

Efficient electrocatalytic reduction of nitrite species on zeolite modified electrode with Cu-ZSM-5



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ABSTRACT

The electrocatalytic reduction of nitrite has been studied on the surface of zeolite modified electrode using exchanged ZSM-5 with copper (ME/Cu-ZSM-5). The process of reduction and kinetics studies were investigated through cyclic voltammetry and chronoamperometry techniques. The *i*-*E* characteristics of ME/Cu-ZSM-5 presented the faradic process associated to redox couple Cu²⁺/Cu⁺ with a $\Delta E = 0.064$ V/SCE. On the other hand, voltammetric studies showed that in presence of nitrite, the cathodic peak current of ME/Cu-ZSM-5 increases followed by a decrease in the corresponding anodic current. This indicated that nitrite species were reduced by a cooperative effect of the acidic properties of zeolite and copper that acts as a redox mediator being immobilized on the electrode surface via an electrocatalytic mechanism. Further experiments showed that electrocatalytic activity increases as Si/Al ratio decreases, the electrocatalytic activity was improved when the material Cu-ZSM-5 was calcined prior to electrode preparation. The values of the rate constant of the catalytic reduction of nitrite and the detection limit obtained were 5.9×10^2 cm³ mol⁻¹ s⁻¹ and 1.4×10^{-5} mol L⁻¹, respectively.

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1. Introduction

The nitrite ion, NO₂⁻, is an intermediate species in the nitrogen cycle, resulting from the oxidation of ammonia or from reduction of nitrate [1]. It is used as an additive in some types of food and its occurrence in soils, waters, foods and physiological systems is prevalent [2]. Nitrite species are widely involved in environmental chemistry and public health; its role was recognized long time ago [3]. Although, naturally occurring concentrations of nitrite are usually of no health significance, wastes from fertilizers or intentional additions of nitrite for corrosion control are potential sources of contamination [4,5]. On the other hand, the nitrite can be combined with blood pigments to produce meta-hemoglobin, which leads to oxygen depletion to the tissues [1,6]. In aqueous solutions, nitrite displays pH-dependent homogeneous-phase equilibria, such as the acid–base equilibrium HNO₂/NO₂⁻ (pK_a = 3.16 [7], 3.37 [8]). Therefore NO₂⁻ predominates in neutral/alkaline pH media, while HNO₂ is the dominant species at pH < 2; accordingly, the electrochemical response of an electrode material will be greatly affected by the

shift from HNO₂ to NO₂⁻ [9–11]. Besides, HNO₂ decomposes to NO in acidic media [10,12,13], which is a reactive molecule on most metal and non-metal electrodes [9–12].

The interest in the electrochemical reduction of nitrite started 10 years ago [14]. The direction electroreduction of the nitrite ion on the most bare electrode surfaces is thermodynamically favorable, however, the charge-transfer kinetics associated with the reaction is slow, consequently, the reduction potential of nitrite is extremely negative [15]. In acidic media, the main focus was on gaseous products: all noble metals react with solution-phase NO (from HNO₂ decomposition) to give N₂O to *E* < -0.1 V vs. SCE [16–18]. Therefore, this electrochemical reduction of nitrite should be catalyzed by a convenient catalyst, which acts like a charged mediator, reducing the potential for nitrite electroreduction [19,20]. In this area, electroreduction of nitrite on modified electrodes, using catalysts such as various metal complexes and polyoxometalates (POM) of both Keggin-type and Dawson-type [15,21–23] are usually immobilized on the electrode surface.

On the other hand, in the so-called zeolite modified electrode (ZME) the charge transfer mediator guest can be immobilized inside of zeolite framework, the ZME's have been employed in oxidation of ascorbic and uric acid, cysteine, methanol and ethanol [24–27], and in the reduction of H₂O₂ [28].

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Particularly, the copper ion in solution and inside of framework of different materials as Cu(II)–hexacyanoferrate(III) and in Dawson heteropolyanion have been employed as charge mediator in the electrochemical reduction of NO_2^- [29–31], however, in these reports the acid media in the solution is necessary for electroreduction of nitrite species, adding HCl or H_2SO_4 . In this context, the ZME modified with Cu-ZSM-5 can be used for this purpose because the redox process attributed to $\text{Cu}^{2+}/\text{Cu}^+$ couple occurs in a potential window between -0.2 and 0.5 V/SCE and the zeolite acid properties [32]. Furthermore, the ZSM-5 zeolite exchanged with Fe^{3+} and Cu^{2+} has been studied in the NO_x removal from gas emissions, pointing out that the system Cu-ZSM-5 showed high catalytic activity and stability in the NO_x reduction to nitrogen [33–36]. So that, the aim of this work is to study the electrocatalytic activity of zeolite modified electrode with zeolite ZSM-5 exchanged with copper toward nitrite electroreduction.

2. Experimental

2.1. Cu-ZSM-5 preparation

The parent zeolite was NH_4 -ZSM-5 with Si/Al ratio = 15 (Zeolyst CBV3024). H-ZSM-5 form was obtained by calcination of parent zeolite on air at 773 K/5 h. The Cu-ZSM-5 was prepared by ion-exchange with a 15% of theoretical exchange; the materials were labeled Cu-ZSM-5. Briefly, 2 g of NH_4 -ZSM-5 were added to a 500 mL of an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.07 M) and stirred for 24 h at room temperature. Then, the solid was filtered, washed three times with de-ionized water and dried at 353 K in air atmosphere. Other NH_4 -ZSM-5 samples from Zeolyst with different Si/Al ratios were also used (25, 40 and 70).

2.2. Working electrode preparation

A polymer suspension was obtained by dissolving 3 mg of poly-methacrylic acid methyl ester, PMMA, (Aldrich, USA) in 1 mL of methyl acrylate, MA, (Aldrich, USA) and 0.2 g of Cu-ZSM-5 or NH_4 -ZSM-5 were added. The resulting mixture was homogeneously dispersed in an ultrasound bath for 30 min. Then, $0.5 \mu\text{L}$ of the resulting suspension were deposited on the surface of glassy carbon electrode and dried with argon at room temperature. The obtained zeolite modified electrodes (ZME) were labeled as ME/Cu-ZSM-5, ME/ NH_4 -ZSM-5 and ME/Cu-ZSM-5C when the zeolite was calcined prior to electrode preparation.

2.3. Solid-state Nuclear Magnetic Resonance ^{27}Al and ^{29}Si MAS

Solid-state ^{27}Al and ^{29}Si Nuclear Magnetic Resonance (NMR) single excitation experiments were performed on a Bruker Avance 400 spectrometer at frequencies of 104.2 and 79.4 MHz, respectively. ^{29}Si NMR spectra were acquired using the combined techniques of Magic Angle Spinning (MAS) and Proton Dipolar Decoupling (HPDEC). Direct pulsed NMR excitation was used throughout, employing 90° observing pulses ($3 \mu\text{s}$) with a pulse repetition time of 40 s. Powdered samples were packed in zirconia rotors. The spinning rate was 5 kHz. Chemical shifts were referenced to TMS. ^{27}Al MAS NMR spectra were acquired using short single pulses ($\pi/12$) and a delay of 0.5 s. The samples were spun at 10 kHz, and the chemical shifts were referenced to an aqueous 1 M AlCl_3 solution.

2.4. Radial distribution function (RDF)

The radial distribution functions were calculated from the full diffraction patterns in order to obtain high values of the angular parameter $h = 4\pi \sin \theta/\lambda$, the diffractogram was measured by step

scanning at angular intervals of 0.08° . For this purpose the X-ray diffraction patterns samples were obtained on a Siemens D500 diffractometer with a molybdenum X-ray anode tube. The $\text{K}\alpha$ radiation (wavelength of 0.70930 \AA) was selected with a diffracted beam monochromator.

2.5. Raman spectroscopy

The Raman spectroscopic measurements were performed at room temperature in a Labram HR800 spectrometer equipped with a laser operating at 784.29 nm, the experiment was obtained in a range between 200 and 1800 cm^{-1} . The microscope used was OLYMPUS BX41 with $100\times$.

2.6. Electrochemical measurements

The electrochemical analyses were carried out at room temperature in a potentiostat-galvanostat VERSASTAT3-400 (Princeton Applied Research). A three-electrode standard electrochemical cell was used for the cyclic voltammetry (CV) measurements at 20 mV s^{-1} . A carbon rod and a calomel (SCE) electrode were used as counter and reference electrode, respectively. Prior to use, the solution was purged with argon for at least 15 min. The i - E characteristics were recorded in the interval from -0.2 V to 0.5 V/SCE. The initial potential was fixed at open circuit potential toward cathodic direction. Solution 0.1 M of NaCl was used as supporting electrolyte.

3. Results and discussion

3.1. Solid-state Nuclear Magnetic Resonance ^{27}Al and ^{29}Si MAS

In a previous work, XRD results of Cu-ZSM-5, did not show major changes in the zeolite framework after copper incorporation [37], however, subtle structural changes cannot be characterized by XRD. In this sense, NMR is most useful as the ^{27}Al and ^{29}Si resonances are very sensitive to chemical environments of aluminum and silicon atoms, respectively. The ^{29}Si MAS NMR spectra displayed in Fig. 1A reveal that the zeolite framework does not change as a consequence of copper incorporation. A careful deconvolution (figure not shown) obtained from spectra reveals the four characteristic peaks associate with the zeolite framework at -113.8 and -107.8 ppm which are normally assigned to resonances from the Si in the SiO_4 tetrahedral around with 4 and 3 Si atoms, i.e., 4Si, 0Al and 3Si, 1Al units, respectively. The shoulder peak centered at about -117.2 ppm is attributed to the existence of crystallographically inequivalent sites in the zeolite. The peak at -103 ppm in the ^{29}Si MAS NMR spectrum could be assigned to the silanols, where the terminal hydroxyl

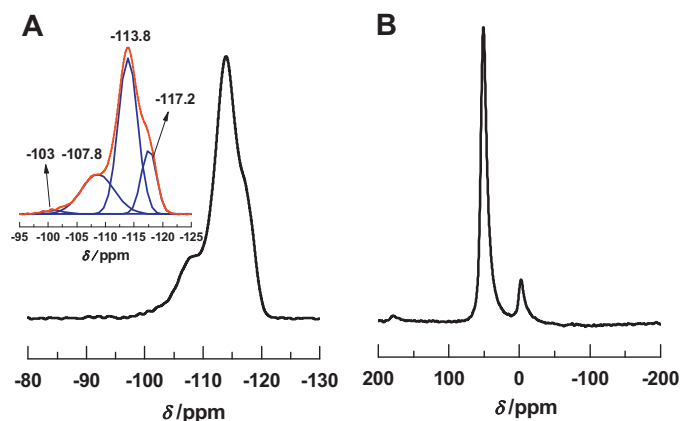


Fig. 1. (A) ^{29}Si MAS RMN and (B) ^{27}Al MAS RMN of Cu-ZSM-5.

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