

Promoting Ethylene Selectivity from CO₂ Electroreduction on CuO Supported onto CO₂ Capture Materials

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Cu is a unique catalyst for CO₂ electroreduction, since it can catalyze CO₂ reduction to a series of hydrocarbons, alcohols, and carboxylic acids. Nevertheless, such Cu catalysts suffer from poor selectivity. High pressure of CO₂ is considered to facilitate the activity and selectivity of CO₂ reduction. Herein, a new strategy is presented for CO₂ reduction with improved C₂H₄ selectivity on a Cu catalyst by using CO₂ capture materials as the support at ambient pressure. N-doped carbon (N_xC) was synthesized through high-temperature carbonization of melamine and L-lysine. We observed that the CO₂ uptake capacity of N_xC depends on both the microporous area and the content of pyridinic N species, which can be controlled by the carboni-

zation temperature (600–800 °C). The as-prepared CuO/N_xC catalysts exhibit a considerably higher C₂H₄ faradaic efficiency (36%) than CuO supported on XC-72 carbon black (19%), or unsupported CuO (20%). Moreover, there is a good linear relationship between the C₂H₄ faradaic efficiency and CO₂ uptake capacity of the supports for CuO. The local high CO₂ concentration near Cu catalysts, created by CO₂ capture materials, was proposed to increase the coverage of CO intermediate, which is favorable for the coupling of two CO units in the formation of C₂H₄. This study demonstrates that pairing Cu catalysts with CO₂ capture supports is a promising approach for designing highly effective CO₂ reduction electrocatalysts.

creasing catalyst roughness,^[5] surface molecular modification,^[6]

Introduction

There are two promising ways to close the anthropogenic CO_2 cycle: one is to transfer CO_2 into value-added products^[1] and the other is to capture CO_2 for sequestration.^[2] In respect of CO_2 conversion, converting CO_2 into energy-dense fuels and chemical feedstocks has attracted widespread concerns because it is a scalable solution for environment and energy needs.^[3] Cu is known to catalyze CO_2 reduction to hydrocarbons in considerable quantities.^[4] However, traditional Cu electrodes suffer from low product selectivity to hydrocarbons, as well as the severe side reaction of hydrogen evolution.

To tune the reaction pathways, many researchers have found that Cu catalysts derived from Cu oxides can enhance the activity and selectivity to hydrocarbons, particularly ethylene (C_2H_4), at negative potentials. Other methods, such as in-

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author(s) of this article can be found under https://doi.org/10.1002/ cssc.201702338. regulating nanostructures,^[7] raising local pH near the electrode surface,^[8] and introducing alkali metal cations, halogen anions and organic functional groups,^[6,9] have also been reported to increase the production of hydrocarbons by CO₂ reduction. For example, Xie et al.^[6] reported that when Cu nanoparticle surfaces were functionalized with N-containing ligands such as amino acids, hydrocarbon generation by CO₂ reduction can be enhanced, owing to the introduction of NH3+ groups that can stabilize the CHO* intermediate through the hydrogen bond between CHO* and NH₃⁺. In addition, boosting the CO₂ pressure is also an effective approach. Sakata and co-workers first reported that increasing the CO₂ pressure drastically improves the activity of CO₂ reduction.^[10] Hori proposed that increasing the CO₂ pressure not only increases the activity, but also affects the selectivity of the products,^[11] a proposal that was then supported in a study by Chaplin and Wragg.^[12] They reported that the boosting the CO₂ pressure could effectively inhibit the hydrogen evolution reaction and suggested that the change in selectivity was caused by promoting the generation of a CO_x^{y-1} intermediate.^[12] For Cu electrodes, increasing CO₂ pressure has been shown to facilitate CO₂ reduction to multi-carbon products.^[13] Melchaeva et al. used CO₂ supercritical fluid as an electrolyte at high pressure and found that the byproducts of CO₂ reduction are inhibited effectively and the selectivity to alcohols is increased.^[14] Koper et al. have shed light on the influence of increasing CO₂ pressure, and found it significantly enhances the C₂H₄ selectivity on Cu catalysts.^[15] All of these results clearly highlight the great importance of the CO₂ pressure



on CO₂ reduction. However, studies of CO₂ pressure require specific reactors and external pressures. We consider whether it is possible to construct a local microenvironment with high CO₂ pressure/concentration around the catalysts under moderate pressure.

To this end, CO_2 capture materials may meet such a requirement. When Cu-based catalysts are supported by CO_2 -capture materials, CO_2 can be adsorbed and potentially form a local microenvironment with high CO_2 concentration around the catalysts. To our knowledge, although many studies have concerned the supports of CO_2 reduction electrocatalysts, the strategy of manipulating the activity and selectivity by tuning CO_2 uptake capacity of the supports has not been reported to date. Among CO_2 capture materials, N-doped carbon materials exhibit excellent performance, owing to their porous structure and the properties brought about by N doping.^[16]

In this study, we synthesized N-doped carbon materials (N_xC) from nitrogen-rich melamine and L-lysine precursors. The CO₂ uptake capability of the N_xC can be controlled by tuning the carbonizing temperature (600, 700, or 800 °C). The target catalysts were prepared by loading CuO onto the N_xC. We found that these catalysts not only enhance the activity of CO₂ reduction, but also tune the selectivity to ethylene, in comparison with CuO supported on non-CO₂-capture materials (e.g., XC-72 carbon black). We also derived a linear correlation of the ethylene selectivity with the CO₂ adsorption capacity of the supports.

Results and Discussion

All of the N_xC samples (N_xC-600 $^{\circ}$ C, N_xC-700 $^{\circ}$ C, and N_xC-800 $^{\circ}$ C) were found by scanning electron mictroscopy (SEM) to have rough and porous structures (Figure 1A-C), which was further confirmed by transmission electron microscopy (TEM; inset). The porosity of the carbon matrix increased with increasing carbonizing temperature. The pore structure will affect the ability of CO₂ adsorption.^[17] To further identify the pore structure of these CO₂ capture materials, nitrogen adsorption-desorption isotherms of the three samples were tested (Figure 1 D). All samples gave rise to a pseudo-type IV curve with a H2-type hysteresis loop at high relative pressure, which is a typical feature of mesoporous materials.^[18] The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. That of N_xC-600 $^{\circ}$ C was only 208 m² g⁻¹, whereas those of N_xC-700 °C and N_xC-800 °C were significantly increased at 478 and 512 m²g⁻¹, respectively. This result indicates that increasing the carbonizing temperature will promote the formation of a larger surface area. The pore size distribution shows the main pore size concentrated around 7.4 nm (inset of Figure 1 D). With regards to CO₂ adsorption capacity, micropores are more important than mesopores.^[19] The microporous areas of N_xC-600 °C, N_xC-700 °C, and N_xC-800 °C are 33, 126, and 113 m²g⁻¹, respectively.

Besides pore structure, the types of doped nitrogen are also very important for the CO_2 adsorption capacity. The nitrogen species were analyzed by the high-resolution N1s X-ray photoelectron spectroscopy (XPS; Figure 2A–C). Three peaks were



Figure 1. A–C) SEM images of the N_xC-600 °C (A), N_xC-700 °C (B), and N_xC-800 °C (C). Insets show TEM images. D) Nitrogen adsorption–desorption isotherms of the three samples.

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Figure 2. A-C) High-resolution N 1s XPS spectra of N_xC-600 °C (A), N_xC-700 °C (B), and N_xC-800 °C (C). D) CO₂ adsorption isotherms at 298 K.

deconvoluted, corresponding to pyridinic N at 398.5 eV, pyrrolic N at 399.9 eV, and graphitic N at 401 eV. $^{\mbox{\tiny [20]}}$ XPS of the three samples showed that pyridinic N is the dominant nitrogen species. N_x C-700 °C had the highest proportion of pyridinic N (60.8%), followed by N_x C-600 °C (52.8%) and N_x C-800 °C (48.1%). Increasing the carbonizing temperatures to 800°C increased the content of graphitic N to 23%, whereas N_x C-700 °C and N_xC-600 °C only have 10 and 18% of graphitic N, respectively. Among three types of nitrogen, pyridinic N has the highest alkalinity, and is of great importance for CO₂ adsorption.^[19] However, in our study, the CO₂ adsorption capacity was not completely consistent with the content of pyridinic N. The CO₂ capture capacities at 298 K of different materials (Figure 2D) followed the order: N_x C-700 °C (2.18 mmol g⁻¹) > N_x C-800 °C $(1.95 \text{ mmol g}^{-1}) > N_x C-600 \,^{\circ}C$ (1.28 mmol g⁻¹). Vulcan XC-72 carbon only has a CO_2 uptake capacity of 0.47 mmol g⁻¹. The lower CO₂ capture capacities of N_xC-600 °C in comparison to N_x C-800 °C may be attributed to the very low microporous area of the former. This result indicates that both large microporous area and high content of pyridinic N play significant roles in capturing CO₂.

Figure 3 A shows the TEM image of CuO without carbon support. It adopts a laminar structure with some dendrites about 70 nm in length. Figure 3B depicts the TEM image of CuO/N_xC-700 °C. The dispersity of CuO was improved signifi-

cantly. The length of laminar structures ranged from 50 to 100 nm and the dendrite width ranged from 7 to 15 nm. CuO/ N_xC-600 °C and CuO/N_xC-800 °C showed similar morphologies to CuO/N_xC-700 $^{\circ}$ C, whereas CuO/XC-72 mainly consisted of a mixture of agglomerated particles and laminar structures with wider dendrites (see the Supporting Information, Figure S1). XRD measurements were carried out to ascertain the CuO phase structures (Figure 3 C). Most of the diffraction peaks $(35.6^{\circ}, 38.8^{\circ}, 48.6^{\circ}, 66.2^{\circ}, and 67.9^{\circ})$ came from monoclinic CuO (PDF#02-1040). The samples showed almost consistent patterns, indicating that the crystal structure of CuO is not influenced by the supports. The total weight contents of Cu in the samples were measured by energy-dispersive X-ray spectroscopy (EDS) to be 22.5, 22.1, 23.2, and 21.2% for CuO/N_xC-600 °C, CuO/N_xC-700 °C, CuO/N_xC-800 °C, and CuO/XC-72, respectively (Table S1). Although the loss of Cu was inevitable during the preparation process, the Cu contents were similar in these four samples. To further confirm the CuO surface state of these samples with different supports, high-resolution Cu2p were collected using XPS (Figure 3D). The Cu2p^{3/2} spectrum was fitted by three peaks at 932.5, 933.6, and 934.8 eV. The relatively weak peak at 932.5 eV represents $\mathsf{Cu}^{\scriptscriptstyle 0}$ and $\mathsf{Cu}^{\scriptscriptstyle +},$ and the other two peaks are associated with Cu^{2+,[21]} The presence of Cu⁰ and Cu⁺ peaks implies that Cu was not completely oxidized to Cu²⁺. Cu²⁺ is the dominant form in all samples, which





Figure 3. TEM images of unsupported CuO (A) and CuO/N_xC-700 $^{\circ}$ C (B). XRD pattern (C) and high-resolution XPS of Cu2p_{3/2} (D) of CuO supported on N_xC-600 $^{\circ}$ C, N_xC-700 $^{\circ}$ C, N_xC-800 $^{\circ}$ C, and XC-72 carbon black.

is in accordance with the XRD results. Note that most of the CuO will be reduced to metallic Cu under the CO_2 electroreduction conditions.

Figure 4A shows the steady-state polarization curves of CO₂ reduction on CuO/N_xC-700°C, CuO/XC-72, and unsupported CuO in CO₂-saturated 0.1 M NaHCO₃ solution (pH 6.8). The steady-state total current was recorded at 2000 s when the contribution of CuO reduction to the total current can be neglected and the faradaic efficiencies (FEs) of gaseous products also reach stable values (Figure S2). The current was normalized by the Cu mass on the electrode surface. CuO/N_xC-700 °C and CuO/XC-72 have total current densities about two times that of unsupported CuO. The FEs for H₂ are 60% on CuO/XC-72, 40% on CuO, and 30% on CuO/N_xC-700 $^{\circ}$ C (Figure 4B–D). Considering the variety of CO₂ reduction products, the neat CO₂ reduction current was calculated by subtracting the hydrogen evolution partial current from the total current. The neat CO₂ reduction currents for different catalysts follows the order $CuO < CuO/XC-72 < CuO/N_xC-600 \circ C \approx CuO/N_xC-800 \circ C < CuO/$ N_x C-700 °C (Figure S3). Such a difference may result from the support effects. As a CO₂ capture material, N_xC-700°C could adsorb CO₂ to form a local microenvironment with high CO₂ concentration, which leads to the promotion of CO₂ reduction and the suppression of hydrogen evolution, as Chaplin and Wragg reported.^[12] In contrast, Vulcan XC-72 has a low CO_2 capture capacity and hydrogen evolution is a significant side reaction under negative potentials (Figure S4).

The main gaseous products of the CO₂ reduction are CO, C₂H₄, and CH₄. In addition, there are trace liquid products (such as formic acid, ethanol, and propanol), and the total FEs of liquid products is less than 10% (Figure S5). As the potential shifts negatively, the FE for CO decreases, whereas those for C₂H₄ and CH₄ increase (Figure 4B–D). This indicates that the intermediate adsorbed *CO can be further reduced to hydrocarbon at a negative potential.^[22] CuO/N_xC-700 °C has a considerably higher C₂H₄ selectivity than CuO and CuO/XC-72 at all tested potential ranges. The highest FE value for C₂H₄ is 36%, obtained on CuO/N_xC-700 °C at -1.25 V, whereas the FE values on CuO and CuO/XC-72 are only 20 and 19%, respectively. This result indicates that using a CO₂ capture material as the support benefits the formation of C₂H₄.

To further explore the influence of CO₂ capture materials, the FEs for products on CuO/N_xC-600 °C and CuO/N_xC-800 °C were also obtained (Figure 5). The FE values for C₂H₄ follow the order CuO/N_xC-700 °C > CuO/N_xC-800 °C > CuO/N_xC-600 °C. In previous studies, the presence of pyridinic N was considered an important factor in promoting C₂H₄ formation by CO₂ reduction on Cu catalysts supported on N-doped carbon.^[23] In



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Figure 4. A) Mass-normalized total current densities of CO₂ reduction on unsupported CuO, CuO/N_xC-700 °C, and CuO/XC-72 at various potentials in CO₂-saturated 0.1 \times NaHCO₃ solution (pH 6.8). B–D) FEs of gaseous products for CO₂ reduction on CuO (B), CuO/XC-72 (C), and CuO/N_xC-700 °C (D). H₂ (orange), CO (violet), CH₄ (red), and C₂H₄ (black); GC sampling was performed at 2000 s during potentiostatic electrolysis.



Figure 5. Product FEs of CO₂ reduction on CuO/N_xC-600 °C (A) and CuO/N_xC-800 °C (B) at different potentials.

this study, this is not the case. In fact, N_xC-600 °C has higher content of pyridinic N than N_xC-800 °C, whereas the FE values for C₂H₄ at -1.15 V are 25% on CuO/N_xC-600 °C and 30% on CuO/N_xC-800 °C. Therefore, other factors besides the concentration of pyridinic N species must greatly influence the C₂H₄ selectivity.

We can exclude some factors from carbon supports. 1) Firstly, the influence of trace metals in the supports can excluded. Although the carbon supports contained trace Fe, Ni, Zn, and Co (Table S2), as detected by inductively coupled plasma mass spectrometry (ICP-MS), they have very poor catalytic activity for CO₂ reduction. The FE for H₂ was almost 100% (Figure S6) with trace CO. 2) The electrical conductivity of carbon supports can also be excluded. The electrical conductivity of the N_xC increased with increasing carbonization temperature from 600 to 800 °C, and XC-72 exhibited the highest value (Figure S7 and



Table S3). This order of conductivity is significantly different from that of C₂H₄ selectivity observed on different carbon supports. 3) The support electronic effects are also not the main reason for the observed dependence of C_2H_4 selectivity on carbon supports. In principle, carbon supports, especially Ndoped carbon, may influence the oxidation state of the metal supported on them through metal-support interactions and thus change the reaction kinetics. However, such support effects will decrease with increasing size of metal nanoparticles. For example, Li et al.^[23] reported that the pyridinic N species in N-doped graphene have little effect on Cu nanoparticles larger than 13 nm for CO₂ reduction. In our study, CuO had particle sizes ranging from 50 to 100 nm. For such large particles, the electronic effect from the supports is little. In fact, we observed no shift in the binding energy of Cu2p in the XPS obtained from different CuO supported samples (Figure 3 d). 4) The Cu loading is the same essentially for four carbon-supported CuO catalysts. And the morphology and size of CuO for three C_xNsupported samples are also similar. So that, the catalyst loading, morphology, and size (or surface area) are unlikely to govern the different C₂H₄ selectivity.

Finally, we found that the CO₂ uptake capacity of the supports correlates well with the C₂H₄ selectivity. Figure 6A shows the potential dependence of C₂H₄ selectivity for four CuO catalysts supported on different carbon supports. To reduce the measurement errors, the tests were repeated three times at each potential. The plot of C₂H₄ selectivity against CO₂ uptake capacity at $P/P_0=1$ is shown in Figure 6B. Clearly, a good linear relationship between the FE for C₂H₄ and the capacity of CO₂ uptake can be observed for all four tested potentials. Considering CO₂ reduction was carried out in CO₂-saturated 0.1 m NaHCO₃ solution, we further tested the CO₂ adsorption capacities in this solution for above carbon supports (Figure S8 and Table S4). The order of adsorption capacities tested in the solution is consistent with that obtained by CO₂ gas adsorption.

It has been generally accepted that the formation of C_2H_4 is mainly through dimerization of two adsorbed *CO intermediates during CO₂ reduction on Cu.^[24,25] Therefore, the high coverage of *CO should be in favor of the formation of C_2H_4 .^[26] In

our study, CO₂ capture materials (e.g., N_xC-700 °C) can maintain a local environment with high CO₂ concentration, and facilitate mass transfer. This may help to increase the *CO coverage on the Cu catalyst surface, and further facilitate the coupling of two CO molecules to form C₂H₄.

Conclusions

We synthesized N-doped carbon materials with different CO₂ uptake capacities for use as supports for CuO electrocatalysts. The target CO₂-reduction catalyst, CuO loaded onto N-doped carbon, exhibits much higher C₂H₄ selectivity than CuO loaded onto common carbon black, as well as unsupported CuO. We found a good linear relationship between C₂H₄ selectivity and CO₂ uptake capacity of the carbon supports, which may guide the preparation of CO₂-reduction catalysts with high C₂H₄ selectivity. Further studies are needed to characterize the oxidation state of Cu catalysts in operando and to reveal the detailed mechanism for boosting C₂H₄ selectivity by CO₂-capture supports.

Experimental Section

Synthesis of N-doped carbon materials

The N-doped carbon materials were prepared by a pyrolysis method. Melamine (2.0 g), L-lysine (1.0 g) and SBA-15 mesoporous silica (0.4 g) were mixed together with deionized water (5 mL) and ethanol (5 mL), and were ultrasonically dispersed for 0.5 h to form a uniform suspension, then dried at 90 °C to form a powder.^[27] The powder was carbonized in two steps by heating under an Ar atmosphere in a tube furnace at 300 °C for 1 h with a heating rate of 3 °C min⁻¹, and then heating up to elevated temperature (600 °C, 700 °C, and 800 °C) for 2 h at 5 °C min⁻¹. The SBA-15 template was then removed by using a 20% HF solution. After centrifugation and washing with deionized water (about 20 mL) several times, as well as drying, the N-doped carbon materials were obtained, and referred as N_xC-600 °C, N_xC-700 °C, and N_xC-800 °C for those obtained at the corresponding carbonized temperature.



Figure 6. A) FEs of C_2H_4 for CO_2 reduction on CuO catalysts supported on four carbon supports at different potentials. B) Linear relationship between the FE for C_2H_4 and the CO_2 uptake capacity on carbon supports at $P/P_0 = 1$ and room temperature.

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Synthesis of CuO supported on N-doped carbon materials

CuO catalysts supported on N-doped carbon materials (CuO/N_xC) were prepared through a reduction and re-oxidation approach. Firstly, CuCl₂·2H₂O (60 mg) and N_xC (50 mg) were dispersed in deionized water (20 mL) in a 100 mL flask, followed by the addition of 0.5 м NaOH solution to afford a neutral system. NaBH₄ (25 mg) was then dissolved in water (20 mL) and the solution was added slowly to the mixture and then kept stirring for 4 h, whereby Cu²⁺ was reduced into metallic Cu nanoparticles. The samples were collected by filtering and washed with deionized water (about 30 mL). Finally, the sample underwent heat treatment at 200 °C for 3 h in air to afford the CuO/N_xC-600 °C, CuO/N_xC-700 °C, or CuO/N_xC-800 °C catalysts. For comparison, we also prepared CuO supported on Vulcan XC-72 carbon black (CuO/XC-72) by a similar procedure. In comparison with the N_xC, XC-72 carbon black has a low CO₂ adsorption capacity. In addition, CuO without carbon support was also prepared.

Material characterization

X-ray diffraction (XRD) was recorded on a Bruker D8 Discover diffractometer detector with Cu_{ka} radiation (40 kV and 40 mA) between 20° and 90°. Transmission electron microscope (TEM) images were acquired on a JEM-1400, and elemental mapping was measured on a Tecnai F30. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) measurements were carried out on a Hitachi 4800. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI 5000 VPIII. N₂ adsorption–desorption isotherms and CO₂ uptake were measured on a TriStar II physisorption analyzer. The contents of Fe, Co, Ni and Zn were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) on an Elan DRC II ICP-MS instrument (PerkinElmer).

Electrochemical measurements

Electrochemical CO₂ reduction was performed on a CHI 760E potentiostat with a three-electrode system at room temperature in 0.1 м NaHCO₃ (pH 6.8), prepared by bubbling CO₂ through a 0.05 м Na₂CO₃ (99.999%, Sigma–Aldrich) solution. To prepare the catalyst ink, the catalyst (3 mg) was ultrasonically dispersed in a mixture of ethanol (500 µL), ultrapure water (500 µL), and Nafion solution (30 μ L, 5 wt%) for 0.5 h to form a homogeneous ink. Then 100 μ L of the as-prepared ink was pipetted onto the carbon paper as a working electrode. The catalyst loading was 0.3 mg cm⁻². A graphite sheet was used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. All potentials in this study are in reference to that of the reversible hydrogen electrode (RHE) according to E(RHE) = E(SCE) + 0.643 V (pH 6.8). A H-type cell separated by a Nafion-117 proton-exchange membrane was used to prevent diffusion of the products to the counter electrode compartment. The electrocatalytic process was performed by potentiostatic electrolysis (-0.95, -1.05, -1.15, and -1.25 V) with continuous bubbling of CO₂. The IR drop was compensated at 70% level during electrolysis. The gaseous products in the cathodic compartment were analyzed by on-line gas chromatography (GC9790II, Agilent).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon capture \cdot CO₂ reduction \cdot copper \cdot electrocatalysis \cdot support effects

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The higher the better: CuO supported on N-doped carbon, a CO₂ capture material, exhibits high faradaic efficiency for CO₂ electroreduction. The higher CO₂ uptake capacity, the higher C₂H₄ selectivity. The local high CO₂ concentration near the Cu catalysts, created by the CO₂ capture materials, is proposed to increase the coverage of CO intermediate, which is favorable for the coupling of two CO units in the formation of C₂H₄.



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Promoting Ethylene Selectivity from CO₂ Electroreduction on CuO Supported onto CO₂ Capture Materials

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