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Simultaneous electrochemical determination of nanomolar concentrations of aminophenol isomers using nanocrystalline zirconosilicate modified carbon paste electrode

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ABSTRACT

Metallosilicates (Metal = Zr, Ti, and Al) modified carbon paste electrodes were fabricated for the simultaneous electrochemical determination of aminophenol isomers. Among the various nanocrystalline metallosilicates investigated in this study, nanocrystalline zirconosilicate modified carbon paste electrode exhibited the highest electro-catalytic activity with excellent stability, sensitivity, and selectivity. The electrochemical behavior of the aminophenol isomers at nanocrystalline zirconosilicate modified carbon paste electrode was investigated in detail. Under the optimum conditions, a wide linear range was obtained from 60 nM to 500 µM for *p*-aminophenol, 120 nM to 500 µM for *o*-aminophenol and *m*-aminophenol. The detection limit was found to be 26 nM, 30 nM, and 30 nM for *p*-aminophenol, *o*-aminophenol, and *m*-aminophenol, respectively. The analytical performance of the sensor was demonstrated in the determination of aminophenol pollutants present in the different environmental water samples.

1. Introduction

It is very important to develop industrial processes, which are highly sustainable with respect to environment and economical growth. Therefore, significant attempts were made to replace the liquid acid based industrial process with heterogeneous solid acid based catalytic process [1–4]. Solid acids such as zeolites are an important class of crystalline porous materials that have been used for numerous catalytic applications because of their uniform channel size, strong acidity, high thermal/hydrothermal stability, and unique molecular shape selectivity [2,5,6]. Crystalline microporous zeolites find extensive applications in water softening, gas separation, and as acid catalysts in the petrochemical/fine chemical syntheses [1,2,7]. Wide application of zeolites in chemical industries has encouraged researchers to make significant contribution in this area. Till today, 194 types of zeolite framework structures are known [8]. However, catalytic applications of zeolites are limited due to diffusion limitations imposed by the zeolite micropores for large organic molecules. To overcome this limitation, zeolites having intra/inter-crystalline mesoporosity have attracted much attention [5,9]. Activity and life time of the catalysts can be enhanced by decreasing the size of zeolite crystals [10]. Several attempts have been made for the preparation of nanosized zeolites [10–14]. Nanocrystalline zeolites with inter/intra-crystalline mesopores were synthesized using soft templates (ionic/non ionic/neutral/polymeric) and hard templates [4,5,13,15]. In recent years, zeolites have attracted an increasing interest in the construction of sensors and biosensors because of their high surface area, porous nature, and ease of surface functionalization with organic groups. There are several reports available in the literature, where zeolite modified electrodes have been used in the electrochemical detection of important inorganic and organic analytes [16–24]. It has been recently reported that nanocrystalline zeolite significantly improves the sensing capability when compared to bulk zeolite [25]. Application of zeolite in the fabrication of sensors is limited because it does not contain any redox metal in the framework structure. It may further be noted that it is difficult to prepare transition metal framework substituted nanocrystalline zeolites. Only a few reports are available in the literature, which deals with the synthesis and applications of transition metal incorporated nanocrystalline zeolites with inter/intra-crystalline mesoporosity [26–28].

Aminophenol isomers (*o*-aminophenol (o-AP), *p*-aminophenol (p-AP), and *m*- aminophenol (m-AP)) are important industrial raw materials that are widely used as chemical inhibitors, petroleum additives, and synthetic intermediates. As a result, large amount

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of aminophenol isomers is inevitably released into the environment as a pollutant. Hence, these compounds are widely distributed in the ecological environment, especially in water bodies. Aminophenol isomers exhibit toxic effect due to their easy penetration through the skin and membranes of humans, animals and plants, which cause genotoxic, mutagenic, and hepatotoxic effects [29]. Therefore, accurate determination of the aminophenol isomers is very important. Aminophenol isomers usually coexist and interfere with each other due to the similar structures and characteristics. Thus, the simultaneous determination of aminophenol isomers is an interesting and challenging research objective [30,31]. Various analytical techniques have been developed for the simultaneous determination of aminophenol isomers such as gas chromatography [32], high performance liquid chromatography [30], capillary electrophoresis [31], micro fluidic devices [33], and spectrophotometry [34]. Although these methods are sensitive, complicated instruments and time-consuming sample pretreatments are required. Compared to these methods, the electrochemical technique has received a great attention due to its high sensitivity, inherent simplicity, miniaturization, fast response and analysis, good reliability, and inexpensive instrumentation. Some reports are available in the literature, which deals with the single electrochemical determination of o-AP [35,36], or p-AP [37–40]. Only a few reports are available for the simultaneous determination of aminophenol isomers [41–43].

Our research is focused on the synthesis and catalytic/electrocatalytic applications of nanocrystalline zeolites [25,28,44–47]. In this study, Zr/Ti/Al framework substituted nanocrystalline ZSM-5 zeolites (Nano-Zr-ZSM-5, Nano-Ti-ZSM-5, and Nano-Al-ZSM-5) modified carbon paste electrodes were constructed for the electrochemical oxidation of aminophenol isomers. To the best of our knowledge, this is the first report, which deals with the simultaneous determination of aminophenol isomers using nanocrystalline zirconosilicate/titanosilicate/aluminosilicate modified carbon paste electrodes.

2. Experimental Section

2.1. Materials

All chemicals used in the study were of AR grade and used as received without further purification. Tetraethylorthosilicate (TEOS, 98%), titanium (IV) butoxide (TBOT, 98%), tetrapropylammonium hydroxide (TPAOH) and propyltriethoxy silane (PrTES, 97%) were purchased from Sigma Aldrich, India. Zirconium (IV) isopropoxide (ZrIPO, 70% solution in propanol) was obtained from Acros Organics, USA. Aminophenol isomers were purchased from SD Fine Chemical Limited, India. Deionized water from Millipore Milli-Q system (Resistivity 18 MΩcm) was used in the electrochemical studies. Electrochemical measurements were performed in phosphate buffer (*Sorenson's buffer*) solution, which was prepared by mixing NaH_2PO_4 and Na_2HPO_4. The standard phosphate buffer solutions with different pH values (lower or higher) were prepared by adding 0.1 M aqueous H_3PO_4 or NaOH solution to 0.1 M aqueous phosphate buffer solution, while magnetically stirring until the pH of the aqueous solution reached the desired value.

2.2. Synthesis of nanocrystalline zeolite materials

In a typical synthesis of Nano-Zr-ZSM-5, 0.663 g of zirconium (IV) isopropoxide was added to 11.86 g of TEOS and the resultant solution was stirred for 15 min at 300 K until mixture became clear solution (Solution A). PrTES (0.87 g) was mixed with TPAOH (10.68 g) and H_2O (10 mL) to form solution B. Solutions A was added slowly to the solution B, followed by the addition of 26.8 mL of H_2O. The resultant gel was further homogenized for 6 h under stirring at 300 K. The final molar composition of the mixture was 0.93 TEOS/0.07 PrTES/0.02 ZrIPO/0.35 TPAOH/40 H_2O. This mixture was transferred to a Teflon-lined stainless steel autoclave, and hydrothermally treated at 443 K for 5 days under static conditions. The final product was filtered, washed with distilled water, and dried at 373 K. The synthesized material was calcined at 823 K for 6 h under air for surfactant removal. Conventional Zr-ZSM-5 was synthesized by following the above mentioned procedure, but in the absence of PrTES.

In a typical synthesis of Nano-Ti-ZSM-5, 0.42 g of titanium (IV) butoxide was added to 11.47 g of TEOS and the resultant solution was stirred for 15 min at 300 K until mixture became clear solution (Solution A). PrTES (1.24 g) was mixed with TPAOH (9.15 g) and H_2O (9 mL) to form solution B. Solutions A was added slowly to the solution B, followed by the addition of 18 mL of H_2O. The resultant gel was further homogenized for 6 h under stirring at 300 K. The final molar composition of the mixture was 0.9 TEOS/0.1 PrTES/0.02 TBOT/0.3 TPAOH/30 H_2O. This mixture was transferred to a Teflon-lined stainless steel autoclave, and hydrothermally treated at 443 K for 5 days under static conditions. The final product was filtered, washed with distilled water, and dried at 373 K. The synthesized material was calcined at 823 K for 6 h under air for surfactant removal. Conventional Ti-ZSM-5 was synthesized by following the above mentioned procedure, but in the absence of PrTES.

Nano-Al-ZSM-5 was synthesized by following the reported procedure using the molar composition 90 TEOS/10 PrTES/1 Al_2O_3/3.3 Na_2O/25 TPAOH/2500 H_2O [25]. Al-ZSM-5 was prepared in the absence of PrTES.

2.3. Instrumentation

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–60° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer, Netherland, using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA) and a proportional counter detector. Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, USA, Autosorb-IQ volumetric adsorption analyzer. Sample was out-gassed at 573 K for 3 h in the degas port of the adsorption apparatus. The specific surface area of zeolites was calculated from the adsorption data points obtained at P/P_0 between 0.05–0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using the Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV, Japan, to investigate the morphology of the zeolites. The detailed TEM structural analysis of the developed morphologies was carried out using FEI, Tecnai G^2 F30, USA, S-Twin microscope operating at 300 kV equipped with a GATAN Orius CCD camera. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was employed using the same microscope, which is equipped with a scanning unit and a HAADF detector from Fischione (model 3000). The compositional analysis was performed by energy dispersive X-ray spectroscopy (EDS, EDAX Instruments) attachment on the Tecnai G^2 F30. The sample was dispersed in ethanol using ultrasonic bath, and dispersed sample was mounted on a Cu grid, dried, and used for TEM measurement.

2.4. Electrode fabrication

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using Potentiostat-Galvanostat BASi EPSILON, USA. A three electrode electrochemical cell was employed with Ag/AgCl as the reference electrode (3 M KCl), zeolite modified carbon paste electrode (3 mm diameter) as the working electrode,