oil (Fluka chemicals) was used as a binder in the preparation of the carbon paste electrode. Mortar and pestle were used for mixing carbon graphite and phosphate mordenite. Ag/AgCl electrode was used as the reference electrode and a platinum wire as the counter electrode in the electrochemical measurements. All experiments were conducted at room temperature and all

solutions were freshly prepared with double distilled water obtained from labstrong nanopure water distiller (Thermoscientific).

2.2. Synthesis and phosphorus modification of mordenite zeolite

Mordenite synthesis was started according to the gel dispersion procedure reported by Hincapie et al [29]. A gel with composition 9.4 Na_2O : Al_2O_3 :40 SiO_2 :1040 H_2O was treated hydrothermally in a PTFE-lined autoclave at 180 °C for 48 h in the absence of both seed and organic template. The Product was washed several times until the pH became less than or equal to 7. The product was then calcined in an air circulating oven at 550 °C. The proton form (acidic mordenite) was obtained by converting it to ammonium form by ion-exchanged using ammonium nitrate which was calcined to get the pure proton form.

Phosphorus modification was done based on the post-synthesis impregnation procedure reported by Dyballa et al [30]. A predetermined amount of mordenite zeolites was suspended in 1.5 ml of 5 wt. % H_3PO_4 and the slurry was allowed to evaporate by heating at 40 °C after which the product was calcined, which called later 5P-MOR.

2.3. Characterization of the phosphate mordenite

The morphology of the mordenite and phosphates mordenite zeolite was investigated by field-emission scanning electron microscopy (FE-SEM) using LYRA 3 Dual Beam (Tescan). The crystallinity was confirmed by using a diffractometer (Miniflex, Rigaku) equipped with Cu $K\alpha$ radiation (1.5405 Å) at 2θ 5° to 50° using a scan rate of 0.03° per step and a counting time of 3 s for each step. ^{27}Al NMR of both parent and modified samples and ^{31}P NMR of the phosphorus mordenite were conducted to investigate the effect of phosphorus impregnation using Bruker Lamda-200 Multi Nuclear Magnetic Resonance (NMR) Spectrometer with Solid state facility.

2.4. Electrochemical characterization

2.4.1. Preparation of zeolite modified electrode

The phosphate mordenite carbon paste electrode was prepared as after the work of Ardakani et al [31]. A mixture of 100 mg containing a constant amount of 30% low viscosity paraffin oil as a binder and different ratios of the graphite to phosphate mordenite zeolite was mixed manually in a mortar. The Paraffin oil was added by means of a dropper and mixed for 20 min until a uniformly wetted paste was obtained. The paste was then packed into the end of 40 mm Teflon tube at the end of which a 0.1 mm hole electrode contact surface was made. Carbon paste electrodes were prepared in the same way without adding zeolites to the mixture. The amount of the 5P-MOR was varied from 5% to 20% with a constant amount of paraffin oil at 30% while graphite was varied with the zeolite amount. The electrodes were named 0-5P-MCPE, 5-5P-MCPE, 10-5P-MCPE, 15-5P-MCPE and 20-5P-MCPE according to whether the carbon paste electrode contains 0%, 5%, 10%, 15% and, 20% of the 5P-MOR, respectively.

2.4.2. Voltammetric measurement using cyclic voltammetry

The electroactive surface area, the current dependence in ferrocyanide and working potential of the phosphate-mordenite carbon paste electrode were obtained by cyclic voltammetry using a CHI 760E Potentiostat equipped with a three-electrode cell. The phosphate mordenite carbon paste electrode (PMCPE) used as working electrode, a platinum wire used as an auxiliary electrode, and Ag/AgCl used as a reference electrode. The electrochemical behavior of 5P-MCPE was examined in potassium ferrocyanide

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