

Enhancing CO₂ER to ethylene over CuO electrodes by Ni and B modification

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Significance and Relevance

The synergistic effects of Ni and B doping on CuO-based catalysts for CO_2 electroreduction (CO_2ER) were investigated. The results reveal that even at low concentrations, Ni significantly enhances the production of both CO and C_2H_4 . Notably, the combined B-Ni modification of CuO demonstrated a pronounced synergistic effect, leading to a substantial increase in ethylene production, a suppression of the hydrogen evolution reaction (HER), improved current density, and enhanced catalyst stability. These findings highlight the potential of multi-level modifications to significantly improve catalyst activity, selectivity, and overall performance for CO_2ER applications.

Preferred and 2^{nd} choice for the topic: CO_2 utilization and recycling - Catalysis to electrify chemical production

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The CO₂ER presents a promising approach to transform CO₂ into valuable chemicals and fuels, such as ethylene, offering solutions to both environmental and energy challenges¹. However, the selectivity of Cu-based electrodes and their long-term stability at high current densities remain significant challenges. To address these issues, this work investigated the synergistic effect of Ni and B as doping agents on a CuO-based catalyst in the production of ethylene through CO₂ER. Ni was selected for its excellent capacity to produce CO, while B was chosen for its ability to dimerize CO, facilitating the production of $C_2H_4^{2,3}$.

Materials and Methods

CuO-based catalyst was synthesized by adding a solution of sodium hydroxide to a copper nitrate aqueous solution. Subsequentially, a suitable amount of nickel nitrate and boric acid was added in the solution, under stirring. Finally, the solution was heated at 373K for 12h into a capped Teflon-lined autoclave. The catalysts obtained were designated as CuONS (nanosheets) for the pristine catalyst, Ni₁CuONS for the catalyst modified with Ni, and B₁Ni₁CuONS for the catalyst modified with both Ni and B. The amount of modifier was set at 1%wt. Scanning Electron Microscope (SEM-EDX), Inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-Ray Diffraction (XRD), Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were employed for characterization. The electrocatalytic tests were conducted at different applied potential (-0.8V, -1V and -1.2V vs RHE) in a gas/liquid phase FlowCell (FC) operating in a three-electrode configuration where the working electrode is a catalyst-based gas diffusion electrode (GDE) with a 10cm² active area.

Results and Discussion

SEM images reveal that all catalysts exhibit a nanosheets morphology. Following modification with B and Ni, the predominant nanosheet morphology is retained; however, the nanosheets become more agglomerated when Ni is added during the synthesis. ICP-OES and EDX analysis revealed that the Ni content is 0.6 wt%, while B is present at trace levels below 0.05 wt%. The presence of the CuO phase in all catalysts was confirmed by XRD. Additionally, the catalyst modified with Ni exhibited a new peak corresponding to the presence of NiOOH. The electrocatalytic behavior was investigated through LSV, revealing a progressive increase in current at the same potential after modification with Ni and B, compared to the pristine CuONS. This improvement is attributed to the lower charge transfer



resistance (R_{ct}), as determined by EIS, for the modified-CuO catalysts. Moreover, the CV in the nonfaradaic region was used to determine the double-layer capacitance (CdL) and, consequently, the Electrochemically Active Surface Area (ECSA). The results revealed that after Ni and B modification, an increase in the ECSA value of pristine CuONS occurred, reaching a higher value for the B and Ni comodified catalyst.

The electrocatalytic activity of the catalysts was studied through a chronoamperometry (CA) test in a three-electrode FC in an alkaline environment (1 M KOH). As shown in Figure 1, the pristine CuONS exhibited good selectivity toward C_2H_4 , which slightly increased after the introduction of Ni into the structure. Moreover, an increase in CO production and a decrease in HER were observed at all applied potentials due to the presence of Ni. After the co-modification of pristine CuONS with Ni and B, an increase in current density was observed, attributed to the higher ECSA value and lower R_{ct} , reaching 140 mA/cm² at -1.2 V (vs. RHE) due to the presence of B. The co-modified CuONS reached a FE toward C_2H_4 of 61% at the same applied potential. Finally, the B_1Ni_1CuONS catalyst was tested for 10 hours under the same conditions, demonstrating good stability and consistent ethylene production, with a maximum FE toward ethylene of 63% and a minimum of 58% at the end of the test.

These results highlight how the synergistic effects of Ni, which selectively favors CO production and suppresses HER, combined with the benefits of B, which boosts current density and promotes CO dimerization, can be utilized to enhance ethylene production at industrial-level.



Figure 1. Current density and Faradaic efficiency (FE) at different applied potentials for all catalysts. The Faradaic efficiencies for C₂H₄, CO, HCOOH, and H₂ are represented by red, green, yellow, and blue colors, respectively.

References

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