



Cite this: *J. Mater. Chem. A*, 2024, 12, 20115

Customized CO₂ electroreduction to methane or ethylene by manipulating *H and *CO adsorption on Cu/CeO_x catalysts†

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The coverage of *CO and *H intermediates on the surface of a catalyst plays a pivotal role in determining the selectivity towards C₁ or C₂ products in the electrochemical CO₂ reduction reaction (CO₂RR). In this study, we engineered two types of interfaces involving copper and rare earth metal oxides, specifically Cu/CeO_x and Cu/CuCeO_x solid solution, which exhibit enhanced binding affinities for *H and *CO adsorbates in the CO₂RR, respectively. As a result, the Cu/CuCeO_x catalyst delivered an ethylene faradaic efficiency of 40.2% at a partial current density of $-245.7 \text{ mA cm}^{-2}$, whereas the Cu/CeO_x catalyst presented a methane faradaic efficiency of 38.6% at a partial current density of $-198.3 \text{ mA cm}^{-2}$. Results of theoretical and experimental analyses have demonstrated that the Cu–Ce–O_x solid solution markedly enhances *CO adsorption by stabilizing Cu⁺ species, thereby favoring its dimerization to ethylene rather than converting to methane through hydrogenation. This investigation elucidates a strategy for directing the selective electroproduction of C₁ or C₂ compounds from the CO₂RR by effectively manipulating *H and *CO adsorption on Cu/CeO_x catalysts.

Received 17th March 2024

Accepted 28th June 2024

DOI: 10.1039/d4ta01808g

rsc.li/materials-a

Introduction

The relentless rise in atmospheric CO₂ levels, predominantly driven by anthropogenic activities, has been identified as a principal factor exacerbating global warming, eliciting widespread concern across the globe.^{1,2} Within this critical context,

the electrochemical carbon dioxide reduction (CO₂RR), especially when powered by renewable energy sources like solar and wind, has emerged as a vital strategy for carbon balance restoration.^{3–5} Distinct from the generation of simpler C₁ products like formic acid (HCOOH) and carbon monoxide (CO),⁶ there is an intensified demand for the production of high energy density hydrocarbons, notably methane (CH₄) and ethylene (C₂H₄), which are envisioned as potential sustainable fuels.^{7–9} To date, copper-based materials, endowed with optimal adsorption energy for the *CO intermediate, have been heralded as the most effective catalysts for facilitating the conversion of CO₂ into valuable hydrocarbons.^{10,11} In pursuit of this, a spectrum of Cu-based electrocatalysts, encompassing metallic Cu, Cu oxides,^{12–14} Cu-integrated metal–organic frameworks (MOFs),^{15,16} and Cu-centric molecules,^{17,18} have been meticulously developed, marking significant strides in the electrocatalytic conversion of CO₂ to CH₄ or C₂H₄. Nevertheless, the design of cost-effective and durable catalysts tailored for the targeted transformation of CO₂ into high-energy products continues to pose a formidable challenge.

The mechanism underlying the CO₂RR involves the initial reduction of CO₂ to adsorbed *CO, succeeded by *CO hydrogenation and/or C–C coupling processes.^{8,19} Recent investigations have illuminated that *CO hydrogenation to *CHO represents the rate-limiting step in CH₄ generation, while *CHO also acts as a pivotal intermediate for multi-carbon (C₂) products.^{4,20} Moreover, the journey from *CO to hydrocarbons encapsulates a multi-step hydrogenation sequence, with *H emerging as a crucial intermediary for hydrocarbon synthesis.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ta01808g>



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fuel conversion systems and exploring efficient electrocatalysts.

Consequently, fine-tuning the adsorption dynamics of *CO and *H presents a promising avenue for steering the CO_2RR towards desired products, particularly for CH_4 and C_2H_4 . For example, Zheng *et al.* showcased that the strategic incorporation of two metal dopants, Zn and Mn, into Cu matrices could simultaneously modulate the coverage of *H and *CO , enabling the fine-tuning of selectivity between CH_4 and C_2H_4 .²¹ Similarly, Sargent *et al.* effectively manipulated *CO coverage through varying CO_2 concentrations, achieving tunable product specificity from C_2H_4 to CH_4 .²² In a parallel vein, Wei and colleagues enhanced the adsorption of the CO intermediate by augmenting polyaniline on Cu substrates, thereby activating CO_2 molecules and yielding a significant faradaic efficiency (FE) for C_2 products.²³ Despite these advances, attaining high selectivity shifts between desired products using analogous materials remains elusive, thereby underscoring the impetus for novel catalyst development.

In this report, we introduce an innovative strategy employing functional rare-earth metal oxides to facilitate selectivity switching between CH_4 and C_2H_4 products by modulating *H and *CO adsorption (Fig. 1). Two distinct electrocatalysts, Cu/CeO_x and a Cu/CuCeO_x solid solution ($0 < X < 2$), were synthesized, with the CeO_x component enhancing *H coverage through expedited water dissociation, while Cu–Ce–O_x solid solutions stabilize Cu⁺ species, augmenting *CO adsorption and catalyzing the C–C coupling process. Electrochemical CO_2RR evaluations revealed that the Cu/CuCeO_x catalyst achieved an ethylene FE of 40.2% at a partial current density of $-245.7 \text{ mA cm}^{-2}$, in contrast to the Cu/CeO_x variant, which exhibited a methane FE of 38.6% at a partial current density of $-198.3 \text{ mA cm}^{-2}$. Density functional theory (DFT) calculations further illustrated that Cu–Ce–O_x solid solutions significantly reduce the formation energy of the *COCHO intermediate, thereby enhancing C_2H_4 production. This paradigm of adjusting CO_2RR selectivity *via* intermediary coverage heralds new avenues for designing innovative Cu-based nanocomposite catalysts.

Results and discussion

The Cu/CuCeO_x catalyst was synthesized utilizing the coprecipitation methodology delineated in previous studies,²⁴ and subsequently subjected to annealing in a mixed atmosphere of 5 vol% H₂/Ar (Fig. 2a and S1†). In contrast, the Cu/CeO_x catalyst was fabricated through a bifurcated procedure: initially, CeO_x was prepared devoid of any Cu precursor *via*

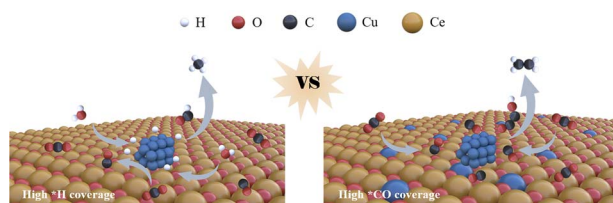


Fig. 1 Diagrams of methane and ethylene production on Cu/CeO_x and Cu/CuCeO_x during the CO_2RR , respectively.

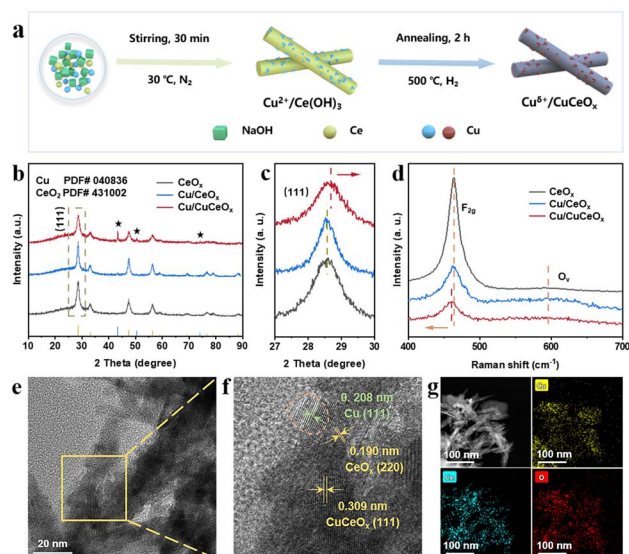


Fig. 2 (a) Synthetic route of the Cu/CuCeO_x catalyst by a coprecipitation method. (b) XRD spectra, (c) local amplification of (111) and (d) Raman spectra for CeO_x, Cu/CeO_x, and Cu/CuCeO_x catalysts (CeO₂, yellow, PDF# 43-1002; Cu, blue, PDF# 04-0836). (e and f) HRTEM images and (g) EDX elemental distribution mapping images of Cu/CuCeO_x.

coprecipitation; thereafter, Cu/CeO_x was produced by an impregnation technique. The X-ray diffraction (XRD) analysis of the synthesized samples (Fig. 2b) reveals diffraction peaks at 28.55° , 32.08° , 47.48° , 56.34° , 59.09° , 69.42° , 76.70° , 79.08° , and 88.43° , congruent with the established cubic fluorite-like structure of CeO₂ (PDF# 43-1002). Additionally, characteristic diffraction peaks of Cu are discernible (indicated by a pentagram at 43.30° , 50.43° , and 74.13°) corresponding to PDF# 04-0836. Notably, the (111) plane of Cu/CuCeO_x exhibits a discernible shift towards higher Bragg angles compared to CeO_x and Cu/CeO_x (Fig. 2c), suggesting the formation of a Cu–Ce–O_x solid solution due to the substitution of a larger cation by a smaller one.^{25–27} As the Cu content continues to increase, some of the copper precipitates out, forming clustered copper species on the Cu/CuCeO_x nanorods.²⁸ And no diffraction peaks corresponding to Cu can be found when the copper loading is below 30 wt%, which may be due to the high dispersion of Cu nanoparticles with too small particle sizes on the surface of the ceria support to be identified by the XRD (Fig. S2†).^{29,30} Raman spectroscopy of the catalysts reveals an intense band around 459 cm^{-1} and another at approximately 595 cm^{-1} , corresponding to the F_{2g} vibration pattern and defect-induced mode (O_v) in a cubic fluorite structure, respectively.³¹ Notably, the F_{2g} bands of Cu/CuCeO_x exhibit a redshift to lower frequencies with increasing Cu loading, compared to pure CeO_x (Fig. S3†), indicative of Cu atom doping into the CeO_x lattice and Cu/CuCeO_x interface formation.^{32,33} This results in extended Ce–O bond lengths at the interface and lattice distortions due to the atomic radius disparity between Cu⁺ and Ce⁴⁺/Ce³⁺,^{34,35} corroborating the XRD findings.

Transmission electron microscopy (TEM, Fig. S4†) images depict the Cu/CuCeO_x as possessing rod-like nanostructures.

The dynamic light scattering in Fig. S5† further illustrates that the particle size distribution between 50 and 200 nm is slightly wider than that presented by TEM, which may be caused by partial rupture or aggregation of cerium dioxide. High-resolution TEM (HRTEM) images (Fig. 2e and f) identify the main interplanar spacings of 0.309 nm corresponding to the Cu–Ce–O_x (111), slightly smaller than the Cu/CeO_x's CeO₂ (111) plane (0.312 nm) observed in Fig. S6.† Other characteristic *d*-spacings at 0.190 and 0.208 nm correspond to the CeO₂ (220) and Cu (111) planes, respectively. Elemental mapping *via* energy-dispersive X-ray spectroscopy (EDS, Fig. 2g) confirms the uniform distribution of Cu, Ce, and O within Cu/CuCeO_x without significant agglomeration. Moreover, inductively coupled plasma atomic emission spectroscopy (ICP-OES) quantified the Ce and Cu composition, aligning closely with theoretical expectations (Table S1†).

The valence states and surface chemistry of Cu, Ce, and O were investigated by X-ray photoelectron spectroscopy (XPS). The Ce 3d XPS spectra for both Cu/CeO_x and Cu/CuCeO_x nanorods, depicted in Fig. 3a, were deconvoluted into eight peaks corresponding to Ce 3d_{5/2} (v, 882.4 eV; v', 884.9 eV; v'', 888.7 eV; v''', 898.2 eV) and Ce 3d_{3/2} states (μ, 900.8 eV; μ', 903.5 eV; μ'', 907.2 eV; μ''', 916.6 eV).^{36,37} Peaks designated v, v', v'', μ, μ', and μ'' are indicative of Ce⁴⁺ species, while the v' and μ' peaks are attributed to Ce³⁺ species, denoting the coexistence of Ce⁴⁺ and Ce³⁺ within the composite matrix.³⁸ The relative abundance of Ce³⁺ to total cerium species was quantitatively assessed and was summarized in Table S1.† The ratio of Ce³⁺ in Cu/CeO_x and Cu/CuCeO_x is 0.114 and 0.128, respectively. A noteworthy observation was the positive shift in the Ce⁴⁺ peaks for Cu/CuCeO_x (Fig. S7†), suggestive of alterations in the central charge distribution between Cu and Ce.³⁹ The Cu/CuCeO_x exhibited a predominance of Ce³⁺ species, which are postulated to facilitate rapid electron transport and mitigate electron localization at the Cu²⁺/Cu⁺ sites within the Cu–Ce–O_x solid solution matrix.⁴⁰ The O 1s XPS spectra are analyzed in Fig. 3b,

which can be resolved into two distinct peaks by deconvolution: one at a lower binding energy of 529.3 eV associated with lattice oxygen (O_{latt}) and another at 531.3 eV, ascribed to adsorbed oxygen species (O_{ads}).⁴¹ The number of oxygen vacancies calculated from the deconvoluted core level O 1s spectra is shown in Table S1.† The Cu 2p XPS spectra (Fig. 3c) exhibit binding energies of 952.7 eV and 932.9 eV, characteristic of Cu⁺ or Cu⁰ species.^{42,43} A minor presence of CuO, attributed to inevitable surface oxidation, was also noted.^{39,44} Given the challenges in distinguishing between Cu⁰ and Cu⁺ based on Cu 2p_{3/2} spectra alone,²⁹ additional analysis was conducted using Cu LMM Auger kinetic energy spectra (Fig. 3d), where peaks at 570.0 and 565.3 eV substantiate the presence of Cu⁺ and Cu⁰ species, respectively.^{45,46} Herein, most of the Cu on the surface is oxidized to monovalent Cu species. The Cu/CuCeO_x sample possesses the most surface monovalent Cu species (0.78), much higher than that of Cu/CeO_x (0.56). The presence of monovalent copper is conducive to the adsorption of *CO.⁴⁷

The CO₂RR catalytic performances of Cu/CuCeO_x catalysts were tested in a flow cell, in which 1.0 M KOH was used as the electrolyte. In this work, all the applied potentials were converted into a reversible hydrogen electrode (RHE) scale without *iR* correction. The linear sweep voltammetry curves (LSV) shown in Fig. 4a were recorded by feeding the CO₂ gas across the 1.0 M KOH interface. Note that the Cu/CuCeO_x catalysts exhibited higher current density responses than those of CeO_x and Cu/CeO_x catalysts, and we assume that the formation of Cu–Ce–O_x solid solutions may enrich active sites that kinetically favored the CO₂RR. To verify the hypothesis, we conducted the cyclic voltammetry (CV) method to estimate the electrochemically active surface area (ECSA) of the catalysts (Fig. S8†). The results show that Cu/CuCeO_x had larger ECSA values than the Cu/CeO_x catalyst, indicating that the generation of Cu–Ce–O_x solid

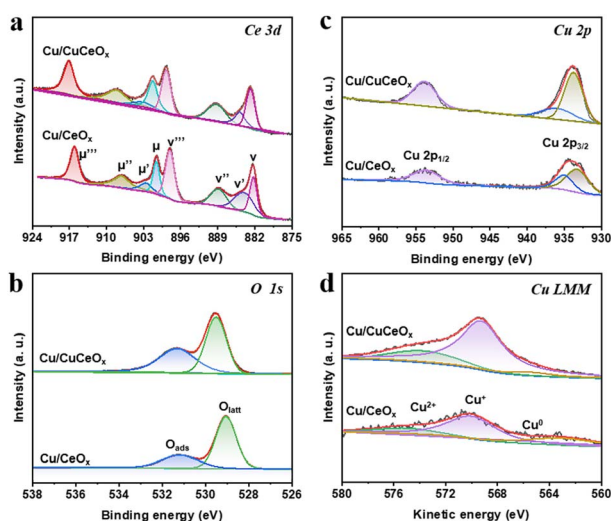


Fig. 3 XPS analysis of (a) Ce 3d, (b) O 1s, (c) Cu 2p, and (d) Cu LMM Auger spectra for Cu/CeO_x and Cu/CuCeO_x.

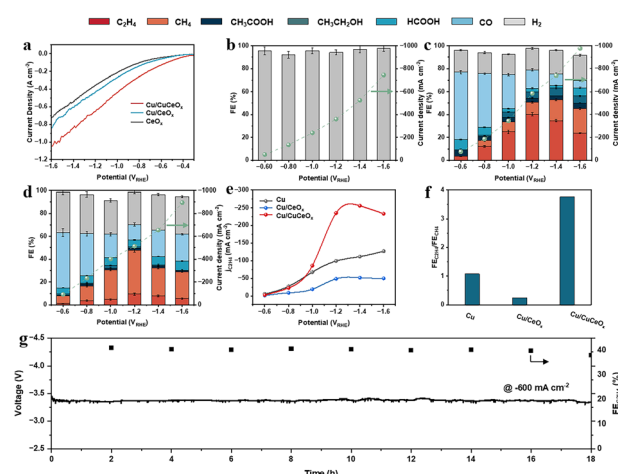


Fig. 4 (a) LSV spectra of CeO_x, Cu/CeO_x, and Cu/CuCeO_x catalysts. (b–d) FEs of products at different applied potentials in 1.0 M KOH electrolyte for CeO_x, Cu/CeO_x, and Cu/CuCeO_x. (e) C₂H₄ partial current densities of Cu, Cu/CeO_x, and Cu/CuCeO_x under different potentials. (f) FE_{C₂H₄}/FE_{CH₄} of CeO_x, Cu/CeO_x, and Cu/CuCeO_x at –1.2 V_{RHE}. (g) Stability test of Cu/CuCeO_x during 18 h of long-time operation at –600 mA cm^{–2}.

solutions favors the kinetics of the CO₂RR *via* generating more interfacial active sites, which is consistent with the results of impedance analysis (Fig. S9†).

The gaseous and liquid products were quantitatively analyzed by on-line gas chromatography (GC, Fig. S10†) and ¹H nuclear magnetic resonance (¹H NMR, Fig. S11†), respectively.⁴⁸ For the pure CeO₂ catalyst, H₂ was the main product (Fig. 4b). As shown in Fig. 4c, the Cu/CuCeO_x catalyst exhibited a high FE_{C₂H₄} of 40.2% at -1.2 V_{RHE}. In comparison, the Cu and Cu/CeO_x catalysts showed lower FE_{C₂H₄} at -1.2 V_{RHE} (Fig. 4d and S12†). For the pure Cu catalyst, the major products were H₂, CH₄, and C₂H₄ species, while FE_{CH₄} and FE_{C₂H₄} were 18.9% and 20.5%, respectively (Fig. S12†). In contrast, for the Cu/CeO_x catalyst, CH₄ emerged as the predominant product, achieving a FE of 38.6% at a potential of -1.2 V_{RHE}. The comparison of FE for H₂ and the CH₄ products over those three catalysts further demonstrated that the formation of H₂ and the CH₄ species was suppressed on the Cu/CuCeO_x catalyst. Furthermore, LSV measurements in an Ar-saturated 1.0 M KOH electrolyte without CO₂ gas revealed that CeO_x exhibited the lowest overpotential at equivalent current densities, further affirming its proficiency in hydrogen evolution (Fig. S13†). Furthermore, the Cu/CuCeO_x catalyst demonstrated the highest partial current density for C₂H₄ production (Fig. 4e), signifying that Cu/CuCeO_x has superior catalytic activity for C₂H₄ synthesis compared to both pristine Cu and Cu/CeO_x. Fig. 4f illustrates that the FE_{C₂H₄}/FE_{CH₄} ratio achieved a maximum of 3.77 on Cu/CuCeO_x, compared to 1.08 and 0.25 for Cu and Cu/CeO_x, respectively, indicating that the formation of Cu–Ce–O_x solid solutions is particularly conducive to C₂H₄ production. Comparative electrochemical evaluations of Cu_{0.1}/CuCeO_x and Cu_{0.5}/CuCeO_x, synthesized *via* the same method, were also performed (Fig. S14†). A 50% increase in Cu loading led to a decline in C₂H₄ selectivity, potentially due to the formation of larger Cu particles, which diminish the number of Cu active sites directly interacting with Ce, thereby inhibiting C–C coupling.³⁶ The long-term stability of Cu/CuCeO_x was assessed through chronopotentiometry, and no significant decrease in Faraday efficiency of C₂H₄ was observed during 18 h of electrocatalysis at -600 mA cm⁻² (Fig. 4g). Post-CO₂RR XPS analysis of the electrode confirmed the persistence of Cu⁺ as the predominant valence state in Cu/CuCeO_x, indirectly evidencing the stabilizing influence of the Cu–Ce–O_x matrix on Cu⁺ species (Fig. S15 and Table S1†). The efficient presence of Cu⁺ was also demonstrated by *in situ* Raman spectra of a wide potential window (Fig. S16†), with characteristic peaks around 150, 230 and 500 cm⁻¹.^{49,50} Moreover, the characteristic peaks of the *CO (2050 cm⁻¹) intermediates were also observed, further indicating the high *CO concentration on the Cu/CuCeO_x catalyst surface.

Subsequent density functional theory (DFT) calculations were conducted for Cu/CeO_x and Cu/CuCeO_x catalysts to rationalize the effects of Cu–Ce–O_x solid solutions on the CO₂RR selectivity toward C₂H₄ (Experimental section in the ESI, Fig. S17 and S18†). Initially, Bader charge analysis was applied to Cu/CuCeO_x (Fig. 5a), revealing that copper integration into the cerium dioxide matrix diminished the charge density around the Cu sites, indicating that the charges of Cu and Ce were

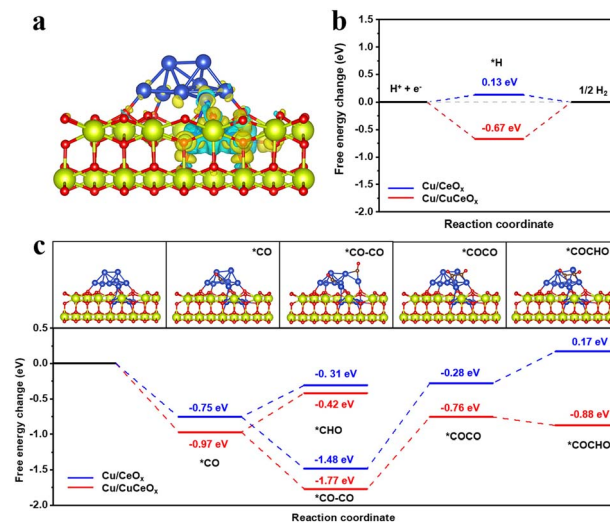


Fig. 5 (a) The Bader charge of Cu/CuCeO_x. (b) Desorption energy diagram of hydrogen on Cu/CeO_x and Cu/CuCeO_x. (c) The free energy change diagram of *CHO or *COCHO generated by *CO over the Cu/CeO_x and Cu/CuCeO_x.

rearranged.⁵¹ The transfer of electrons from Cu to Ce³⁺ results in higher Cu⁺ in Cu/CuCeO_x, which is conducive to promoting the adsorption of *CO on the surface and enhancing C–C to achieve high selectivity of C₂H₄. This alteration favorably impacts the protonation of *COCO intermediates, thereby facilitating C₂H₄ formation. In addition, the hydrogen evolution reaction (HER) performance of both Cu/CeO_x and Cu/CuCeO_x was assessed (Fig. 5b). The Gibbs free energy ($|\Delta G_{H^*}|$) for the HER on Cu/CeO_x is 0.13 eV lower than that of Cu/CuCeO_x (0.67 eV), thus allowing the promotion of the surface *H coverage and the hydrogenation.

The free energy diagrams depicting the formation of *CHO or *COCHO from *CO on the Cu/CeO_x or Cu/CuCeO_x catalysts are presented in Fig. 5c. Moreover, Cu/CuCeO_x also exhibits significantly stronger *CO adsorption than Cu/CeO_x, enhancing the local *CO concentration and favoring the C–C coupling process on the Cu/CuCeO_x catalyst. According to previous reports,⁵² the formation of CH₄ and C₂H₄ is primarily governed by distinct rate-determining steps: the hydrogenation of *CO to *CHO for CH₄, and the coupling of *CO with *CHO for C₂H₄, respectively.^{20,53} For the Cu/CeO_x catalyst, the ΔG value of the CO hydrogenation is 0.44 eV lower than that of the Cu/CuCeO_x catalyst, suggesting that Cu/CeO_x has a higher selectivity for producing CH₄. In contrast, the formation of the *COCHO intermediate of the Cu/CuCeO_x catalyst (0.12 eV) requires less free energy change than that of the Cu/CeO_x catalyst (0.45 eV), indicating a more favorable C₂H₄ pathway. Our computational findings corroborated that surfaces characterized by relatively high *H and low *CO coverage are conducive to the promotion of CH₄ production. Conversely, surfaces with a rich presence of *CO and moderate levels of *H are advantageous for the synthesis of C₂H₄.

Lastly, *in situ* infrared spectroscopy was employed to analyze potential surface intermediates on Cu/CeO_x and Cu/CuCeO_x

under various potential conditions, further elucidating the catalytic mechanism (Fig. S19†). Not only the peak of CO₂ can be observed in a pronounced absorption band of 2400–2300 cm⁻¹,^{54,55} but also the characteristic peak of CO (2050 cm⁻¹) can also be identified,⁵⁶ which serves as evidence for the activation and reduction of CO₂.⁵⁷ In addition, a distinct *CHO peak, key intermediate for CH₄, was further found at 1226 cm⁻¹.⁵⁸ In contrast, in the Cu/CuCeO_x spectrum, the characteristic peak of *CHO is significantly weakened and replaced by *COCHO at 1550 and 1185 cm⁻¹,^{59–62} indicating that Cu/CuCeO_x catalysts are more inclined to produce C₂, which is consistent with the results calculated by DFT.

Conclusions

In summary, this study successfully demonstrates the selective electroreduction of CO₂ to CH₄ or C₂H₄ by finely tuning *H and *CO adsorption on Cu/CeO_x catalysts. Our innovative approach, involving the manipulation of Cu/CeO_x and Cu/CuCeO_x interfaces, significantly influences the catalytic selectivity towards desired C₁ or C₂ products. Notably, the Cu/CuCeO_x electrocatalyst demonstrated a peak FE_{C₂H₄} of 40.2% and *j*_{C₂H₄} of -245.7 mA cm⁻², while the Cu/CeO_x electrocatalyst showed good CO₂RR performances with a maximum FE_{CH₄} of 38.6% and *j*_{CH₄} of -198.3 mA cm⁻². This advancement is underpinned by the enhanced *CO adsorption facilitated by the stabilization of Cu⁺ species within the Cu–Ce–O_x solid solution. Our findings pave the way for the development of tailored catalysts capable of directing CO₂ electroreduction towards specific hydrocarbons, addressing critical needs in CO₂ mitigation and sustainable fuel production.

Data availability

All the data supporting this article have been included in the main text and the ESI.†

Author contributions

M. K. proposed, designed, and supervised the project. T. H., Y. B., Z. C., and J. P. wrote the manuscript. T. H., Y. B., and Z. C. performed the experiments and analyzed the data. All authors discussed the results and revised the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This work was supported by the Shanghai Pujiang Program (22PJ1400200), the National Natural Science Foundation of China (no. 52122312 and 22209024), Tongcheng R&D Foundation (no. CPCIF-RA-0102), and the State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University.

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