



Research Paper

Understanding the Electrochemically Induced Conversion of Urea to Ammonia Using Nickel Based Catalysts



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ABSTRACT

In this paper, the mechanism of the electrochemically induced hydrolysis of urea to ammonia (eU2A) at 70 °C in alkaline medium using nickel electrodes was investigated. The intermediates and products in the bulk solution were monitored by Fourier Transform Infrared spectroscopy (FTIR). The intermediates and products of the reaction on the catalyst surface were analyzed by *in-situ* Raman spectroscopy. Urea electrolysis and thermal hydrolysis of urea to ammonia (in the bulk solution) take place in parallel to the eU2A process. The ammonia production rate depends strongly on the amount of nickel oxyhydroxide as well as the concentration of OH⁻ ions. The redox couple of Ni²⁺ and Ni³⁺ ions plays an important role in the mechanism of the reaction.

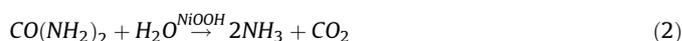
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1. Introduction

The Environmental Protection Agency (EPA) regulation of nitrogen oxides (NOx) emissions is of significant concern these days [1]. To meet the stricter regulations, selective catalytic reduction of NOx using ammonia as reducing agent is proved to be an effective method to eliminate NOx [2]. However, handling ammonia is difficult in most cases since it is toxic and corrosive, thus its transportation and storage becomes costly [3]. Therefore, on-site generation of ammonia from urea has gained attention. Commercial urea to ammonia (U2A) systems have been implemented in power plants [4–6]. However, the U2A process used in power plants requires high temperature and pressure, which creates limitations in mobile engines, especially during start up of the engine. Urea to ammonia reaction could be promoted using catalysts such as urease [7] or a number of oxides such as alumina, silica, and palladium complexes [8,9]. However, these catalysts have limitations including activity and operating temperature. To address these concerns, Botte proposed an electrochemical process to convert urea to nitrogen (N₂), hydrogen (H₂), and ammonia (NH₃) using nickel based electrodes in alkaline media [10]. At certain operating conditions, the conversion of urea to ammonia

–electrochemically induced urea to ammonia, eU2A– dominates the process and minimum N₂ is produced [10].

In previous studies, we have demonstrated that the eU2A is enabled by applying a cell voltage on a Ni anode and Ni cathode at 1.65 V [11]. At relatively low temperature, 70 °C, urea was hydrolyzed to ammonia in alkaline media due to the applied electrochemical potential at higher rates than the thermal hydrolysis of urea at the same conditions. It was proposed that the eU2A takes place according to the following reactions at the anode (Eqs. (1) and (2)) and cathode (Eq. (3)):



It was hypothesized that Ni(OH)₂–(Ni²⁺) undergoes oxidation to its active form NiOOH–(Ni³⁺) which catalyzes the decomposition of urea as per Eqs. (1) and (2). Therefore at 70 °C, the urea to ammonia reaction was induced in the presence of electrochemically produced NiOOH catalyst. Daramola et al. [12] studied the dissociation rates of urea in the presence of NiOOH using density functional theory (DFT) methods. The authors proposed a possible mechanism for the dissociation of urea, in which the urea adsorbs on the catalyst surface and through the H donation on the NiOOH

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catalyst surface could lead to the production of ammonia leaving CNO^- still adsorbed on the catalyst surface [12]. However, the mechanism of the urea decomposition to ammonia via the electrochemical process is still unclear; in particular, the formation of CNO^- has not been investigated experimentally.

The purpose of this paper is to gain a better understanding of the eU2A process in alkaline media. Cyclic voltammetry (CV) was used to analyze the oxidation and reduction processes. Constant potential eU2A experiments were conducted and compared with the thermal hydrolysis of urea (THU) process. *In-situ* Raman spectroscopy was used to monitor the intermediates and products during the reaction on the catalyst surface. *Ex-situ* Fourier Transform Infrared (FTIR) was conducted to identify the intermediates and products in the bulk solution during the reaction. By comparing time-dependent Raman and FTIR spectra for both the eU2A and THU experiments, a promising pathway for the eU2A is proposed.

2. Experimental Methods

2.1. Reagents and experimental setup

Urea (purity, 99.8%) and KOH (purity >85%) used in the experiments were supplied by Fisher Scientific. Ultra-pure water (Alfa Aesar, HPLC grade) was used throughout, unless otherwise specified. As shown in Fig. 1, the electrochemical tests were carried out in a three neck flask using a Solartron 1281 Multiplexer Potentiostat with Ni foil (2.0 cm x 3.0 cm, purity >99%, Alfa Aesar) as working electrode, Ni foil (2.0 cm x 3.0 cm, purity >99%, Alfa Aesar) as the counter electrode, and Hg/HgO as the reference electrode (Koslow Scientific). Both the working and counter electrodes were polished with sandpaper (320 and 600 grits Gator Finishing) to remove any impurities and oxides that could have formed during manipulation (for example, during spot welding of the current collectors) followed by sonication in DI water for 10 min. Ni wires (diameter 1.0 mm, purity 99.5%, Alfa Aesar) were used as current collectors. The current collectors were spot welded on the nickel foils using a Miller[®] resistance spot welder (SSW-2020ATT) operating at 9 A for 1 second. The reference electrode was supported using a Luggin capillary filled with the supporting electrolyte (KOH at the concentration according to each experiment).

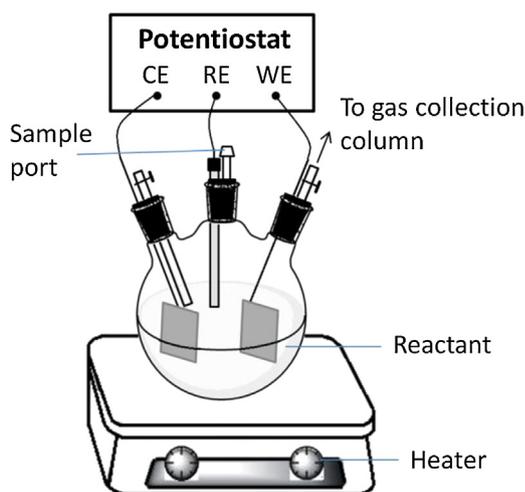


Fig. 1. Schematic representation of the reaction vessel. Both the working and counter electrodes are Ni foil, while the reference electrode is Hg/HgO. Temperature was set at 70 °C. Sample ports allowed collecting gases and liquid.

A total of 125 ml of reactant solution was used for each experiment. The solution was heated to 70 °C using a heat jacket with a temperature controller (Econo Temperature controller 12125-14). All the experiments were conducted at 70 °C unless specified differently, which follows previous investigation by Lu and Botte [11]. The fifth pseudo-steady state voltammograms are reported. All the voltammograms in this study were performed between 0.20 V and 0.65 V vs. Hg/HgO at a scan rate of 10 mV s⁻¹. Constant potential experiments were performed to determine the ammonia production rate as a function of time in the eU2A process. In such experiments, samples of 0.5 ml solution were collected from the reactor every 30 minutes. The concentration of ammonia was measured using an ammonia ion selective electrode as described in Section S1 in Supporting Information (SI). Experiments were also performed at constant temperature without an applied potential, the THU mode. The gases other than ammonia and CO₂ generated during the experiments were trapped in a gas collection column and analyzed by a gas chromatograph (Agilent Technologies 7890 B) equipped with a Molsieve 13X column and a thermal conductivity detector as described in Section S2 in SI.

2.2. Ex-situ FTIR

Ex-situ Fourier Transform Infrared spectroscopy (FTIR) for both the eU2A and THU were conducted using a Bruker Vertex 80 Instrument Spectrum One Fourier Transform Spectrometer. Sampling was performed every one hour by placing 20 μl electrolyte from the bulk solution into a disposable KBr pellet. FTIR spectra were then collected in the wave numbers of 68–4451 cm⁻¹ and the single-beam spectrum of the KBr pellet was acquired before each measurement to compensate for background.

2.3. In-situ Raman Spectroscopy

An *in-situ* electrochemical cell was built to identify the intermediates of the reactions on the catalyst surface during the eU2A process, a schematic of the cell is shown in Fig. 2 and its dimensions are shown in Fig. S3 (refer to SI). The electrochemical tests were carried out using a Solartron 1252A potentiostat in a three-electrode cell setup with Ni foil (1.0 cm x 1.0 cm, purity >99%, Alfa Aesar) as working electrode, Ni foil (0.5 cm x 2.0 cm, purity >99%, Alfa Aesar) as counter electrode, and Hg/HgO as reference electrode (Koslow Scientific). Both the working and counter electrodes were polished with sandpaper (320 and 600 grits Gator Finishing) to remove any impurities and oxides that could have formed during manipulation (for example, during spot welding of the current collectors) followed by sonication in DI

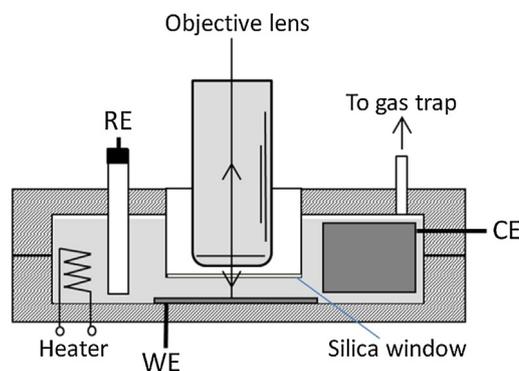


Fig. 2. Electrochemical cell for *in-situ* Raman spectroscopy. eU2A reaction of 5.0 M urea in the presence of 5.0 M KOH at 0.462 V was conducted in the cell at 70 °C. Raman spectra of intermediate species and products were obtained with the laser focused onto the working electrode surface through a silica window.

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