

Unraveling the Mechanism of Cu/CeO₂ Interface Modulation for CO₂ Electroreduction Into C₂₊/CH₄

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Cu shows unique characteristics for electrochemical CO₂ reduction reaction (CO₂RR) to hydrocarbons and oxygenates due to the moderate adsorption energy of the key intermediate *CO. However, it remains a challenge to selectively control CO₂RR towards C₁ (e.g., CH₄) or C₂₊ (e.g., C₂H₄ and C₂H₅OH) through simple interface engineering. Herein, a series of inverse catalysts, composed of CeO₂ nanoparticles over Cu substrate (Cu-CeO₂-x), are subtly designed to tackle the issues. It is verified CeO₂ decoration induces highly active Cu/CeO₂ interfacial sites that enhance the adsorption and conversion of CO₂ and *CO intermediates into C₂₊ or CH₄, while the Cu sites are conducive to *CO generation. With the increase of CeO₂ deposition, the C₂₊ and CH₄ selectivity present a volcano-type and increasing tendency with maximum faradic efficiency of 62.6% and 51.3%, respectively. In-situ infrared spectroscopy and theoretical calculations reveal that moderate CeO₂ loading allows the Cu/CeO₂ interfacial sites to cooperate efficiently with the Cu sites to promote the coupling of *CO/*CHO intermediates, thus enhancing the C₂₊ selectivity. In contrast, excessive CeO₂ loading suppresses the C–C coupling but boosts unilaterally the hydrogenation, thus promoting the CH₄ production. This work provides effective strategies to regulate the CO₂RR selectivity by modulating metal/oxide interfaces.

99%) over different catalysts.^[3] However, the manufacture of deep-reduction products (CH₄, C₂₊, etc.) still remains a great challenge to regulate their production yield and selectivity.^[4]

Cu-based materials are the main catalysts reported so far capable of catalyzing the deep reduction of CO₂ to CH₄ or C₂₊ due to their moderate adsorption energy for the key CO₂RR intermediate *CO, thus favoring the further reduction of *CO.^[5] However, more than 16 kinds of CO₂RR products have been detected over Cu-based catalysts alone, implying relatively complex reaction pathways and intermediates. Consequently, the proportional relationship among the adsorption energies of different intermediates over Cu catalyst alone inherently limits its product selectivity in CO₂RR.^[6] To address this challenge, researchers have proposed a series of improvements upon Cu-based catalysts including morphological size optimization,^[7] selective exposure of crystallographic surfaces,^[8] valence modulation,^[9]

alloying,^[10] and defect engineering.^[11]

It is well recognized that the intimate metal/oxide interfacial interactions can effectively improve molecular adsorption and activation in multiphase catalytic reactions.^[12] Among them, CeO₂ often served as a component or carrier of multiphase catalysts in three-way catalysis, water-gas shift, and CO₂ hydrogenation reactions, owing to the unique characteristics of Ce³⁺/Ce⁴⁺ transition which contributes to its excellent redox properties and abundant oxygen vacancies.^[13] In recent years, Cu/CeO₂ composites have been reported to catalyze CO₂RR to deep-reduction products with high activity and selectivity. The results illustrate that

1. Introduction

Electrochemical CO₂ reduction reaction (CO₂RR) into commercially valuable fuels and chemicals using renewable electricity (solar and wind, etc.) is a promising strategy to lower CO₂ emissions and build a carbon-neutral cycle.^[1] Typically, the CO₂RR products can be mainly divided into two main categories that are 2e[−] reduction compounds (CO, HCOOH) and deep-reduction (>2e[−]) compounds (CH₄, C₂H₄, C₂H₅OH, CH₃COOH, etc.).^[2] Numerous works have shown that the 2e[−] products CO and HCOOH have achieved high Faraday efficiencies (even up to

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DOI: 10.1002/adfm.202420161

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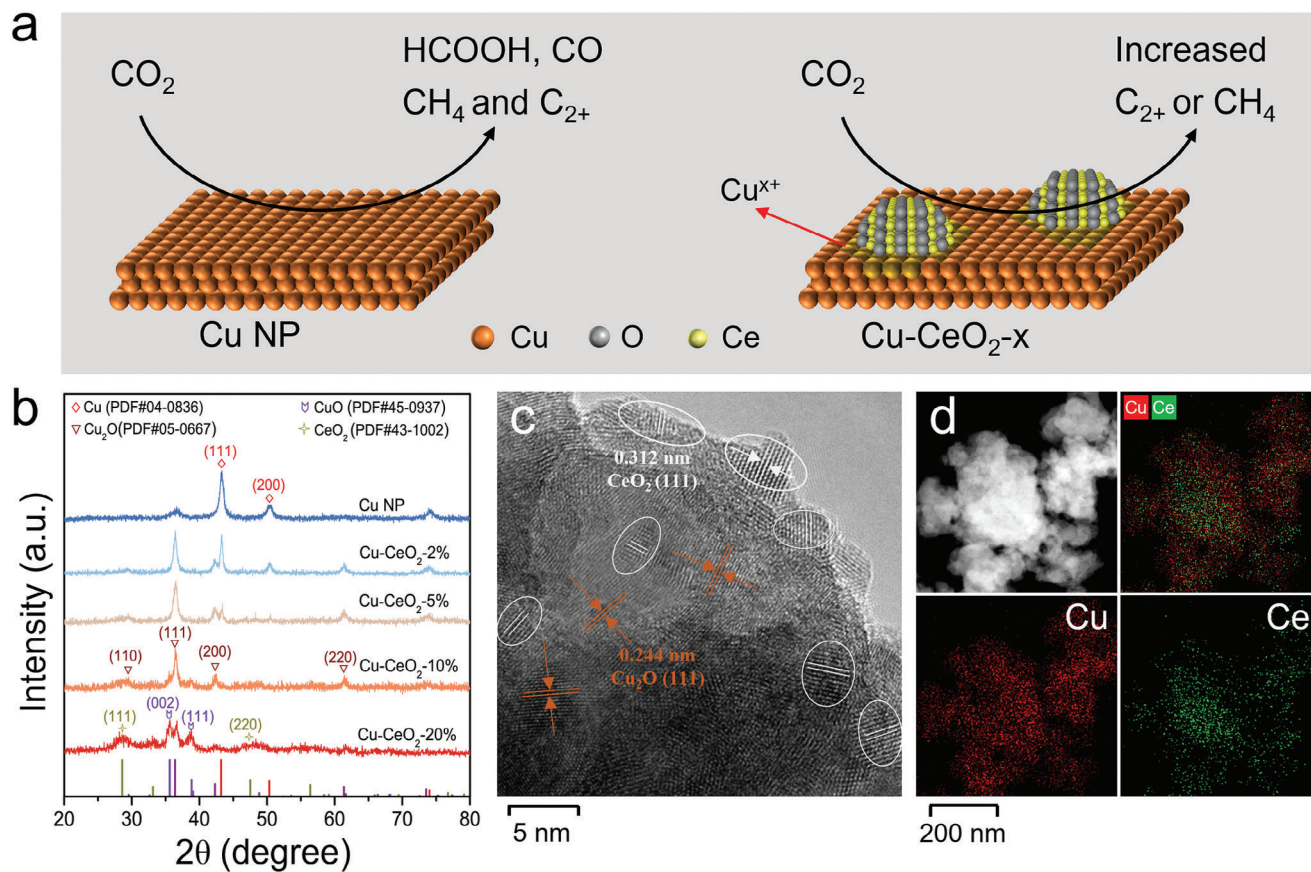


Figure 1. The structural and morphological characterizations of catalysts. a) The schematic diagram of Cu-CeO_{2-x} catalysts. b) The XRD patterns of prepared catalysts. The HRTEM image c) and relative EDS mappings d) of Cu-CeO₂-5%.

Cu/CeO₂ interface can stabilize highly active Cu⁺ or Cu²⁺, promote the adsorption of CO₂ and reaction intermediates such as CO, reduce the activation energy during CO₂RR, and inhibit the HER.^[4a,14] However, some work indicates that the Cu/CeO₂ composites like single-atomic Cu-doped CeO₂ and Cu/CeO_{2-x} heterodimers exhibit an enhanced CH₄ selectivity,^[14a,15] while others like CuO/CeO₂ catalysts instead display high-performance C₂₊ yielding.^[16] Despite the progress made in Cu/CeO₂ electrocatalysts for CO₂RR, the effect of the Cu/CeO₂ interface interaction on the distribution of CO₂RR products remains unclear, while the deep insight into the regulation for interface adsorption site and their structure-activity relationship needs to be built.

Herein, we synthesize a series of inverse catalysts that are Cu nanoparticles (Cu NP) loaded with CeO₂ (Cu-CeO_{2-x}, x indicates the loading amount mol% of CeO₂), which can modulate the product selectivity of C₂₊ or CH₄ for CO₂RR by adjusting the relative CeO₂ loading amount. The characterizations including XRD, TEM, EDS mapping, CO₂-TPD, and CO Drifts illustrate that CeO₂ loading induces highly active Cu/CeO₂ interface which can promote the adsorption of CO₂ and intermediates CO. With the increase of CeO₂ loading, the C₂₊ and CH₄ product selectivity shows a volcano-type and increasing trend, respectively, in which Cu-CeO₂-5% shows the maximum FE_{C₂₊} of 62.6% with corresponding partial current density (*j*_{C₂₊}) of −250.4 mA cm^{−2} and Cu-CeO₂-20% shows the maximum FE_{CH₄}

of 51.3% with corresponding *j*_{CH₄} of −153.9 mA cm^{−2}. In situ attenuated total reflection-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) and DFT calculations illustrate that moderate CeO₂ loading content with sufficient Cu/CeO₂ interfacial sites and Cu sites is conducive to the coupling of weakly adsorbed CO over Cu sites with the strongly adsorbed *CHO intermediate at adjacent Cu/CeO₂ interface, which favors the C₂₊ pathway. On the contrary, when the Cu/CeO₂ interfacial sites increase accompanied by the decline of Cu sites, the strong adsorption and activation ability of Cu/CeO₂ interfacial sites promote the further hydrogenation of *CHO to produce CH₄.

2. Results and Discussion

The Cu-CeO_{2-x} inverse catalysts (Figure 1a) with different CeO₂ loading were prepared via impregnation method. The Powder X-ray diffraction (XRD) patterns of these catalysts are displayed in Figure 1b. With the increase of the CeO₂ content, Cu NP is gradually transformed into Cu₂O or even CuO, implying that the interfacial interaction between Cu and CeO₂ leads to the spontaneous electron transfer from Cu to CeO₂.^[17] Only a very weak peak ascribed to CeO₂ (111) is observed when the loading is 20%, indicating the relatively good dispersion of CeO₂. The actual Ce/Cu atomic ratio of Cu-CeO₂-2%, Cu-CeO₂-5%, Cu-CeO₂-10%, and Cu-CeO₂-20% are 1.7%, 4.5%, 9.4%, and 19.1% via the

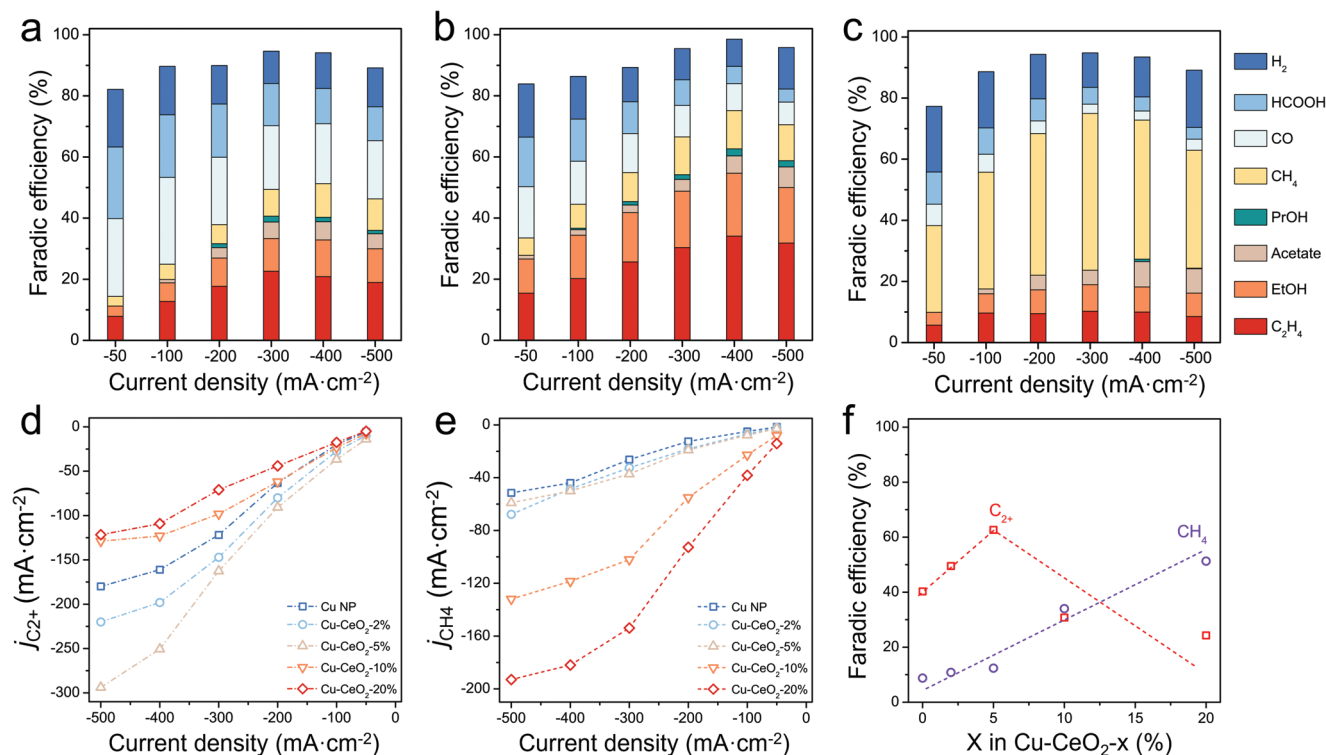


Figure 2. The CO₂RR performance of catalysts. The FEs for Cu NP a), Cu-CeO₂-5% b), and Cu-CeO₂-20% c) at different current densities. The j_{C2+} d) and j_{CH4} e) for the five catalysts. f) The correlation between the CeO₂ molecular fractions and the CH₄ FEs at j_{total} of -300 mA cm⁻² or C₂+ FEs at j_{total} of -400 mA cm⁻².

ICP-OES measurements, respectively, which are close to the theoretical values. The X-ray photoelectron spectra (XPS) were employed to characterize the electronic structure of elements like Cu and Ce, as displayed in Figure S1 (Supporting Information). For Cu 2p and Cu LM2, it shows the coexistence of Cu⁰, Cu⁺, and even a small amount of Cu²⁺ on the Cu NP surface owing to partial oxidation. After the CeO₂ loading, the Cu-CeO₂-x catalysts are dominated by Cu⁺ and Cu²⁺, in which Cu-CeO₂-20% apparently shows much higher Cu²⁺ ratio. Based on the relative peak area in Cu 2p spectra, the Cu²⁺ are calculated to be 13.6%, 26.9%, 33.5%, 45.2%, and 56.7% for Cu NP, Cu-CeO₂-2%, Cu-CeO₂-5%, Cu-CeO₂-10%, and Cu-CeO₂-20%, respectively. These results illustrate that Cu is gradually transformed into Cu⁺ and Cu²⁺ with the CeO₂ loading consistent with the XRD results, while the surface displays much more high-valence Cu.

Here, Cu-CeO₂-5% and Cu-CeO₂-20% are selected as representatives to make the comparison with Cu NP. The TEM and SEM images displayed in Figures S2 and S3 (Supporting Information) reveal that little morphological difference is observed after the CeO₂ loading. For the high-resolution TEM (HRTEM) images, Cu NP shows the typical d-spacing of 0.208 nm ascribed to Cu (111) in Figure S4a (Supporting Information). After CeO₂ loading, two lattice spacings of 0.244 nm for Cu₂O (111) and 0.312 nm for CeO₂ (111) are found for both Cu-CeO₂-5% and Cu-CeO₂-20% in Figures 1c and S4b (Supporting Information), while Cu-CeO₂-20% also exhibits the d-spacing of 0.254 and 0.231 nm ascribed to CuO (111) and CuO (002), respectively. This result further confirms the oxidation of Cu induced by the CeO₂ loading, while

Cu-CeO₂-20% apparently shows much more d-spacing of CeO₂. The EDS mappings of Cu and Ce validate the relatively uniform dispersion of Ce over the catalyst surface for both Cu-CeO₂-5% (Figure 1d) and Cu-CeO₂-20% (Figure S4c, Supporting Information). From above results, it can be concluded that small CeO₂ particles are uniformly loaded on the surface of Cu-CeO₂-x catalysts and form the Cu/CeO₂ interface, which induces the electron transfer from Cu to CeO₂.

The CO₂RR performance of the Cu-CeO₂-x catalysts was tested in a home-made flow cell with 0.5 M KHCO₃ as electrolyte via chronopotentiometric method in a cathodic current range of -50 to -500 mA cm⁻². As shown in Figures 2a-c and S5-S6 (Supporting Information), the products detected are mainly H₂, CO, CH₄, HCOOH, C₂H₄, EtOH, Acetate, and *n*-PrOH. Compared with Cu NP, Cu-CeO₂-x catalysts show apparently much higher selectivity of deep-reduction (>2e⁻) products. This result may be ascribed to the strong interfacial interaction of Cu/CeO₂ which can promote the further reduction of CO intermediates.^[18] With the increase of CeO₂ loading, the product's faradic efficiencies of C₂+ and CH₄ display a volcano-type and increasing trend, respectively (Figure 2f). Consequently, Cu-CeO₂-5% shows the best C₂+ selectivity with maximum FE_{C2+} of 62.6% and j_{C2+} of -250.4 A cm⁻² under total current density (j_{total}) of -400 mA cm⁻², while Cu-CeO₂-20% displays the optimal CH₄ selectivity with maximum FE_{CH4} of 51.3% and j_{CH4} of -153.9 mA cm⁻² under j_{total} of -300 mA cm⁻². For the pristine CeO₂ as compared in Figure S7 (Supporting Information), mainly H₂ and CO are detected, while H₂ is the dominant product. That means Cu is the only active site

for CO₂RR to generate value-added products and CeO₂ itself basically makes no contribution to the CO₂RR performance. The long-term stability test of Cu-CeO₂-5% and Cu-CeO₂-20% are carried out in a MEA device under j_{total} of -400 and -300 mA cm⁻², respectively, as shown in Figure S8 (Supporting Information). The FE_{C_2+} of Cu-CeO₂-5% and FE_{CH_4} of Cu-CeO₂-20% remain at 55.4% with j_{C_2+} of -221.6 mA cm⁻² and 42.3% with j_{CH_4} of -126.9 mA cm⁻² after electrolyzing of 30 and 24 h, respectively, displaying good stability under high current densities. The electrochemical impedance spectroscopy (EIS) of Cu NP, Cu-CeO₂-5%, and Cu-CeO₂-20% were measured under -0.8 V (vs. RHE) shown in Figure S9 (Supporting Information). The charge transfer resistance (R_{ct}) of the electrode follows in the order: Cu-CeO₂-20% > Cu NP > Cu-CeO₂-5%. That means enough Cu/CeO₂ interfacial sites with moderate CeO₂ loading can enhance the reaction dynamics, while much higher CeO₂ coverage (Cu-CeO₂-20%) will slightly decrease the charge transfer. Generally, the disparity of the R_{ct} among them is small.

It is well known that Cu^{x+} (Cu⁺ or Cu²⁺) may be reduced to Cu⁰ during CO₂RR cathodic voltage, resulting in the loss of Cu^{x+} dominance for CO₂RR.^[19] Herein, the morphological and structural characterizations of Cu NP, Cu-CeO₂-5%, and Cu-CeO₂-20% were carried out after electrolyzing. From the XRD patterns shown in Figure S10 (Supporting Information), all three catalysts show the main diffraction peaks of metal Cu, verifying the reduction of Cu^{x+}. Moreover, the peaks belonging to Cu₂O are also obviously observed for Cu-CeO₂-5% and Cu-CeO₂-20% while that of Cu-CeO₂-20% is much stronger. The Rietveld refinement results with 2θ range from 30 to 80° in Figure S10b and Table S1 (Supporting Information) reveal that Cu-CeO₂-20% shows much higher Cu₂O content (27.8 wt.%) than Cu-CeO₂-5% (12.4 wt.%). The XPS measurement was carried out to further study the surface valence state after electrolysis. From the Cu 2p and Auger Cu LM2 spectra in Figure S11 (Supporting Information), the mixture of Cu⁰, Cu¹⁺, and Cu²⁺ are all observed over the surface of Cu NP, Cu-CeO₂-5%, and Cu-CeO₂-20%. After deconvolution, the relative ratio of the high-valence Cu (Cu⁺ + Cu²⁺) can be obtained according to the relative peak area of Cu²⁺ and Cu⁺ combining the Cu 2p and Auger Cu LM2 spectra (Figure S11 and Table S2, Supporting Information),^[19] which are calculated to be 46%, 73.4% and 90.7% for Cu NP, Cu-CeO₂-5% and Cu-CeO₂-20%, respectively. These results illustrate that the formed Cu/CeO₂ interface for CeO₂ loading is favorable for the Cu⁺ and Cu²⁺ stabilization during the CO₂RR process and the stabilization effect is enhanced while increasing the CeO₂ loading amount. From the results of HRTEM and EDS mappings in Figure S12 (Supporting Information), the relatively uniform dispersion of CeO₂ can still be observed on the surface of Cu-CeO₂-5% and Cu-CeO₂-20%, implying the stable Cu/CeO₂ interface even under high-current CO₂ electrolyzing. The Raman spectra are obtained for Cu-CeO₂-20% before and after CO₂RR to study whether the reconstruction occurs to form the Ce-Cu-O solution that is recognized as the active sites for CO₂RR to CH₄,^[20] while the CeO₂-loaded Cu catalysts with different Cu content (1 to 15 wt.%) are also characterized as comparison (Figure S13, Supporting Information). Apart from the broader F_{2g} peak at 454 cm⁻¹ for CeO₂, Cu-CeO₂-20% shows another three peaks at 250–300, 300–350, and 600–650 cm⁻¹, mainly ascribed to Cu_xO species (Cu₂O+CuO) (Figure S14, Supporting Information).^[21] After CO₂RR measurement,

the four peaks nearly show little change other than the relatively weaker intensity of the three peaks belonging to the Cu_xO species owing to the reduction under cathodic conditions. This result illustrates that the inverse Cu-CeO₂-20% catalyst for high CH₄ selectivity shows mainly Cu/CeO₂ interfacial sites and no apparent reconstruction to Cu-Ce-O solid solution occurs after CO₂RR. Therefore, above results verify that the Cu/CeO₂ interfacial sites are indeed active for CO₂ deep reduction to C₂₊ or CH₄.

CO₂-TPD was employed to investigate the CO₂ adsorption ability and surface states of the catalysts. To approximate the CO₂RR condition, the catalysts were pre-reduced under H₂/He atmosphere at 300 °C. As shown in Figure 3a, the desorption peaks of Cu NP mainly lie in two temperature intervals that are low-temperature region (<200 °C, I) for the weak CO₂ chemisorption and medium-temperature region (250–450 °C, II) for the strong CO₂ chemisorption over Cu.^[22] After CeO₂ loading, both Cu-CeO₂-5% and Cu-CeO₂-20% show a new desorption peak in the high-temperature region (450–650 °C, III) in which peak III-1 and III-2 may be ascribed to the strong CO₂ adsorption over CeO₂ and Cu/CeO₂ interface, respectively. Comparing the peak areas of the three groups of desorption peaks shown in Figure 3b, it can be found that the area of peak II associated with the strong CO₂ adsorption over Cu is significantly reduced after CeO₂ loading, owing to the convergence of Cu surface by CeO₂. The more loading of CeO₂ is, the more the peak area decreases. Moreover, the area of peak III ascribed to CeO₂ introduction is also higher for more CeO₂ loading (Cu-CeO₂-20%). All these results suggest that the presence of Cu/CeO₂ interface can apparently promote CO₂ adsorption and enrichment, which may be beneficial to enhance the catalytic activity of CO₂RR.

The CO adsorption ability of the three groups of catalysts was studied using in situ CO Drifts. Like the CO₂-TPD, the catalysts were also pre-reduced under H₂/He atmosphere before testing. As displayed in Figure 3c, all three catalysts exhibit one prominent band in the CO absorption region of 2150–2050 cm⁻¹, in which the peak of Cu NP is located at 2096 cm⁻¹ corresponding to the Cu⁰-adsorbed carbonyl species. After CeO₂ loading, this band shifts to the higher wavenumber toward 2116 cm⁻¹ correlated to the Cu⁺-adsorbed carbonyl species, suggesting the presence of Cu⁺ on the surface of Cu-CeO₂-x catalysts.^[23] This result further confirms that the loading of CeO₂ can promote the stabilization of high-valence Cu consistent with the XRD and XPS results. From the results of the corresponding peak areas in Figure 3d, it follows in the order of Cu-CeO₂-20% > Cu-CeO₂-5% > Cu NP, implying that the Cu/CeO₂ interface can obviously enhance the CO adsorption. From the characterization results of CO₂-TPD and in situ CO-DRIFTS, it can be concluded that the Cu/CeO₂ interface of the Cu-CeO₂-x catalysts can reinforce the adsorption of reactants CO₂ and CO, which may improve the CO₂RR performance and promote the CO₂ deep reduction.

To investigate the intrinsic reason for the different CO₂RR performance and selectivity, in situ ATR-SEIRAS was applied to probe the reaction intermediates over Cu NP, Cu-CeO₂-5%, and Cu-CeO₂-20%. As shown in Figure 4a–c, three common infrared absorption peaks located at 2030–2080, 1380–1420, and 1050–1090 cm⁻¹ are observed for all three catalysts, which are attributed to the atop-adsorbed *CO (*CO_{atop}), *COOH and *CHO species, respectively.^[24] Among them, *COOH is the intermediate of CO₂ reduction to CO, while *CHO from CO hydrogenation

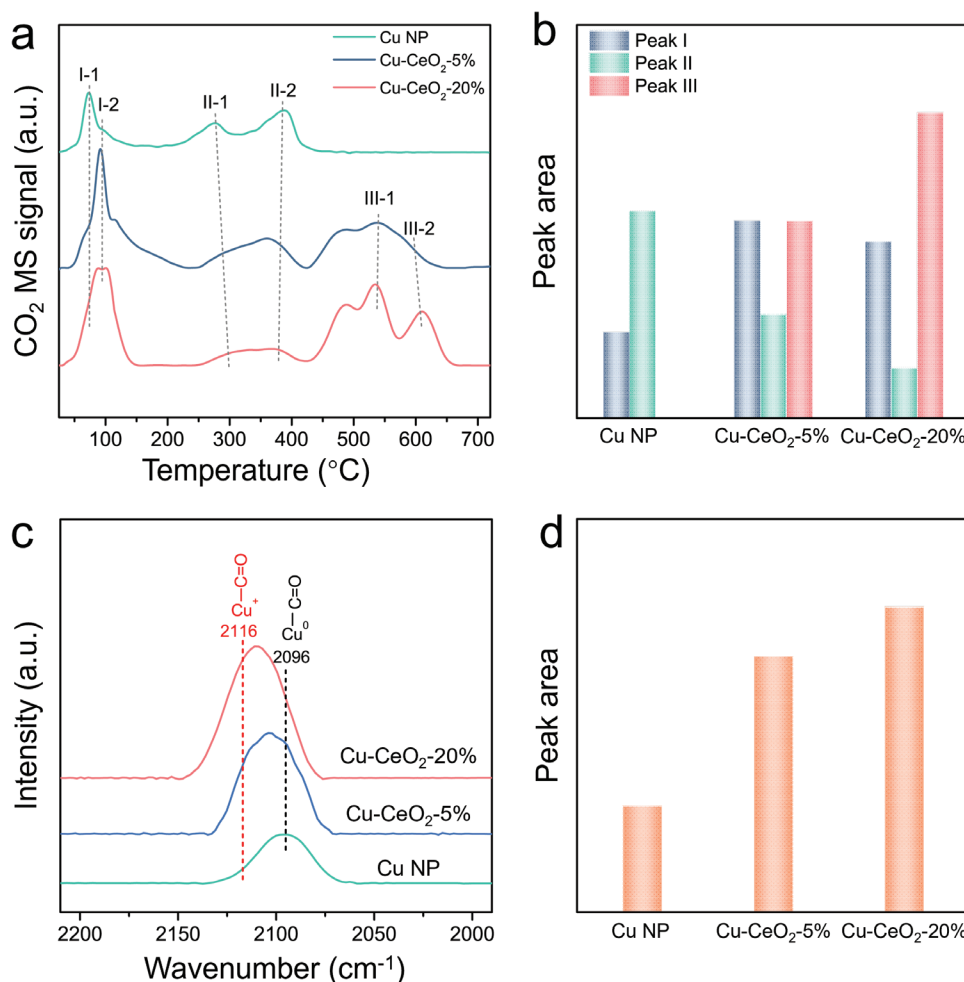


Figure 3. The CO_x-adsorption characterizations of catalysts. a) The CO₂-TPD spectra. b) The relative CO₂ desorption peak area. c) In situ CO DRIFTS spectra. d) The relative peak area of CO adsorption.

and *CO itself are regarded as the key intermediates for CO₂ deep-reduction. These intermediate bands over Cu-CeO₂-20% and Cu-CeO₂-5% catalysts are much stronger than those over Cu NP, indicating that the presence of Cu/CeO₂ interfacial sites can enhance the adsorption and transformation of CO₂ and *CO which is especially critical for the deep reduction of CO₂ to produce C₂₊ or CH₄. In addition, Cu-CeO₂-5% shows a prominent band located at 1568 cm⁻¹ attributed to the adsorbed species of OC*CHO,^[25] arising from the coupling of *CO with *CHO intermediates. The coupling process to produce OC*CHO is regarded as the rate-determining step for one of the reaction pathways over the Cu-based catalysts to generate C₂₊ products by deep reduction of *CO. However, this band is not obviously observed over Cu NP and Cu-CeO₂-20%. On the one hand, the probability of this coupling process occurring over these two catalysts is much lower than that of Cu-CeO₂-5% seen from the CO₂RR performance, leading to the band coverage by other intermediate signals. On the other hand, the reaction pathways to produce C₂₊ products over these two catalysts may be different from that of Cu-CeO₂-5%.

As the adsorbed *CO and *CHO are the key reaction intermediates for CO₂RR to C₁ or C₂₊ products, we further make

the comparison of the relative peak of Cu NP, Cu-CeO₂-5%, and Cu-CeO₂-20%. As shown in Figure 4d, the total peak area of these two intermediates (*CO and *CHO) gradually increased as the potential became more negative for Cu-CeO₂-5% and Cu-CeO₂-20% owing to the increasing reaction rate, while the relative value became decreased at -1.2 V (vs RHE) for Cu NP. The total contents of the two key intermediates basically follow in the order of Cu-CeO₂-5% > Cu-CeO₂-20% > Cu NP regardless of potential. That means the Cu/CeO₂ interfacial sites can promote the CO₂ transformation to adsorbed *CO and *CHO for further reduction, while moderate Cu/CeO₂ interfacial sites (Cu-CeO₂-5%) are conducive to produce more intermediates of *CO and *CHO. The relative ratio of *CHO intermediates for these catalysts is obtained based on their peak area to the total area of these two intermediates (Figure 4e). Compared with Cu NP, the CeO₂-modified catalysts exhibit much lower ignition bias and much higher ratio of *CHO, further verifying that the Cu/CeO₂ interfacial sites can evidently enhance the *CO hydrogenation to *CHO which is always regarded as a rate-determining step for the CO₂ deep reduction to produce CH₄ or C₂₊. Furthermore, Cu-CeO₂-20% shows apparently much higher *CHO ratio than Cu-CeO₂-5%, even though it has much lower total value of these two

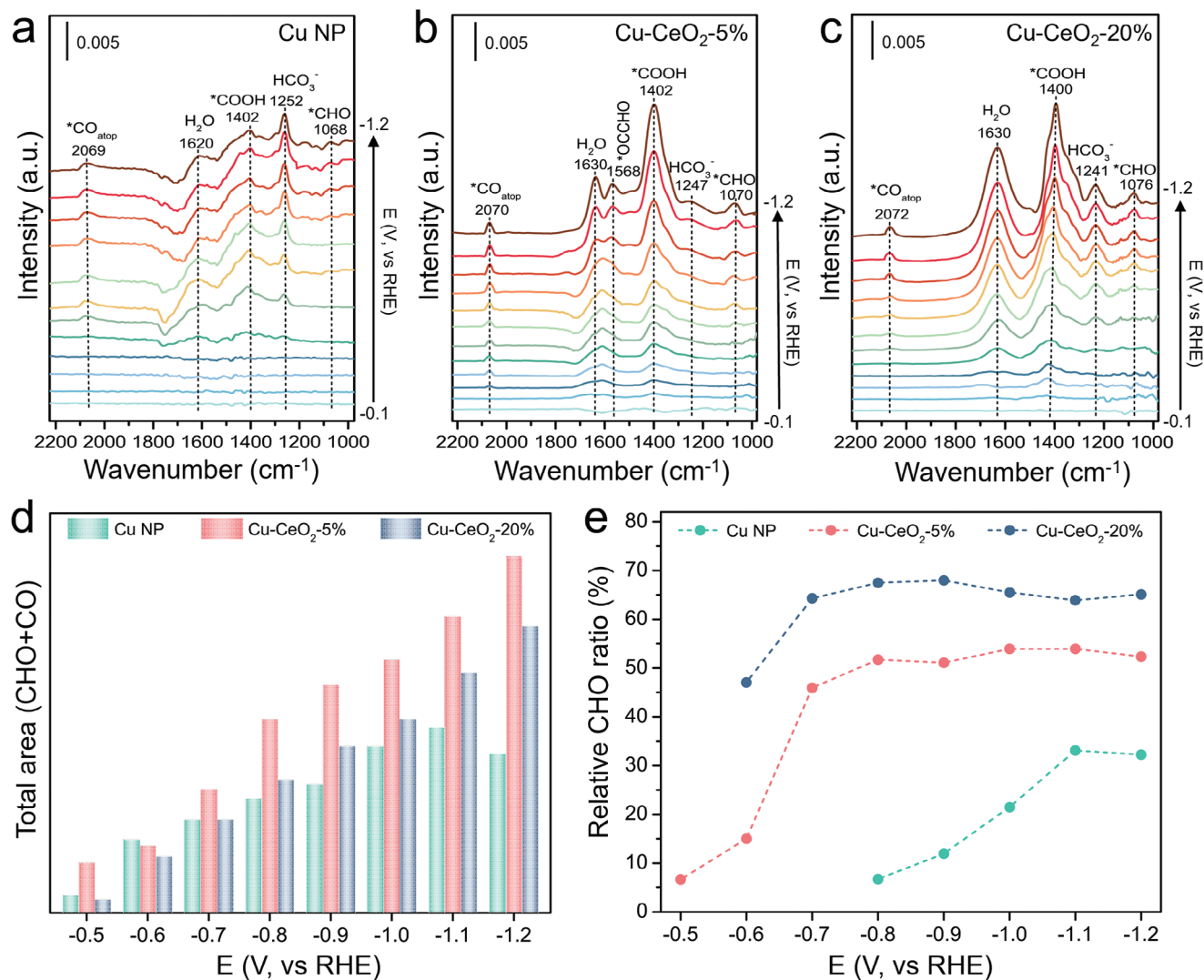


Figure 4. a–c) The in-situ ATR-SEIRAS spectra Cu NP a), Cu-CeO₂-5% b), and Cu-CeO₂-20% c). d) The total peak area of *CO and *CHO. e) The relative *CHO ratio in the total area of *CO and *CHO.

intermediates owing to the larger coverage of surface Cu sites. Combined with the CO₂RR results, it can be deduced that enough amount of both *CO and *CHO intermediates is conducive for their coupling toward C₂₊ pathway over moderate CeO₂-loading Cu surface. On the contrary, relatively larger amount of *CHO intermediates accompanied with much lesser *CO intermediates will inhibit the C-C coupling process, while the further hydrogenation of *CHO is preferred toward CH₄ pathway over high CeO₂-loading Cu surface.

Theoretically, we resorted to DFT calculations to rationalize the CeO₂ content-dependent CO₂RR performance. Taking CO/CH₄ and C₂H₄/CH₃CH₂OH as the representative C₁ and C₂ products, we determined and compared the CO₂RR energetics over Cu (111) surface and CeO_{2-x}/Cu (111) interface (Figure 5). Regarding the C₁ production (left column in Figure 5), it is evident that bare Cu(111) surface and CeO_{2-x}/Cu(111) interface play very different roles in *CO formation, *CO hydrogenation, and *CH₃ formation, as indicated by green, red, and or-

ange dash circles, respectively. Cu(111) is prone to convert CO₂ into *CO (small barrier of 0.28 eV) but subsequent conversion to *CHO (endothermic by 0.75 eV) and CH₄ (huge barrier of ≈1.8 eV for CH₃-O or CH₃-OH bond cleavage) is difficult. In contrast, CeO_{2-x}/Cu(111) interface shows an opposite trend that *CO formation is less favored (barrier of 0.73 eV) but the hydrogenation of *CO and other intermediates generally gets promoted with enhanced thermodynamics. Particularly for the *CH₃ formation, while the CH₃-O bond cleavage being similar to that on Cu(111) surface, we observe an obvious decrease of ≈0.7 eV in the CH₃-OH dissociation barrier at the Cu/CeO₂ interface (1.15 vs 1.88 eV). Such significant promotion is attributed to the distinct transition structure that gains proper accommodation of OH and CH₃ moieties via interfacial Ce and Cu atoms at the same time (Figure S15, Supporting Information). Moreover, we note that typical electro-reductive conditions such as negative potentials and surface *H coverage could further lower the CH₃-OH dissociation barrier (Figure S16,

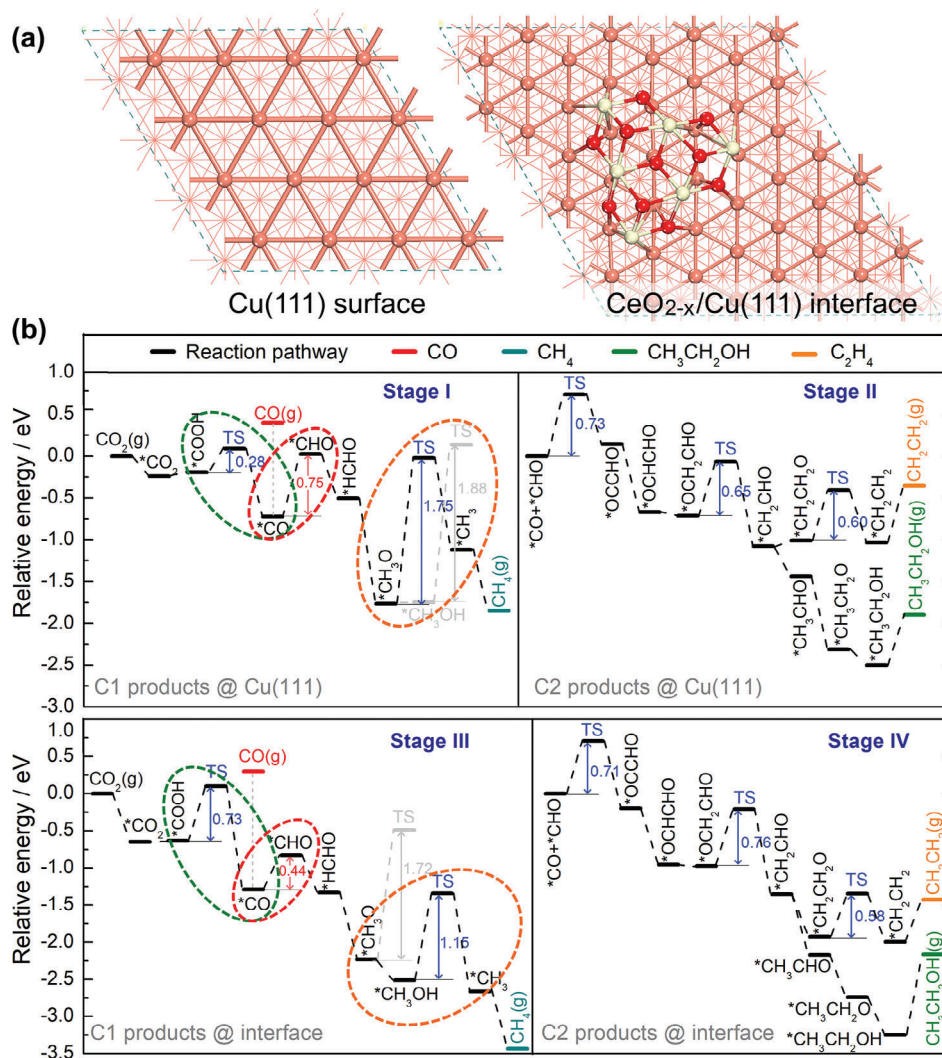


Figure 5. a) Optimized calculation models as well as b) CO₂RR energetics for C₁ and C₂ production over Cu (111) surface and CeO_{2-x}/Cu(111) interface. The cerium, oxygen, and copper atoms are presented as ivory, red, and orange balls, respectively.

Supporting Information), facilitating the CH₄ production at the Cu/CeO₂ interface.

Regarding the C–C coupling for C₂ production, DFT calculations exclude the *CO-*CO pathway owing to the extreme instability of the *OCCO intermediate, consistent with the previous reports.^[26] Alternatively, the *CO-*CHO pathway is likely responsible for the C₂ products, through which no obvious difference in coupling barriers is observed between the two sites despite more intensive exothermic energetics at the interface (right column in Figure 5). It implies that the C₂ production is readily to proceed as long as *CO and *CHO gather together with comparable concentrations. Overall, these results bring us three important features of CO₂RR on Cu-CeO_{2-x} catalysts. First, efficient CO₂ reduction requires the cooperation of bare Cu surface (*CO formation) and Cu/CeO₂ interface (*CO hydrogenation); Secondly, the product selectivity to CH₄ or C₂₊ depends on the relative surface concentration of *CO and *CHO intermediates, and thus could be tuned by altering the relative content of Cu/CeO₂ interface sites and bare Cu surface sites. Thirdly, CO₂ reduction ignites over

the Cu NP surface (Stage I in Figure 5), and the as-formed *CO diffuses to the CeO_{2-x}/Cu (111) interface and gets hydrogenated into *CHO (Stage III), which triggers either the C₂ production upon comparable *CO and *CHO concentrations (Stage IV), or deep hydrogenation into CH₄ upon insufficient *CO concentration (Stage III).

In addition, regarding the typical competitive reaction of hydrogen production (HER), two key processes of Heyrovsky (H⁺ + e⁻ + * → *H) and Tafel (H* + H* → H₂) reactions are widely conceived to be responsible for the hydrogen production activity.^[27] We have previously determined an energy barrier of 0.56 eV for Heyrovsky reaction at the water/copper interface using state-of-the-art constrained molecular dynamics simulations.^[28] As for the Tafel reaction, given the significant charge redistribution around the Cu/CeO₂ interface region (Figure S17a, Supporting Information), the hydrogen adsorption energy was computed to be ≈ -0.3 eV at the interface whereas -0.41 eV on bare Cu(111) surface (Figure S17b, Supporting Information), corresponding to a H–H coupling barrier of 0.64 and 0.72 eV, respectively. Thus,

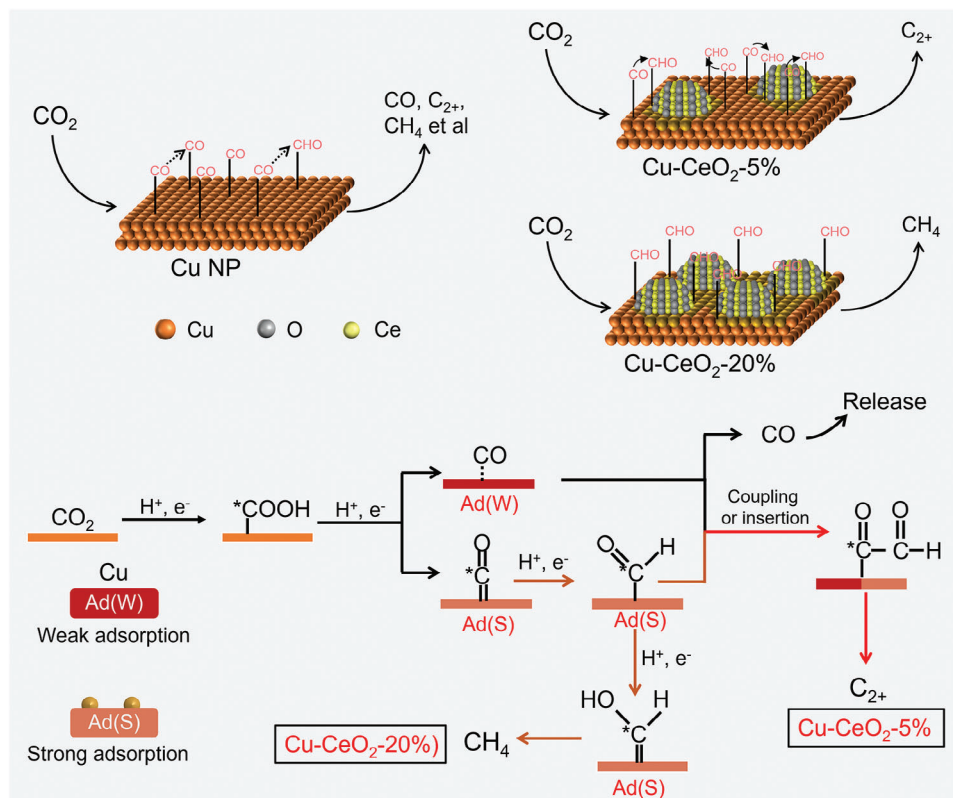


Figure 6. Schematic diagram of CO₂RR mechanism over different catalysts.

it is anticipated that HER generally shows a reaction barrier of 0.6–0.7 eV over the CeO₂/Cu composites, which is higher than the hydrogenation barrier of 0.3–0.6 eV for the key intermediates in CO₂ reduction (e.g., *CO₂, *CO, *COOH).^[28,29] Such difference in barrier heights signifies a preference of CO₂ reduction over HER for the Cu/CeO₂ reverse catalyst, rationalizing the relatively low H₂ production as observed in experiments (Figure 2).

Summarizing above experimental characterization and DFT results allows to figure out the regulation mechanism that determines the varied CO₂RR selectivity along with different CeO₂ content (**Figure 6**). (1) The adsorption of key intermediates, such as *CO and *CHO, is significantly stronger at Cu/CeO₂ interfacial sites than that over Cu sites (CO desorption energy of 1.59 vs 1.12 eV; Figure 5). Thus, the formed *CO desorbs more easily over Cu surface, resulting in low C₂₊ and CH₄ selectivity for Cu NP. (2) Effective C–C coupling requires *CHO at Cu/CeO₂ interfacial sites and *CO over Cu sites, and accordingly moderate CeO₂ loading content (Cu-CeO₂-5%) exposes matched Cu/CeO₂ interfacial sites and Cu sites and thus enhances evidently the C₂₊ selectivity. (3) Too much CeO₂ deposition causes excessive interfacial sites surpassing the Cu sites, leading to declined *CO formation and suppressed *CO*CHO coupling.^[30] The strong adsorption and activation capability of the Cu/CeO₂ interfacial sites drives further hydrogenation of *CHO toward CH₄ production for Cu-CeO₂-20%. The comparison of various strategies with respect to the regulation of the CO₂RR selectivity to C₂₊ or

CH₄ is thoroughly discussed as displayed in Table S3 (Supporting Information).

3. Conclusion

In this work, a series of Cu-loaded CeO₂ inverse catalysts (Cu-CeO₂-x) are designed to apply to CO₂RR. The dominant CO₂RR products of the Cu-CeO₂-x can be regulated from C₂₊ to CH₄ by adjusting the relative CeO₂ loading content. The characterization and theoretical results illustrate that the CeO₂ loading produces highly active Cu/CeO₂ interfacial sites for Cu-CeO₂-x catalyst, which can enhance the adsorption and transformation of reactants CO₂ and intermediates like *CO conducive to the CO₂ deep reduction to high-value products like C₂₊ or CH₄. Moreover, moderate CeO₂ loading content with sufficient Cu/CeO₂ interfacial sites and Cu sites is conducive to the integration of the intermediates over interfacial sites (*CHO) and adjacent Cu sites (*CO), thus enhancing C₂₊ selectivity. However, much more CeO₂ loading content accompanied by significantly decreased catalytic centers inhibits the C–C coupling. The strong adsorption and activation of intermediates like *CO and *CHO over the Cu/CeO₂ interfacial sites prefer multiple hydrogenations to produce CH₄. Consequently, Cu-CeO₂-5% exhibits the best C₂₊ selectivity with maximum FE_{C₂₊} of 62.6% (*j*_{C₂₊} = –250.4 A cm^{–2}) at *j*_{total} of –400 mA cm^{–2}, while Cu-CeO₂-20% has the best CH₄

selectivity with maximum FE_{CH_4} of 51.3% ($j_{CH_4} = -153.9$ mA cm⁻²) at j_{total} of -300 mA cm⁻². This work provides a deep insight into the regulation of interface adsorption sites and their structure-activity relationship over CO₂RR for the metal-oxides catalysts.

4. Experimental Section

Chemicals: Cu nanoparticles (30 nm, 99.9%) and methanol (99.5%) were purchased from Macklin. Ce(NO₃)₃ · 6H₂O (99.5%) was obtained from Aladdin. The carbon paper with gas diffusion layer (GDL) was purchased from Toray Industries.

Synthesis of Cu-CeO_{2-x} Inverse Catalysts: A series of Ce(NO₃)₃ · 6H₂O methanol solutions with different concentrations (0.04, 0.1, 0.2, and 0.4 mmol L⁻¹) were prepared in 3 mL glass vials. Then 128 mg commercial Cu NP (2 mmol) were dispersed into the solution under moderate sonication for 30 min. The slurry was slowly stirred under slight vacuuming at room temperature until the methanol volatilizing. The obtained solid was calcined in a tube furnace under Ar atmosphere at 350 °C for 2 h to get the corresponding Cu-CeO_{2-x} inverse catalysts ($x = 2\%, 5\%, 10\%, 20\%$, mol%).

Material Characterization: X-ray diffraction patterns (XRD) were characterized on an ARL EQUINOX 1000 diffractometer (Thermo Scientific, USA) by using Cu K α rays ($\lambda = 0.15406$ nm) radiation in the 2θ range of 10–80°. Transmission electron microscopy (TEM) images were obtained on JEM-F200 at 200 kV equipped with energy dispersive spectroscopy (EDS). Thermo Scientific K-Alpha spectrometer was served to collect X-ray photoelectron spectra (XPS). The Raman spectra were recorded in a LabRam HR Evolution laser confocal micro-Raman spectrometer with laser wavelength of 532 nm. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was employed to determine the actual Ce and Cu content of samples in a PerkinElmer 8300 spectrometer. All samples were digested in concentrated HNO₃ and diluted in DI water with specific concentrations prior to measurements.

CO₂ temperature programmed desorption (CO₂-TPD) was performed on a TP-5076 TPD/TPR dynamic adsorber (Xianquan, China) equipped with a mass spectrometry (MS) detector in a quartz tubular microreactor. 50 mg of the sample was first activated in 5% H₂/He at 300 °C for 30 min and then cooled down to 25 °C. The adsorption was carried out at 25 °C for 30 min under constant stream of pure CO₂ (20 mL min⁻¹). Subsequently, CO₂ desorption was started in flowing He (20 mL min⁻¹) under temperature from 25 to 750 °C with heating rate of 10 °C min⁻¹. The CO₂ signal ($m/z = 44$) was continuously recorded online in a mass spectrometer (EXQ, Hiden).

The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to simulate the CO adsorption over Cu-CeO_{2-x} catalyst during CO₂RR process, which was performed on a Thermo Nicolet 6700 Spectrometer (Thermo Fisher, USA) equipped with high-temperature reaction cell and MCT detector. The IR spectra were obtained with a resolution of 64 scans and 4 cm⁻¹ in absorbance units. 100 mg of catalyst was first heated up to 300 °C and kept for 30 min in flowing He gas (40 mL min⁻¹), and then switched to 5 vol% H₂/He treatment for another 30 min. The sample was cooled down to 25 °C in flowing He (40 mL min⁻¹) and the spectra were taken for a background. Afterward, the gas was changed to CO/He (2 vol%, 30 mL min⁻¹) and retained for 30 min until saturation coverage. At last, the gas was switched to He (40 mL min⁻¹) and retained for 10 min before the spectra were collected.

The Attenuated Total Reflection-Surface Enhanced Infrared Absorption Spectroscopy (ATR-SEIRAS) was performed on an INVENIO R FT-IR (Bruker) spectrometer equipped with an MCT detector. 10 mL of 0.5 M KHCO₃ solution was used as the electrolyte, and the Pt sheet and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. For the working electrode, 30 μ L of catalyst ink (5 mg mL⁻¹) was dropped onto a semi-cylindrical Si crystal and then vacuum dried, and a stainless-steel wire was glued to lead out. Pure CO₂ (20 mL min⁻¹) gas was continuously pumped into the electrolyte during the experiments. The

working electrode was first pre-reduced at -0.8 V (vs. RHE) for 10 min to make the working electrode at a steady state. Then the ATR-SEIRAS tests were performed between -0.1 and -1.2 V (vs. RHE) with pre-recorded background spectra. All spectra were recorded by absorbance that was $\log(R/R_0)$. The spectral resolution and scan rate was 4 cm⁻¹ and 3 mV s⁻¹, respectively. The scan time was 0.5 min.

Preparation of Gas Diffusion Electrodes: A 12 mg of catalyst powder was dispersed in 4 mL of isopropanol solution containing 20 μ L of Nafion ionomer solution (5 wt.% H₂O) and ultrasonicated for 30 min to obtain a uniform catalyst ink. The catalyst ink was then drop-cast onto the carbon paper equipped with gas diffusion layer (GDL) (Toray, Japan) to achieve a catalyst loading of 1 mg m⁻² to obtain the gas diffusion electrode (GDE).

Electrochemical Measurements: CO₂ electrolyzing experiments were implemented on a customized three-chamber flow cell with an effective area of 1 cm² (1 cm $\times$ 1 cm) by a CHI1140E workstation with three electrode system. The prepared GDE, Ni foam, and Ag/AgCl (saturated KCl solution) were served as cathode working electrode, counter electrode, and reference electrode, respectively. A piece of proton exchange membrane (Nafion-117) was used to separate cathode and anode compartments. The electrolyte was 0.5 M KHCO₃ aqueous solution (99.99%, Macklin Inc.). Using a syringe pump, the cathode and anode chambers were constantly fed with the electrolyte with a flow rate of 1.0 mL min⁻¹. 20 sccm of CO₂ feedstock (99.99%) was supplied to the cathode gas chamber controlled by a mass flow meter. The CO₂ electrolysis was conducted by chronopotential method. All recorded potentials were transformed to reverse hydrogen electrodes (RHE) according to the equation

$$E_{RHE} = E_{Ag/AgCl} + E^{\theta}_{Ag/AgCl} + 0.059 \times \text{pH (V)} \quad (1)$$

Using a gas chromatography spectrometry (GC-2014C, Shimadzu) with the online system, the gas products were analyzed, in which H₂ and CO were quantified by thermal conductivity detector (TCD) and flame ionization detector (FID1), while CH₄ and C₂H₄ were detected on FID2. The faradaic efficiency of gas products was determined through the equation:

$$FE (\%) = \frac{Q_x}{Q_{total}} \times 100\% = \frac{n_x \times C_x \times v \times t \times F}{I \times t \times V_M} \times 100\% \\ = \frac{n_x \times C_x \times v \times F}{I \times V_M} \times 100\% \quad (2)$$

The liquid products were then analyzed using a Bruker AVIII (600 MHz) nuclear magnetic resonance hydrogen spectrometer (¹HMR). Specifically, after 20 min of electrolysis, 500 μ L of cathodic electrolyte containing the liquid products was mixed with 100 μ L of D₂O containing 20 ppm (v/v) dimethyl sulfoxide ($\geq 99.9\%$, Alfa Aesar) as internal standard. Then the 1D ¹HMR spectra of the liquid products under different current densities were measured. The product amount was quantified by the peak area of the corresponding species. The Faradaic efficiency of the liquid product y was then determined by the following equation:

$$FE (\%) = \frac{Q_y}{Q_{total}} \times 100\% = \frac{n_y \times C_y \times v_L \times t \times F}{I \times t} \times 100\% \\ = \frac{n_y \times C_y \times v_L \times F}{I} \times 100\% \quad (3)$$

n_x, n_y : electrons transferred for reduction to product x, y; C_x, C_y : volume fraction or molar concentration of product x or y quantified by GC or HMR; v : gas flow velocity of outlet, L s⁻¹; v_L : Cathode liquid flow rate, L s⁻¹; F : Faradic constant, 96500 C mol⁻¹; I : average current during electrolysis, A; V_M : gas molar volume, 22.4 L mol⁻¹.

Computational Methods: All spin-polarized density functional theory (DFT) calculations were carried out using the Vienna ab initio Simulation Package. Electronic exchange and correlation were treated within the generalized gradient approximation (GGA), and the projector-augmented wave (PAW) method with an energy cutoff of 450 eV was employed to describe the interaction between atomic cores and electrons, with the Ce

(5s, 5p, 6s, 5d, 4f), Cu (3d, 4s), O (2s, 2p), C (2s, 2p), and H (1s) shells being treated as valence electrons. Throughout the calculations, the on-site Coulomb interaction correction with an effective U value of 5.0 eV for the Ce 4f orbitals to better describe the localized electron states, consistent with previous reports was applied.^[31] The transition states (TSs) of surface reactions were located by using a constrained minimization method until the Hellman-Feynman forces on each ion were less than 0.05 eV Å⁻¹.^[32] The DFT-D3 scheme was applied throughout the calculations to take the van der Waals (vdW) interaction into account.

The Cu NP catalyst was constructed as a four-layer $p(4 \times 4)$ Cu(111) surface with a 12 Å vacuum gap separating periodic cells. The bottom two layers of Cu substrate were kept fixed while other atoms were allowed to relax during structural optimization. The Cu-CeO_{2-x} interface was constructed by adopting a well-established CeO₂/Cu(111) composite model,^[33] which composes of a Ce₆O₁₃ triangle island (featuring CeO₂(111) lattice structure) over a large three-layer $p(4\sqrt{3} \times 4\sqrt{3})$ Cu(111) supercell. Given that the typical reductive environment of CO₂RR, three apex oxygen atoms in the original Ce₆O₁₃/Cu(111) model were removed owing to their surmountable oxygen vacancy formation energy of ≈ 2.5 eV (relative to the value of ≈ 3.3 eV for side oxygens), giving rise to a CeO_{2-x}/Cu(111) composite structure containing 6 Ce, 10 O, and 144 Cu atoms. Considering the large size of lattice parameters (17.78 $\times$ 17.78 Å²), the Brillouin-zone integration was treated using a $1 \times 1 \times 1$ k-points mesh. During all calculations, the bottom layer of Cu substrate remained fixed while the other Cu and ceria layers were allowed to relax. Note that such model agrees well with experimental observation of CeO₂(111) and Cu(111) facets as well as plenty of oxygen vacancies in the synthesized Cu/CeO₂ inverse catalysts (Figures 5 and S13–S15, Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This project was supported financially by the National Key R&D Program of China (2021YFB3501900), the National Natural Science Foundation of China (22475031 and 22273021), the National Youth Top-notch Talent Support Program of China, and Shanghai Science and Technology Development Funds (22QA1402900).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

C₂₊/CH₄ selectivity, CO₂RR, Cu/CeO₂ interface, strong/weak adsorption

Received: October 22, 2024

Revised: January 5, 2025

Published online: January 23, 2025

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