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Research on the Electrochemical Catalytic Reduction Performance of NO to Ammonia with Cu–Co Alloy

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ABSTRACT
Nitric oxide (NO) removal is crucial for mitigating environmental issues such as acid rain, photochemical smog, and ozone depletion. Electrochemical NO reduction reaction (NORR) offers a sustainable pathway to simultaneously eliminate NO and produce value-added ammonia (NH_3), leveraging renewable electricity and operating under mild conditions. In this study, a Cu–Co alloy supported on carbon paper was evaluated as an electrocatalyst for NORR in a three-electrode H-type cell with 3% NO concentration. The performance was compared against bare carbon paper. Results demonstrate that the Cu – Co alloy significantly enhances NH_3 yield and Faradaic efficiency due to improved selectivity and suppression of the competing hydrogen evolution reaction. This work highlights the potential of Cu – Co alloys for efficient NO conversion under low-concentration conditions relevant to industrial exhaust treatment.

KEYWORDS
NO reduction; Electrocatalytic reduction; Ammonia production

1 Introduction

Removal of nitrogen monoxide, mainly generated from combustion of fossil fuels in automobiles and plant [1], is pivotal and urgent for protection of environment since it has various harm including acid rains, photochemical smog, and ozone depletion [2].

Conventional methods to remove nitrogen monoxide are SCR (selective catalytic reduction) and SNCR (selective non-catalytic reduction), where NH_3 is added to convert NO to harmless N_2 [3-4]. Electrochemical NO reduction is promising because electricity can be generated from green energy sources, such as solar, wind, and geothermal power, in addition to moderate reaction condition required. NO can be reduced to numerous products, including NH_3, NH_3OH, amino acids etc. depending on the electrical potential applied [5]. Ammonia is considered valuable industrial ingredient, agricultural necessity, and newly proposed energy source for replacing fossil fuels [6]. However, till now, Harber-Bosch process that needs high energy for high pressure and temperature required is still the main method to produce NH_3 industrially, which poses threat to already depleting unsustainable energy source. Besides, reducing NO to NH_3 has a thermodynamical preference than N_2 reduction to NH_3, another method proposed for ammonia production, as the former one has higher standard reduction potential [7], demonstrating the opportunity for NO reduction reaction (NORR) as a new, efficient method. Therefore, converting NO to NH_3 is advantageous as it removes NO and produces value-added NH_3 simultaneously.

Electrochemical NORR focuses on improvement of conversion efficiency as the main challenge is the competition with hydrogen evolution reaction which most transition metal catalysts favor except Cu, as a result of which foam Cu has been proved to be the metal catalyst with highest NORR reactivity and selectivity. Use of catalyst successfully changes electronic structure and intrinsic thermodynamic activity of reactants, thus improving selectivity, yield, and Faradic efficiency (FE). Theoretical research indicates that Cu is located near the apex of the NORR volcano diagram and is the material closest to the ideal NORR catalyst. However, the intrinsic catalytic activity of Cu is limited, which leads to relatively high adsorption energy for NO, thereby restricting the activity of NORR. Generally, methods to reduce the adsorption energy of Cu include doping second-phase elements into Cu or optimizing its catalytic performance through surface modification. Studies have shown that intermetallic compounds with metal-like properties can effectively regulate electronic structure due to their excellent electrical conductivity and the synergistic effect among metal atoms, thereby enhancing catalytic activity. The crystal structure (hexagonal close-packed Co nanosheets), crystal face (Ni (210)), coordination structure (Ru-LCN), and single-atom catalyst (CuFe DS/NC) has been researched and discussed for different ways to design catalysts, and many catalysts have shown great performance overall. Co, as another common transition metal, has good electrical conductivity and stability at the electroreduction potential. Metal Co is conducive to the dissociation of H_2O and provides the necessary protons to promote the formation of NH_3. However, most of current investigations are based on high concentration of NO, alleviating from real industrial exhaust gas. So, research based on low NO concentration is crucial for this study area [7].

In this paper, comparison is made between Cu-Co alloy on carbon paper and carbon paper itself to test the performance of electrocatalysis of Cu-Co alloy in NO reduction to NH_3 under the condition of 3% NO. This work

underscores the promise of Cu–Co alloy catalysts for efficient NO-to-NH_3 conversion under low-concentration conditions, offering a viable strategy for simultaneous pollutant removal and value-added chemical production in industrial exhaust treatment.

2 Methodology

In this study, the Autolab electrochemical workstation was used to investigate the electrocatalytic reduction reaction process. A three-electrode system was adopted, with the CuCo alloy catalyst electrode as the working electrode (WE), the Ag/AgCl electrode as the reference electrode (RE, the potential conversion to the standard hydrogen electrode is shown in Formula 1), and the Pt sheet electrode (1×1cm) as the counter electrode (CE). This research used three-electrode system in a typical H-type, two-compartment cell using 0.5 M $NaSO_4$ as electrolyte, with one chamber submerging WE (NO in delivery tube) and RE, and another chamber submerging RE. It should be installed as shown in Figure 1. The concentration of NO was introduced at 3% and the flow rate was 10 mL min^{-1}. Before the reaction, Ar gas is introduced for 20 minutes to expel the gas in the electrolyte, and then NO is introduced until the system stabilizes.

$$E_{RHE} = E_{Ag/AgCl} + 0.197V + 0.0591 \times pH \quad (1)$$

Figure 1 Diagram of the electrocatalytic reduction of NO reaction apparatus

Cu-Co alloy powder was synthesized by chemical synthesis method combined with constant current reduction method. Using hydrophobic carbon paper as the substrate, the Cu-Co alloy was coated on the surface of the carbon paper by drop coating method to prepare the catalyst electrode. A period of pre-reduction is carried out before the reaction to activate the catalyst electrode. The research was conducted using carbon paper as the comparison electrode. The reduction product of NO, ammonia, was detected by spectrophotometry. The characteristic absorbance of ammonia at a specific wavelength (697 nm) was determined through a color reaction to establish a linear relationship between absorbance and concentration. The standard curve is shown in Figure 2. Faradic efficiency and ammonia formation rates were calculated using the following equation.

$$FE(\%) = \frac{nFCV}{Q} \times 100\% \quad (2)$$

$$R(NH_3) = \frac{CV}{StM} \quad (3)$$

Here, F is the Faraday constant (96,485 C mol^{-1} e^-), C is the product concentration, V is the electrolyte volume, Q is the total transferred charge, S is the electrode area, t is the reaction time, and M is the molar mass of the product.

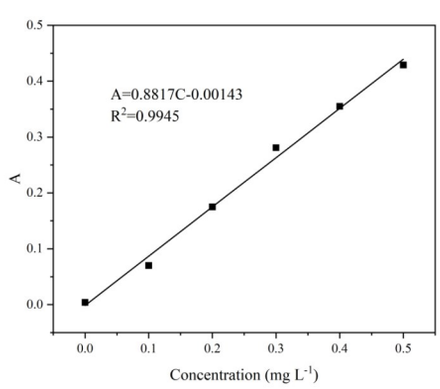

Figure 2 The standard curve of ammonia

3 Results and discussion

3.1 LSV test

The reduction performance of the catalyst electrode was studied through LSV testing. As shown in Figure 3, both the CuCo alloy catalyst electrode and the carbon paper electrode without catalyst loading exhibit an increase in current at a certain potential, demonstrating reduction performance. Compared with carbon paper, the LSV curve of CuCo electrode shows a significant enhancement, with a lower reduction potential and a greater reduction current density under the same conditions. This indicates that the CuCo catalyst has been successfully loaded onto the surface of CP and exhibits superior electrochemical reduction performance compared to CP.

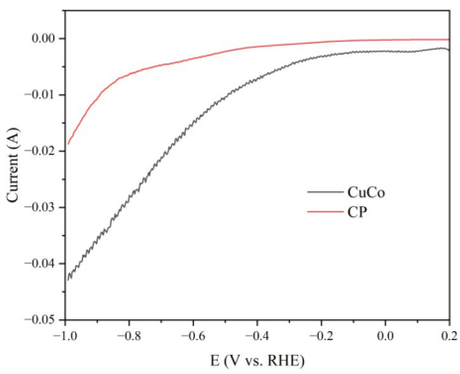

Figure 3 LSV curves of CuCo electrode and CP electrode

3.2 Performance of reduction

Under the above conditions, the catalytic reduction performance of CuCo electrode and CP electrode was compared and analyzed. At a reduction potential of -1.0 V, samples of the electrolyte were taken every 20 minutes to test the ammonia concentration produced therein. The results are shown in Figure 4. As can be seen from the figure, with the increase of time, the ammonia concentration in the product gradually increases, which proves that NO is reduced to ammonia products under the action of the catalytic electrode. The increase in ammonia production concentration of CP is very limited, indicating that CP has almost NO ability to reduce NO. The significant increase in ammonia production concentration of CuCo demonstrates its advantages in the ammonia production process of NO reduction. With the increase of time, the ammonia production maintains a stable rate of increase, indicating that the catalyst has stable catalytic reduction performance [8].

The current response during this reduction process was tested, and the results are shown in Figure 5. It can be seen that the CP current signal is relatively weak, with the current within 30 mA and a low current density. CuCo has a relatively large current, reaching up to 0.043 A within 120 minutes. The higher current density leads to better electro-reduction performance. Throughout the entire reduction process, the continuous and stable current indicates the reduction stability of the catalytic electrode. As time goes by, the current gradually increases slightly. This is because as the reaction product ammonia is generated, the concentration of the electrolyte gradually increases, enhancing the conductivity and further improving the reducing capacity.

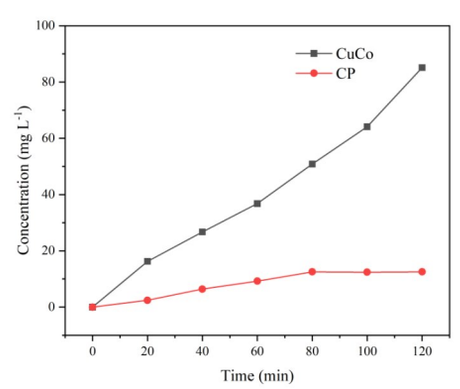

Figure 4 Comparison of ammonia production performance between CuCo electrode and CP electrode

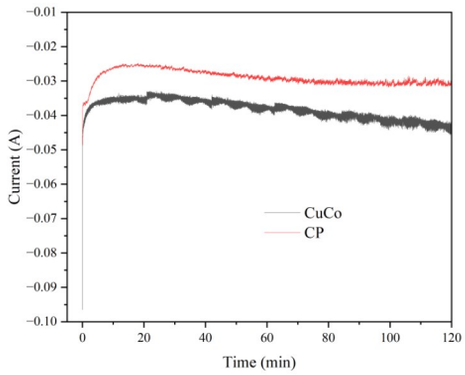

Figure 5 The i-t curve of the reduction process

3.3 Optimization of reduction potential

The reduction potential was optimized. The reduction reactions were carried out for 2 hours under the conditions of -0.3 V, -0.5 V, -0.8 V and -1.0 V respectively. The Faraday Efficiency and ammonia yield were tested, and the results are shown in Figure 6. As the voltage increases, the ammonia yield gradually rises. This is because a higher voltage provides a greater current density for the reduction reaction, thereby generating more ammonia as the reduction product. The FE curve shows a volcanic graph trend. When the voltage is lower than -0.8 V, the Faraday efficiency gradually increases with the increase of voltage, and the current utilization rate gradually increases. When the voltage exceeds -0.8V, the Faraday efficiency actually decreases. Although there is a higher current density at this time, side reactions such as hydrogen production gradually occur, and the current utilization rate becomes even lower. Therefore, the optimal reduction potential of CuCo is -0.8 V, at which point the Faraday efficiency reaches 71.3% and the ammonia production rate is 248.4 μmol h^{-1} cm^{-2}.

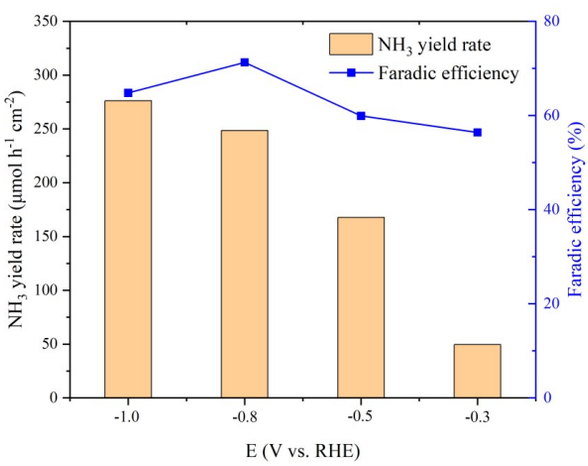

Figure 6 Experiments on the reduction potential conditions of CuCo electrodes

3.4 Comparison between alloy electrodes and single-metal electrodes

Single-metal powders of Cu and Co were synthesized respectively using the same synthesis method and loaded onto the surface of CP to prepare single-metal catalytic electrodes. The reduction performance of the CuCo catalytic electrode and the single-metal catalytic electrode was tested respectively at the optimal reduction potential and compared with that of the CP electrode. The results are shown in Figure 7. It can be found that all three metal electrodes exhibit Faraday efficiency and ammonia production rate far superior to those of the CP electrode, and have excellent electroreduction performance. Compared with single-metal electrodes, CuCo electrodes have higher FE and ammonia production rates, demonstrating the synergistic catalytic effect of multiple metal doping and the enhanced performance on catalytic activity.

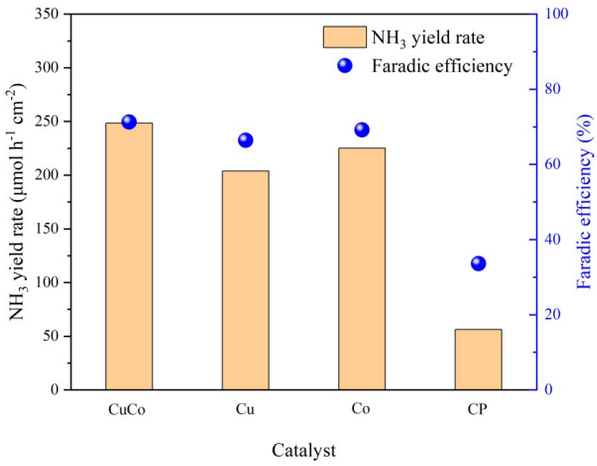

Figure 7 Comparison of electrode reduction performance

4 Conclusion

In this study, CuCo alloy powder was synthesized and loaded onto hydrophobic carbon paper to prepare CuCo alloy catalyst electrodes, which were then applied to the catalytic reduction of NO for ammonia production. The paper studied the reduction conditions and ammonia production performance of the CuCo catalytic electrode. Compared with the carbon paper electrode without catalyst loading, the CuCo electrode exhibits a lower reduction potential and a higher current density, with a stable and efficient increase in ammonia production concentration. The reduction potential was optimized and compared with the corresponding single-metal catalytic electrode. The optimal reduction potential of CuCo was -0.8 V, showing a higher Faraday efficiency (71.3%) and a higher ammonia production rate (248.4 μmol h^{-1} cm^{-2}). This study highlights the prospects of CuCo alloy catalysts in the reduction of NO to ammonia production, providing a feasible strategy and an environmentally friendly innovative idea for industrial waste gas treatment.

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