Journal of Energy Chemistry 65 (2022) 367–370

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

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Letter

Cascade electrocatalytic reduction of carbon dioxide and nitrate to ethylamine

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CO_2 utilization, including electrochemical reduction of CO_2 to fuels and useful chemicals, is explored to valorize carbon emissions [1–12]. The value of CO_2 electroreduction products originates from their C–H, C–C, and C–O bonds. To further increase the value and expand the scope of products, it is desirable to integrate C–N bond formation with the electrochemical reduction of CO_2. One of such possibilities is to include nitrate (NO_3^-) as a reactant, whose excessive presence in water can pose risk to drinking water and cause geological issues such as eutrophication [13,14]. The co-reduction of CO_2 and NO_3^- or NO_2^- was initially studied several decades ago and urea was found to be the C–N product [15–18]. More recent efforts include replacing NO_3^- with N_2 in the electrosynthesis of urea and using ammonia (NH_3) or amines as the N source to generate acetamides from the ketene intermediate of the CO reduction catalyzed by Cu [19,20]. In addition, we have recently developed an electrocatalytic reaction that is able to synthesize methylamine from the co-reduction of CO_2 and NO_3^- enabled by a molecular cobalt catalyst loaded on carbon nanotubes [21]. The key step of this cascade reaction is the formation of formaldoxime by the spontaneous condensation reaction between formaldehyde (HCHO) and hydroxylamine (NH_2OH), which are intermediates of the corresponding electrochemical CO_2 and NO_3^- reduction reactions respectively. This initial success inspired us to explore the direct electrosynthesis of ethylamine, which is a widely used aliphatic amine in chemical synthesis and pharmaceutical chemistry [22], from cheap and abundant inorganic reactants such as CO_2 and NO_3^-.

Herein, we report the first electrochemical conversion of CO_2 and NO_3^- to ethylamine, a 20-electron 21-proton reduction cascade (Fig. 1). The reaction proceeds under ambient conditions in a near-neutral aqueous electrolyte catalyzed by oxide-derived Cu nanoparticles (Fig. 1a). Acetaldoxime is identified as the key intermediate to ethylamine (Fig. 1b) and is formed from the condensation reaction between acetaldehyde, an active reaction intermediate for CO_2 reduction to ethanol, and NH_2OH, an active reaction intermediate for NO_3^- reduction to NH_3. Further reduction of acetaldoxime leads to the final product, i.e. ethylamine. Mechanistic analysis indicates that the overall yield of ethylamine is limited by the competing reduction of acetaldehyde to ethanol and NH_2OH to NH_3.

The Cu catalyst is derived in-situ from 8 nm CuO nanoparticles under reductive electrolysis conditions (experimental details are provided in Supporting Information) [23]. Potentiostatic electrolysis at −1 V vs. the reversible hydrogen electrode (RHE; all potentials are referenced to the RHE scale unless otherwise noted) is carried out with the CuO nanoparticles loaded on carbon fiber paper as the working electrode, during which CuO is transformed into metallic Cu with the average particle size increased to 30 nm, as revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Fig. S1). When CO_2 reduction electrolysis is performed in a 1.0 M $KHCO_3$ aqueous electrolyte, various gas and liquid products including H_2, CO, CH_4, C_2H_4, $HCOO^-$, ethanol and 1-propanol are detected (Fig. 2a). The total Faradaic efficiency (FE; all selectivity values are based on FE unless otherwise noted) of CO_2 reduction is ~ 71% including FE(C_2H_4) of 36.3% and FE(ethanol) of 14.3%, which is similar to the selectivity of previously reported oxide-derived Cu catalysts [24–26]. In addition, we have identified small amounts of other C_{2+} products such as acetate, (hydrolyzed) acetaldehyde, 2-propanol and acetone by examining the proton nuclear magnetic resonance (^{1}H NMR) spectrum of the post-electrolysis electrolyte (Fig. S2). This Cu catalyst is also active for NO_3^- reduction. NH_4^+ is generated with a high FE of 73.5% and a partial current density $j(NH_4^+)$ of 40.2 mA cm^{-2} from electrolysis performed at −1 V in an Ar-saturated aqueous electrolyte containing 0.1 M KNO_3 and 1.0 M $KHCO_3$; H_2 is the other product with a FE of 30.5%, and no NH_2OH is detected (Fig. 2a).

These results encouraged us to apply the catalyst to the co-reduction of CO_2 and NO_3^-. Electrolysis at −1 V in a CO_2-saturated 0.1 M KNO_3 + 1.0 M $KHCO_3$ aqueous electrolyte expectedly yields many products (Fig. 2a). In general, CO_2 reduction, H_2 evolution, and NO_3^- reduction are competing reactions in this case (Tables S1, S2). Interestingly, among all the major CO_2 reduction products, the production rates of CO, C_2H_4, $HCOO^-$, ethanol and 1-propanol are barely affected, whereas CH_4 formation is greatly suppressed by the presence of NO_3^- (Tables S1, S2). These different responses to the addition of NO_3^- appear to indicate that there is more than one type of active sites for CO_2 reduction on the catalyst surface.

Despite the complexity in product distribution, the concurrent reduction of CO_2 and NO_3^- is essential for the desired C–N coupling reaction. Indeed, acetaldoxime, which is a 16-electron 17-proton

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https://doi.org/10.1016/j.jechem.2021.06.007

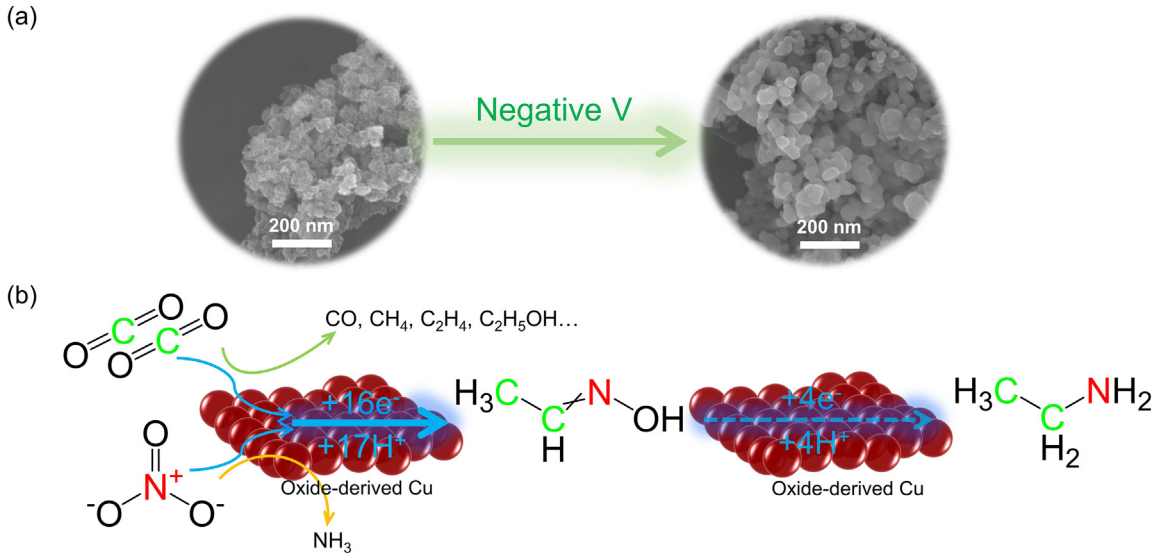

Fig. 1. Schematic illustration. (a) In-situ formation of oxide-derived Cu catalyst under reductive potential. (b) Electrochemical co-reduction of CO_2 and NO_3^- to synthesize acetaldoxime and ethylamine.

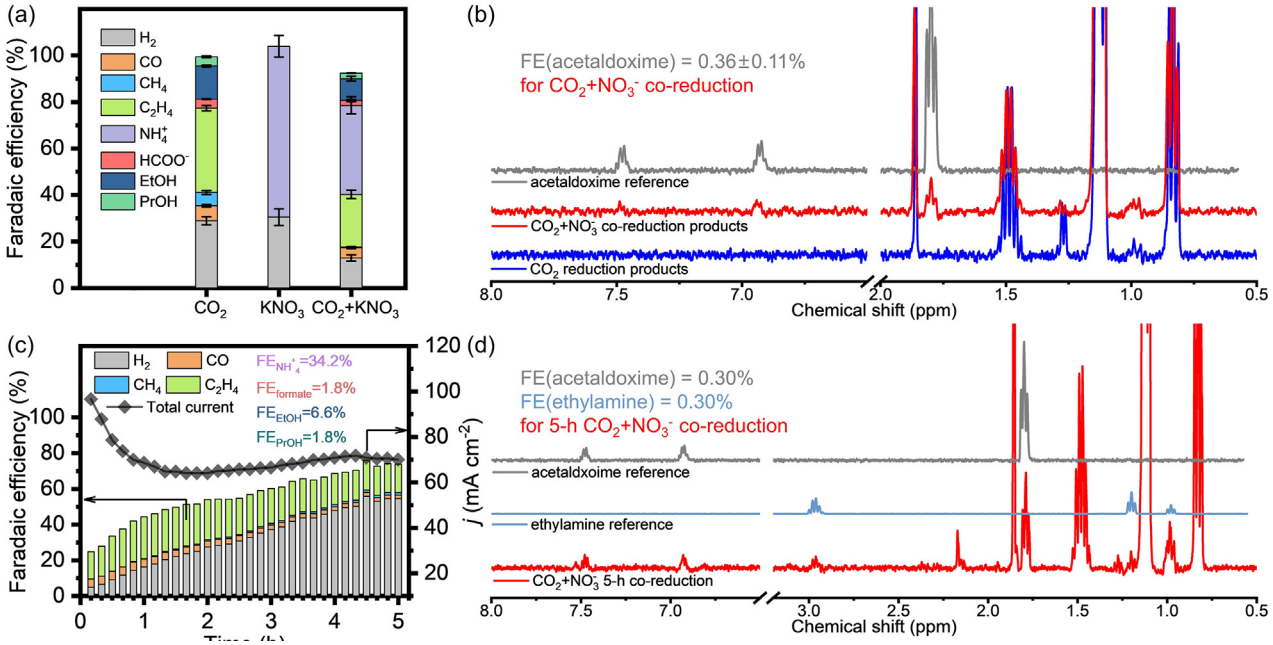

Fig. 2. (a) Product distribution (FE) for CO_2 reduction, NO_3^- reduction, and CO_2 and NO_3^- co-reduction. 1 h electrolyses were performed. (b) ^{1}H NMR spectra of the post-electrolysis solutions corresponding to (a). (c) Product distribution and total current density for a 5 h co-reduction electrolysis; the average liquid product FEs were measured after the electrolysis. (d) ^{1}H NMR spectrum of the post-electrolysis solution corresponding to (c). The standard ^{1}H NMR spectra of acetaldoxime and ethylamine are presented as references in (b) and (d).

reduction product from CO_2 and NO_3^-, is identified by ^{1}H NMR spectroscopy in the electrolyte after 1 h of electrolysis (Fig. 2b, S3), despite its low FE of 0.36%. Increasing the concentration of KNO_3 in the range of 0.04 M to 0.16 M does not seem to improve the production of acetaldoxime (Fig. S4). Extending the co-reduction electrolysis to 5 h causes a gradual increase of FE(H_2) (Fig. 2c), possibly due to proton donation from the NH_4^+ product near the electrode surface. More importantly, in addition to acetaldoxime, ethylamine, a 20-electron 21-proton reduction product, is formed (Fig. 2d, S5). To the best of our knowledge, this is the first direct electrosynthesis of ethylamine from CO_2 and NO_3^-, both of which are environmentally concerning species that need remediation.

Based on our recent discovery that the condensation between HCHO and NH_2OH leads to the formation of formaldoxime and methylamine in electrochemical CO_2 and NO_3^- co-reduction [21], we hypothesized that the formation of ethylamine in this system follows a similar reaction pathway where acetaldoxime is the initial C–N coupling product formed from the acetaldehyde-NH_2OH condensation and further reduction of acetaldoxime yields ethylamine. Acetaldehyde and NH_2OH are known to be reaction intermediates for electrochemical CO_2 reduction to ethanol and NO_3^-

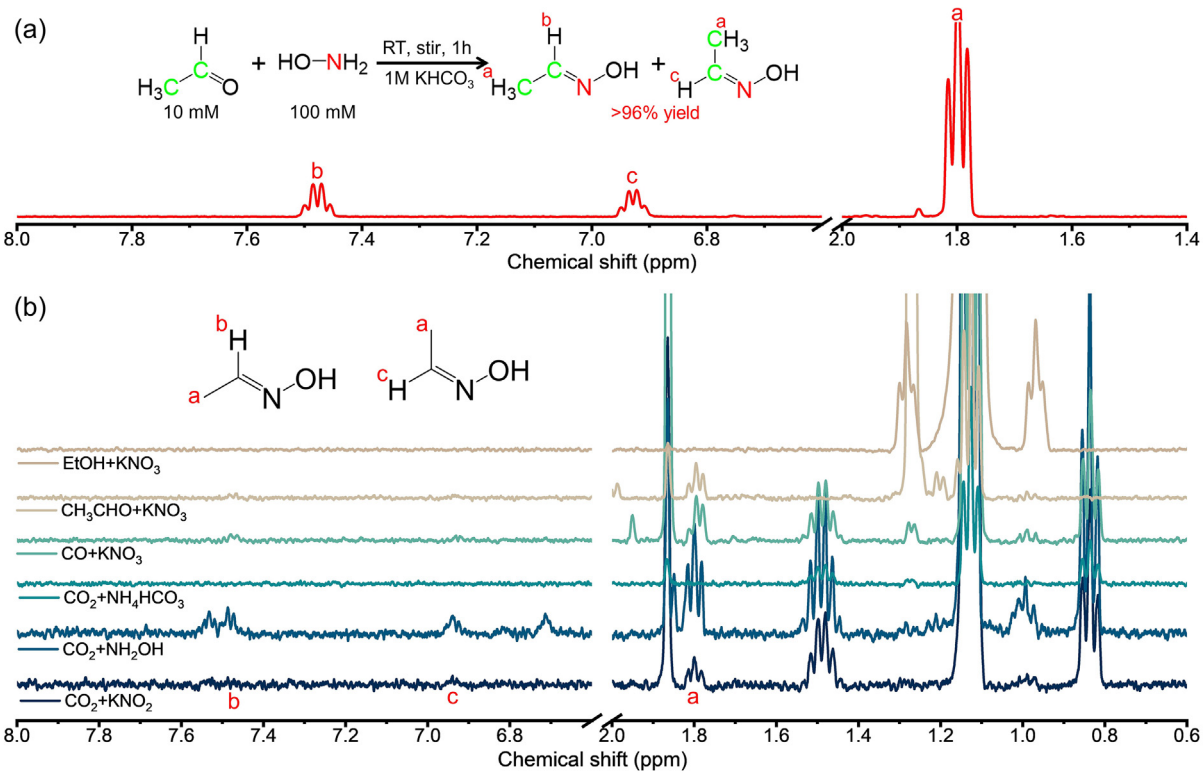

Fig. 3. (a) ^{1}H NMR spectrum of the product solution after mixing acetaldehyde and NH_2OH. (b) ^{1}H NMR spectra of the post-electrolysis solutions after performing potentiostatic electrolyses with varied C and N sources.

reduction to NH_4^+, respectively [27–30]. To test this hypothesis, we first examined the reactivity between acetaldehyde and NH_2OH in 1.0 M aqueous $KHCO_3$ at room temperature and observed over 96% conversion of acetaldehyde in 1 h (Fig. 3a). Secondly, we conducted a series of controlled electrolyses where the C or N source was varied (Fig. 3b, S6 and S7). When CO or acetaldehyde, both of which are intermediates on the pathway of CO_2 reduction to ethanol on Cu [28,31,32], is co-reduced with NO_3^-, acetaldoxime is formed in either case; however, using ethanol as the C source does not yield any acetaldoxime. When NO_2^- or NH_2OH, both of which are intermediates for NO_3^- reduction to NH_4^+/NH_3 [29,33], was co-reduced with CO_2, acetaldoxime formation is confirmed in either case; however, no acetaldoxime is produced in the case of NH_4HCO_3 as the N source. These results confirm that acetaldehyde and NH_2OH are indeed the reactants of the C–N bond formation step. Finally, electroreduction of acetaldoxime was performed, confirming that ethylamine formation from acetaldoxime reduction is plausible under the reaction conditions (Figs. S8, S9). Therefore, as shown in Fig. 4, in the overall reaction from CO_2 and NO_3^- to ethylamine, CO_2 and NO_3^- reduction reactions first proceed separately to acetaldehyde and NH_2OH respectively, and then these two intermediates react chemically to form acetaldoxime which is further reduced to ethylamine.

This catalytic cascade enables the capability to synthesize C_{2+} amines solely from low-cost and abundant inorganic reactants such as CO_2 and NO_3^- powered by renewable electricity, although the yield is still too low for any immediate application. Our analysis suggests that the low yield of ethylamine is caused by several factors. First and foremost, the reduction of acetaldehyde and NH_2OH directly competes with the coupling reaction between these two intermediates. Unfortunately, both reduction reactions are likely to be fast, because acetaldehyde and NH_2OH are barely detected among the final products of separate CO_2 and NO_3^- reduction reactions respectively, which is also supported by the fact that ethanol and NH_3 are generated at much higher rates than acetaldoxime or ethylamine in the co-reduction of CO_2 and NO_3^- (Tables S1, S2). Fast reduction of the coupling intermediates probably poses a substantial limit on the rate of the C–N coupling reaction which requires at least one of the intermediates to migrate. Secondly, the reduction of acetaldoxime to ethylamine is not kineti-

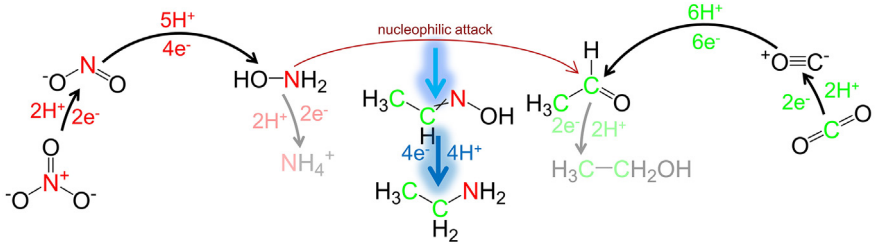

Fig. 4. Proposed reaction pathway to form acetaldoxime and ethylamine from electrochemical co-reduction of CO_2 and NO_3^-. The reaction intermediates shown here have been confirmed experimentally.

cally favorable, which is reflected in the result that ethylamine is only detected as a product after the 5 h electrolysis (Fig. 2). The difficulty of reducing acetaldoxime can also be comprehended by comparing it with other reduction reactions. The FE of H_2 evolution is less than 30% in either CO_2 or NO_3^- reduction (Fig. 2a). However, in the electroreduction of 0.1 M acetaldoxime, the H_2 selectivity is as high as 62% (Fig. S8), which further increases to ~ 90% when the acetaldoxime concentration is reduced to 10 mM (Fig. S9). Therefore, acetaldoxime reduction is significantly slower than CO_2 reduction, NO_3^- reduction, or H_2 evolution. Lastly, the overall yield is also affected by the diverse reaction pathways of CO_2 reduction on Cu. Acetaldehyde, as both a possible product and an intermediate to ethanol [34,35], is not formed with high selectivity, which sets the upper limit for the yield of any product derived from it.

In summary, we have developed the first electrochemical synthesis of acetaldoxime and ethylamine from CO_2 and NO_3^- co-reduction using an oxide-derived Cu catalyst. This reaction provides another successful example of utilizing the C–N coupling reaction between the aldehyde and hydroxylamine intermediates near the electrode surface that are generated from CO_2 and NO_3^- reduction reactions respectively. This work demonstrates the possibility of electrocatalytically synthesizing C_{2+} organonitrogen compounds from cheap and abundant inorganic feedstocks.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the US National Science Foundation (Grant CBET-2028351). Z.T. acknowledges the Tully Graduate Research Fellowship in Chemistry by Yale University. Y.W. acknowledges the Dox Fellowship by Yale University. H.W. acknowledges the Sloan Research Fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2021.06.007.

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