

Component-Specific Functions of Cu, Zn, and Zr in Inverse ZnZrO_x/Cu Catalysts for CO₂ Hydrogenation to Methanol

Yu Gao, Erfan Shahroudi, Stefan Bouts, Yonghui Fan, Yin Li, Peeranat Chaipornchalerms, Junbu Wang, Konstantin Klementiev, Nikolay Kosinov,* and Emiel J. M. Hensen*



Cite This: *J. Am. Chem. Soc.* 2026, 148, 7378–7387



Read Online

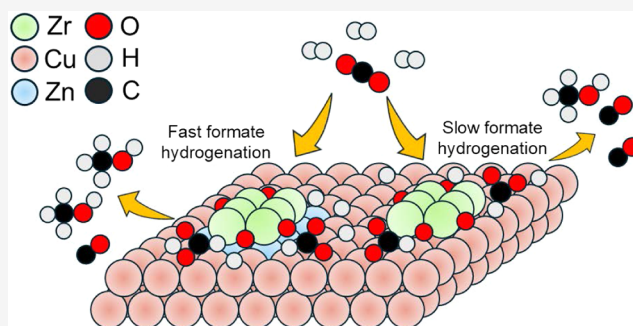
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Cu-based ternary catalysts often outperform their binary counterparts in the hydrogenation of CO₂ to methanol. Unraveling the underlying synergistic effects among multiple components remains challenging and requires comprehensive *operando* characterization. In this study, we present a detailed investigation into the synergistic Cu–Zn–Zr interactions in inverse ZnZrO_x/Cu catalysts, which show strong promise for enhancing the synthesis of methanol from CO₂. *In situ* X-ray diffraction revealed that ZrO₂ clusters effectively stabilize Cu nanoparticles against sintering during the H₂ reduction. *Operando* X-ray absorption spectroscopy at the Cu, Zn, and Zr K-edges demonstrated that the enhanced reducibility of Zn and Zr species arises from synergistic Cu–Zn–Zr interactions. Upon H₂ reduction, partially reduced ZrO₂ facilitated CO₂ adsorption and activation. Initially dispersed Zn²⁺ species were partially transformed into the CuZn alloy, which remained stable under reaction conditions. Notably, the CuZn alloy significantly enhanced the hydrogenation of key formate reaction intermediates to methanol. Moreover, Zn incorporation in Cu inhibited methanol decomposition to CO. The combined effects of efficient H₂ activation on highly dispersed metallic Cu, enhanced CO₂ activation by reduced ZrO₂ clusters, and rapid formate hydrogenation facilitated by the CuZn alloy rendered inverse ZnZrO_x/Cu catalysts superior in methanol formation rates as compared to inverse ZnO_x/Cu, ZrO_x/Cu catalysts, a commercial CuZnAl catalyst, and previously reported CuZnZr catalysts.



INTRODUCTION

The catalytic conversion of CO₂, a major greenhouse gas, with renewable hydrogen into chemicals is considered a promising strategy to mitigate climate change.¹ Among various products, methanol is particularly attractive due to its versatility as a platform chemical for producing a wide range of fuels and chemicals.² Commercial methanol synthesis is typically carried out using Cu/ZnO/Al₂O₃ (CuZnAl) catalysts and CO₂-containing synthesis gas (a mixture of CO and H₂) at a mild temperature (200–300 °C) and high pressure (50–100 bar). Although mechanistic studies have shown that CO₂ is the primary reactant hydrogenated to methanol over these catalysts, operating with high CO₂ concentrations introduces significant kinetic and thermodynamic challenges.^{3,4} A key practical limitation is catalyst deactivation, primarily due to Cu particle sintering and oxidation at the higher H₂O pressures in the reactor.^{5,6} Therefore, developing more robust and efficient catalysts for the direct hydrogenation of CO₂ to methanol remains a critical challenge.

Cu/Zn/ZrO₂ (CuZnZr) compositions have been recently explored as promising alternative catalysts for methanol synthesis. The stronger surface basicity of ZrO₂ compared to Al₂O₃ enhances CO₂ adsorption, while its lower hydrophilicity

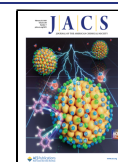
facilitates H₂O desorption, thereby mitigating Cu and Zn oxidation and reducing catalyst deactivation.^{7,8} In addition, interfacial sites between different catalyst components can significantly influence the catalytic performance. Although pure Cu exhibits low activity for methanol synthesis,^{9,10} CO₂ can be converted into formate (HCOO*) intermediates at Cu–ZrO₂ or Cu–ZnO interfacial sites, where these species are stabilized before undergoing hydrogenation to methoxy groups and ultimately methanol.^{11,12} Consequently, tailoring interfacial properties represents an effective strategy to regulate the catalytic performance. One promising approach involves constructing inverse catalysts, in which oxide clusters are dispersed on metallic surfaces, thereby strengthening metal–support interactions (MSI) compared to bulk oxides.¹³ Ma and coworkers showed the potential of inverse ZrO₂/Cu catalysts for CO₂ hydrogenation to methanol, reporting high methanol

Received: November 10, 2025

Revised: January 22, 2026

Accepted: January 26, 2026

Published: February 9, 2026



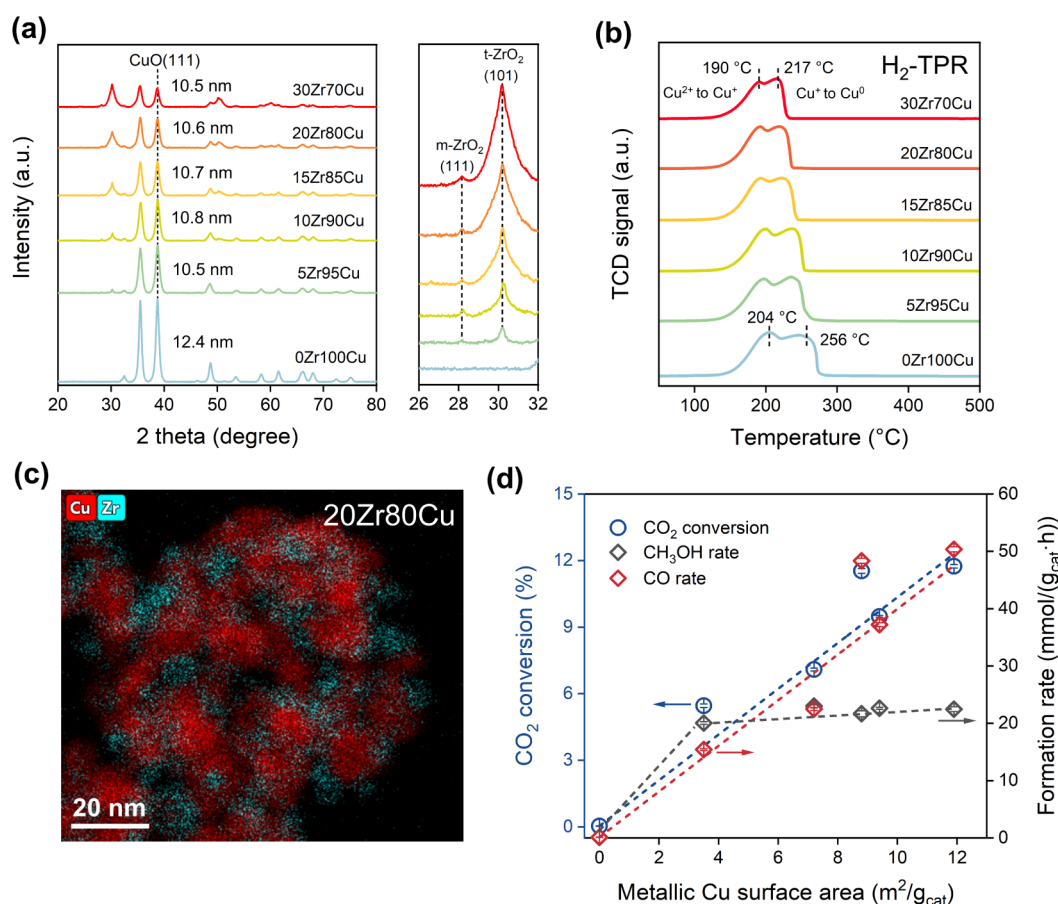


Figure 1. (a) XRD patterns of as-prepared inverse ZrO_2/Cu samples recorded at $\lambda = 0.154$ nm. The Scherrer equation was used to determine the particle sizes from the width of the $\text{CuO}(111)$ peak; (b) H_2 -TPR profiles of the inverse ZrO_2/Cu samples; (c) HAADF-STEM-EDX maps of as-prepared $20\text{Zr}80\text{Cu}$; and (d) CO_2 conversion and CO and CH_3OH formation rates as a function of metallic Cu surface area (reaction conditions: $\text{CO}_2/\text{H}_2/\text{N}_2$ (10/30/10 mL/min), 50 mg of catalyst, 250°C , and 30 bar; reaction data recorded after 12 h on stream, metallic surface areas derived from N_2O titration).

space–time–yield (STY) and promising stability.^{14,15} However, a systematic investigation of inverse Cu catalysts incorporating various promoter metal oxides for methanol synthesis is still lacking.

Herein, we systematically investigated inverse Cu -based catalysts synthesized via flame spray pyrolysis (FSP) for the hydrogenation of CO_2 to methanol. Among the various promoted inverse Cu catalysts (Zr , Si , Al , Ti , Ce , Ga , and Zn), inverse ZrO_2/Cu exhibited the highest mass- and surface area-normalized CH_3OH formation rates, although with moderate CH_3OH selectivity. Inverse ZnO/Cu also exhibited promising surface area-normalized activity, together with a high CH_3OH selectivity of 86%. Building on these results, we developed inverse ZnZrO_x/Cu catalysts that exhibit enhanced performance in methanol synthesis, achieving a maximum methanol rate of 35.0 $\text{mmol}/(\text{g}_{\text{cat}}\cdot\text{h})$ at 250°C and 30 bar, surpassing the performance of a commercial CuZnAl catalyst. To establish structure–performance relationships in this ternary system, we employed *operando* X-ray diffraction and spectroscopy techniques. *In situ* X-ray diffraction (XRD) results revealed a strong stabilization of Cu nanoparticles by ZrO_2 clusters, with Cu particle sizes remaining unchanged during H_2 reduction. *Operando* X-ray absorption spectroscopy (XAS) data at the Cu , Zn , and Zr K -edges were simultaneously recorded to probe the electronic structure of the ternary Cu – Zn – Zr catalysts. The Cu species remained fully metallic

throughout the H_2 reduction and CO_2 hydrogenation, serving as the primary sites for H_2 dissociation. Facile H^* spillover promoted the reduction of the ZrO_2 species, thereby enhancing CO_2 activation. *In situ* IR spectroscopy revealed that the CuZn alloy, formed during H_2 reduction, markedly accelerated the hydrogenation of formate (HCOO^*) intermediates to CH_3OH . This was further corroborated by formic acid (HCOOH) hydrogenation experiments, which confirmed the role of the CuZn alloy in facilitating CH_3OH formation. Additionally, incorporation of Zn was found to suppress CO formation via CH_3OH decomposition, thereby improving CH_3OH selectivity during CO_2 hydrogenation. The synergistic interplay among small metallic Cu nanoparticles, the CuZn alloy species, and reducible ZrO_2 clusters contributes to the superior performance of inverse ZnZrO_x/Cu catalysts in CO_2 hydrogenation to CH_3OH .

RESULTS AND DISCUSSION

ZrO_2 Promotion for CH_3OH Synthesis

A series of inverse ZrO_2/Cu samples with varying Zr content was synthesized by FSP, denoted as $x\text{Zr}y\text{Cu}$ ($x + y = 100$; $x = 0, 5, 10, 15, 20, \text{ and } 30$). The XRD patterns revealed characteristic diffraction lines of CuO in all as-prepared ZrO_2/Cu samples, along with diffraction lines of both tetragonal ZrO_2 ($t\text{-ZrO}_2$) and monoclinic ZrO_2 ($m\text{-ZrO}_2$) (Figure 1a).

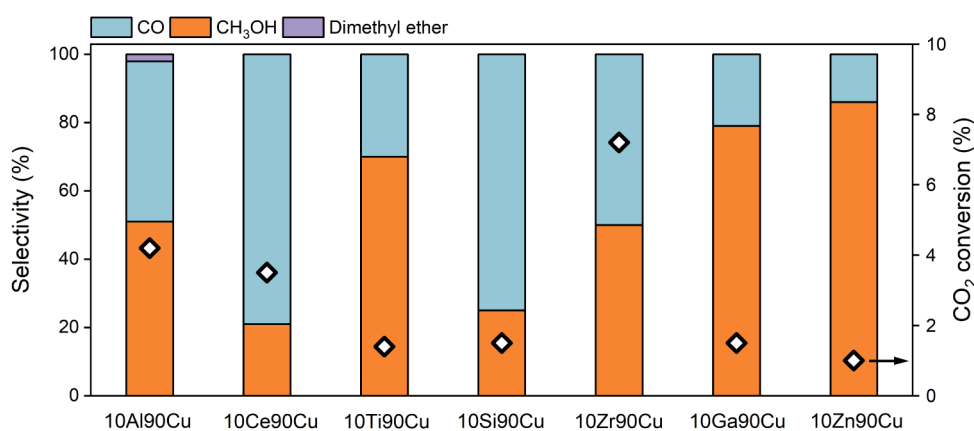


Figure 2. CO₂ hydrogenation performance over various inverse Cu catalysts (reaction conditions: CO₂/H₂/N₂ (10/30/10 mL/min), 50 mg of catalyst, 250 °C, and 30 bar; reaction data after 12 h on stream).

The presence of Zr in inverse ZrO₂/Cu samples led to CuO diffraction peaks that were broader than those in the FSP-prepared CuO sample, which indicates that ZrO₂ already stabilized small CuO particles during FSP synthesis. The stabilization effect extended during catalyst reduction. H₂-TPR results show that the reduction features of Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰ shifted to lower temperatures with increasing Zr content (Figure 1b), consistent with the easier reducibility of smaller CuO nanoparticles.¹⁶ High-resolution transmission electron microscopy (HRTEM) images and high-angle annular dark-field scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (HAADF-STEM-EDX) maps for the as-prepared 20Zr80Cu sample show small ZrO₂ clusters homogeneously distributed over CuO nanoparticles (Figure 1c and Figure S1). The CO₂ hydrogenation performance of these samples was evaluated using a feed of CO₂/H₂/N₂ (10/30/10 mL/min) at 250 °C and 30 bar, after reduction in 20 vol % H₂ in He at 300 °C for 1 h. The inverse ZrO₂/Cu catalysts demonstrated enhanced CO₂ conversion and CO formation rate with increasing Zr content up to 20 mol %, followed by a slight decrease at a Zr content of 30 mol % (Figure S2). Notably, while the pure Cu catalyst exhibited a low CH₃OH formation rate of 0.1 mmol/(g_{cat}·h), introducing just 5 mol % Zr enhanced the rate to 20.0 mmol/(g_{cat}·h). These findings highlight that incorporating a small amount of ZrO₂ into Cu catalysts can significantly boost the CH₃OH synthesis from CO₂. The CH₃OH formation rate increased with Zr content up to 10 mol % and then leveled off. Previous studies have also shown that inverse ZrO₂/Cu catalysts exhibit significantly higher CH₃OH STY compared to conventional Cu/ZrO₂ catalysts, even when they contain comparable metallic Cu surface areas.^{14,15,17} Moreover, inverse ZrO₂/Cu catalysts displayed higher CH₃OH selectivity than conventional Cu/ZrO₂ catalysts at equivalent CO₂ conversions. This improvement is attributed to the distinct interfacial sites formed between Cu nanoparticles and ZrO₂ clusters in the inverse configuration.¹⁷ Further studies revealed that both CO₂ conversion and CO formation rates scale with the metallic Cu surface area, as determined by N₂O titration at 50 °C, across the inverse ZrO₂/Cu catalysts (Figure 1d, Figure S3, and Table S1). In contrast, the CH₃OH formation rate shows only a weak dependence on the Cu surface area. Similar trends were observed when normalizing the activity to the total specific surface area measured by N₂ physisorption (Figure S6 and Table S1). Notably, the 5Zr95Cu catalyst, despite its

relatively low Cu surface area and CO₂ conversion, achieves a CH₃OH formation rate comparable to that of catalysts with higher CO₂ conversions. These findings suggest that CH₃OH synthesis is not strictly governed by Cu surface area but is likely associated with Cu–ZrO₂ interfacial sites.^{15,17} Increasing Zr content beyond 5 mol % enhances Cu surface area, CO₂ conversion, and CO formation rate but does not appreciably improve CH₃OH formation, indicating saturation of the beneficial Cu–ZrO₂ interfacial sites.¹⁵ This saturation promotes CO formation via the reverse water–gas shift (RWGS) reaction, resulting in a decline in CH₃OH selectivity with increasing CO₂ conversion (Figure S2). On the other hand, the decreased CH₃OH selectivity at higher CO₂ conversions may also result from CH₃OH decomposition.¹⁸

The structural and chemical promotion of ZrO₂ clusters on the hydrogenation of CO₂ to CH₃OH over Cu nanoparticles motivated the exploration of other compositions, particularly those exhibiting high CH₃OH selectivity. Accordingly, a series of inverse Cu samples comprising 10 mol % of promoters (Al, Ce, Ti, Si, Ga, and Zn) and 90 mol % Cu were synthesized by FSP. The samples are denoted 10x90Cu, where x represents the promoter. Among the prepared samples, 10Zr90Cu exhibited the highest CO₂ conversion and CH₃OH formation rate (Figures 2 and S7). Notably, 10Zn90Cu demonstrated the highest CH₃OH selectivity of 86%, indicating that Zn promotion favors CH₃OH formation over CO,¹⁹ albeit at a lower CO₂ conversion rate. However, this catalyst showed continuous deactivation during a 12 h stability test (Figure S8), indicating that Zn is ineffective in stabilizing Cu nanoparticles against sintering. In contrast, 10Zr90Cu was stable during similar stability test. As metallic Cu dominates in reduced inverse catalysts, the specific surface area after H₂ reduction was used as an approximate measure of the active surface area (Figure S6 and Table S1). When normalized to the specific surface area, 10Zn90Cu demonstrated the second-highest CH₃OH formation rate after 10Zr90Cu (Figure S7). These findings underscore the promise of 10Zr90Cu and 10Zn90Cu for CH₃OH synthesis, with the former increasing the level of CO₂ conversion and the latter improving the CH₃OH selectivity. Notably, N₂O titration revealed a negligible metallic Cu surface area in 10Zn90Cu after H₂ reduction (Figure S4 and Table S1), indicating that Zn species covered the surface.

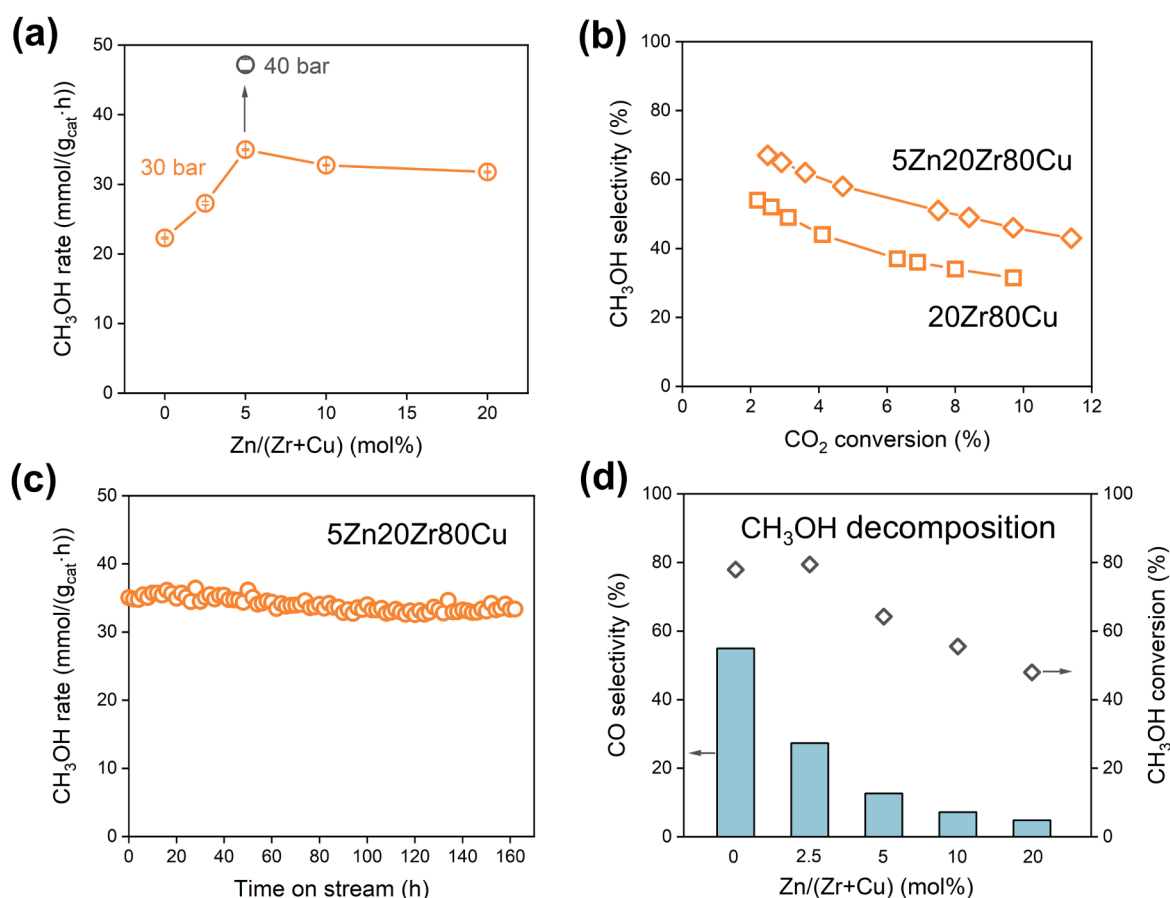


Figure 3. (a) CH₃OH formation rate of inverse ZnZrO_x/Cu catalysts during CO₂ hydrogenation (reaction conditions: CO₂/H₂/N₂ (10/30/10 mL/min), 50 mg catalyst, 250 °C, 30 bar; reaction data after 12 h on stream); (b) CH₃OH selectivity as a function of CO₂ conversion for 20Zr80Cu and 5Zn20Zr80Cu. The results were obtained by changing the contact time between the catalyst bed and reactants; (c) stability test of 5Zn20Zr80Cu during CO₂ hydrogenation; and (d) CH₃OH conversion and CO selectivity of inverse ZnZrO_x/Cu catalysts during CH₃OH decomposition (reaction conditions: 2 vol % CH₃OH in He (50 mL/min), 30 mg catalyst, 250 °C, and 1 bar; reaction data recorded after 3 h on stream).

Inverse ZnZrO_x/Cu Catalysts

Based on the observed potential of ZrO₂ for enhancing CO₂ conversion and ZnO for improving CH₃OH selectivity, both promoters were combined to further enhance CH₃OH synthesis by CO₂ hydrogenation. Starting from the most active 20Zr80Cu sample, a series of inverse ZnZrO_x/Cu samples with varying Zn content (i.e., Zn/(Zr + Cu) ratios of 0.025, 0.05, 0.10, and 0.2) were prepared by FSP and denoted as *x*Zn20Zr80Cu (*x* = 2.5, 5, 10, and 20). XRD patterns revealed that the CuO particles became smaller with increasing Zn content, confirming the stabilizing effect of Zn species on CuO (Figure S9). Notably, Zn species remained highly dispersed even at a high Zn content of 10 mol %, as indicated by the absence of ZnO diffraction lines. X-ray photoelectron spectroscopy (XPS) results revealed that the surface atomic Cu/Zn ratio in inverse ZnZrO_x/Cu samples is 2–4 times higher than that in the bulk (Figure S10 and Table S2). The high dispersion of Zn species in the inverse ZnZrO_x/Cu catalyst was further supported by HAADF-STEM-EDX maps (Figure S11). Spatial Pearson correlation coefficients derived from EDX pixel maps consistently showed stronger Cu–Zn than Zn–Zr proximity across all as-prepared inverse ZnZrO_x/Cu samples (Figure S12 and Table S3), suggesting that Zn preferentially decorates the CuO surface. Cu–Zn interactions were evident from H₂-TPR profiles (Figure S13),²⁰ where the

reduction feature of Cu²⁺ to Cu⁺ became less pronounced and the Cu⁺ to Cu⁰ peak shifted to higher temperatures with increasing Zn content. The CO₂ hydrogenation performance of inverse ZnZrO_x/Cu catalysts demonstrated an initial increase in the CH₃OH formation rate with increasing Zn content, with 5Zn20Zr80Cu exhibiting the highest rate of 35.0 mmol/(g_{cat}·h), followed by a slight decrease for 10Zn20Zr80Cu and 20Zn20Zr80Cu (Figure 3a). Under the applied reaction conditions, 5Zn20Zr80Cu also showed a CH₃OH rate higher than that of a commercial CuZnAl catalyst (31.7 mmol/(g_{cat}·h)). Moreover, it outperformed most state-of-the-art catalysts reported in the literature (Figure S14 and Table S4). The substantial improvement in CH₃OH selectivity upon Zn promotion is illustrated in Figure 3b. It was established that Zn promotion in 5Zn20Zr80Cu enhanced CH₃OH selectivity relative to 20Zr80Cu at the same CO₂ conversion: at 10% CO₂ conversion, CH₃OH selectivity was 47% for 5Zn20Zr80Cu and 31% for 20Zr80Cu. Moreover, 5Zn20Zr80Cu displayed stable catalytic performance during a 160 h stability test (Figure 3c). Increasing the reaction pressure to 40 bar resulted in a significant increase in the CH₃OH formation rate to 47.2 mmol/(g_{cat}·h) for the 5Zn20Zr80Cu catalyst (Figure 3a). Notably, trace amounts of methyl formate (HCOOCH₃) were detected during CO₂ hydrogenation for both the 20Zr80Cu and 5Zn20Zr80Cu

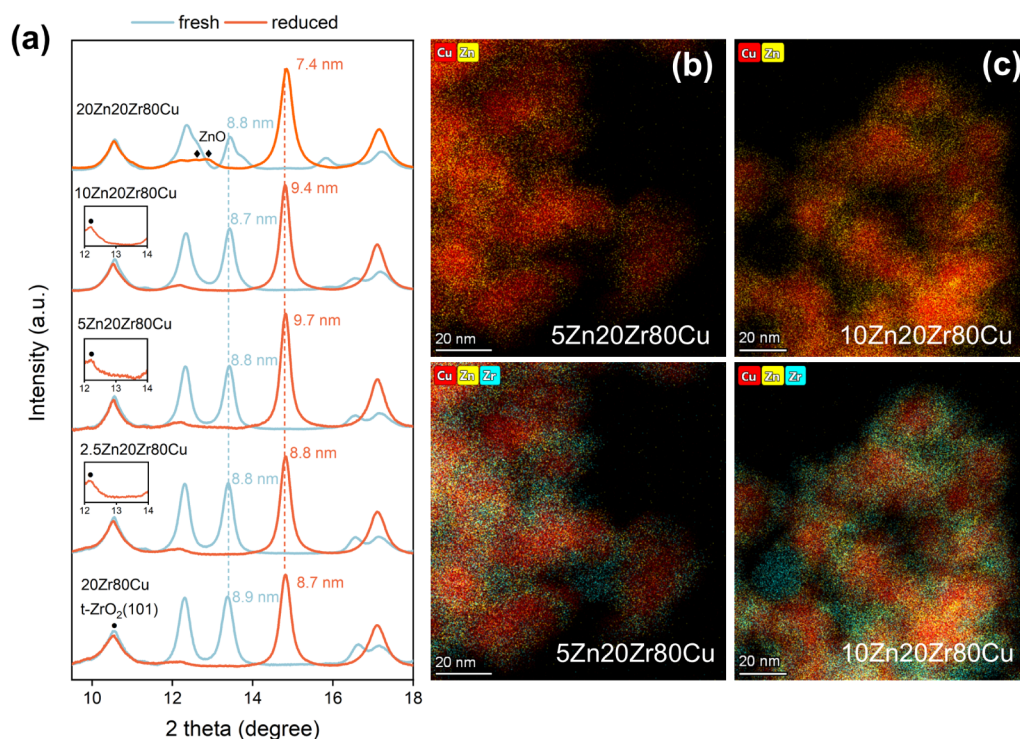


Figure 4. (a) *In situ* XRD patterns of the inverse Cu catalysts recorded at $\lambda = 0.054$ nm. The H_2 reduction was performed at 1 bar and 300°C with a feed of H_2/He (4/16 mL/min) for 30 min, and EDX maps of (b) $5\text{Zn}20\text{Zr}80\text{Cu}$ and (c) $10\text{Zn}20\text{Zr}80\text{Cu}$ after H_2 reduction at 300°C for 1 h. Samples were exposed to air after H_2 reduction.

catalysts (Figure S15), indicating CH_3OH decomposition.²¹ CH_3OH decomposition may affect the observed CH_3OH formation rate and product distribution, as CO is the main product.¹⁸ To investigate this, CH_3OH decomposition experiments were conducted using a feed of 2 vol % CH_3OH in He at 250°C and 1 bar. As shown in Figure 3d and Figure S16, both CO formation rates and the CO selectivity among products such as HCOOCH_3 , CH_4 , and CO_2 were significantly suppressed by the addition of Zn, i.e., from 44.8 mmol/(g_{cat}·h) in $20\text{Zr}80\text{Cu}$ to 2.5 mmol/(g_{cat}·h) in $20\text{Zn}20\text{Zr}80\text{Cu}$, and from 54.9% in $20\text{Zr}80\text{Cu}$ to 4.8% in $20\text{Zn}20\text{Zr}80\text{Cu}$, respectively. This strong suppression of CH_3OH decomposition to CO by Zn incorporation contributed to the improved CH_3OH selectivity for the inverse ZnZrO_x/Cu catalysts during CO_2 hydrogenation (Figure 3b).

A kinetic study showed that the apparent activation energy (E_a) increased with increasing Zn content, from 57 kJ/mol for $20\text{Zr}80\text{Cu}$ to 81 kJ/mol for $5\text{Zn}20\text{Zr}80\text{Cu}$, followed by a decrease to 60 kJ/mol for $20\text{Zn}20\text{Zr}80\text{Cu}$ (Figure S17). The higher E_a for inverse ZnZrO_x/Cu catalysts than for $20\text{Zr}80\text{Cu}$ is likely due to differences in the active sites. These catalysts exhibited CO_2 reaction orders between 0.10 and 0.20, suggesting strong CO_2 adsorption and high surface coverage with CO_2 -derived intermediates (Figure S18). This also indicates that the role of ZrO_2 clusters in the CO_2 hydrogenation reaction relates to CO_2 adsorption and activation. Moreover, the catalysts exhibited comparable H_2 reaction orders of 0.40–0.55 (Figure S18), suggesting that Zn incorporation did not significantly promote H_2 activation. This is further supported by H_2 – D_2 exchange measurements, where both $20\text{Zr}80\text{Cu}$ and inverse ZnZrO_x/Cu catalysts exhibited a similar onset temperature of HD formation at $\sim 120^\circ\text{C}$ (Figures S19 and S20). In contrast, a ZnZrO_x catalyst showed

activity only in HD at $\sim 235^\circ\text{C}$, indicating that H_2 activation predominantly occurs on metallic Cu sites. Previous studies by Burch et al. have highlighted the role of ZnO in facilitating H^* spillover via surface hydrides or hydroxyls in Cu/ZnO catalysts for CH_3OH synthesis.^{22–24} The apparent absence of an enhanced H^* spillover in inverse ZnZrO_x/Cu catalysts is likely due to the formation of distinct Zn-containing active sites.

Active Sites for CH_3OH Synthesis

We used *in situ* synchrotron XRD and *operando* XAS to characterize the active phase in inverse ZnZrO_x/Cu catalysts. The metal Cu particle sizes in $20\text{Zr}80\text{Cu}$ and inverse ZnZrO_x/Cu catalysts remained nearly unchanged after H_2 reduction (Figure 4a and Figure S21). The particle sizes derived from the CuO(111) and Cu(111) diffraction peaks differed by only ~ 1 nm, underscoring the strong stabilization of Cu nanoparticles promoted by ZrO_2 clusters. Although ZrO_2 nanoparticle supports can disperse Cu clusters effectively,^{25,26} our results show that ZrO_2 clusters can also efficiently stabilize Cu nanoparticles. The ZrO_2 clusters in the inverse Cu catalysts demonstrated slightly smaller particle sizes after H_2 reduction (Table S5). Unlike previously reported inverse ZnZrO_x/Cu samples prepared by coprecipitation, which contained ZnO clusters, the FSP-prepared inverse ZnZrO_x/Cu samples in this study contain highly dispersed Zn.^{15,27} ZnO diffraction features were absent in $2.5\text{Zn}20\text{Zr}80\text{Cu}$, $5\text{Zn}20\text{Zr}80\text{Cu}$, and $10\text{Zn}20\text{Zr}80\text{Cu}$ after H_2 reduction (Figure 4a). The enhanced Zn dispersion is further supported by the EDX maps (Figures 4b, c, and Figure S22). Additionally, high spatial Pearson correlation coefficients between both Zn–Zr and Cu–Zn pairs were determined from the EDX maps of the inverse ZnZrO_x/Cu catalysts after H_2 reduction (Figure S23 and Table S6). These findings suggest that the enhanced Zn dispersion in

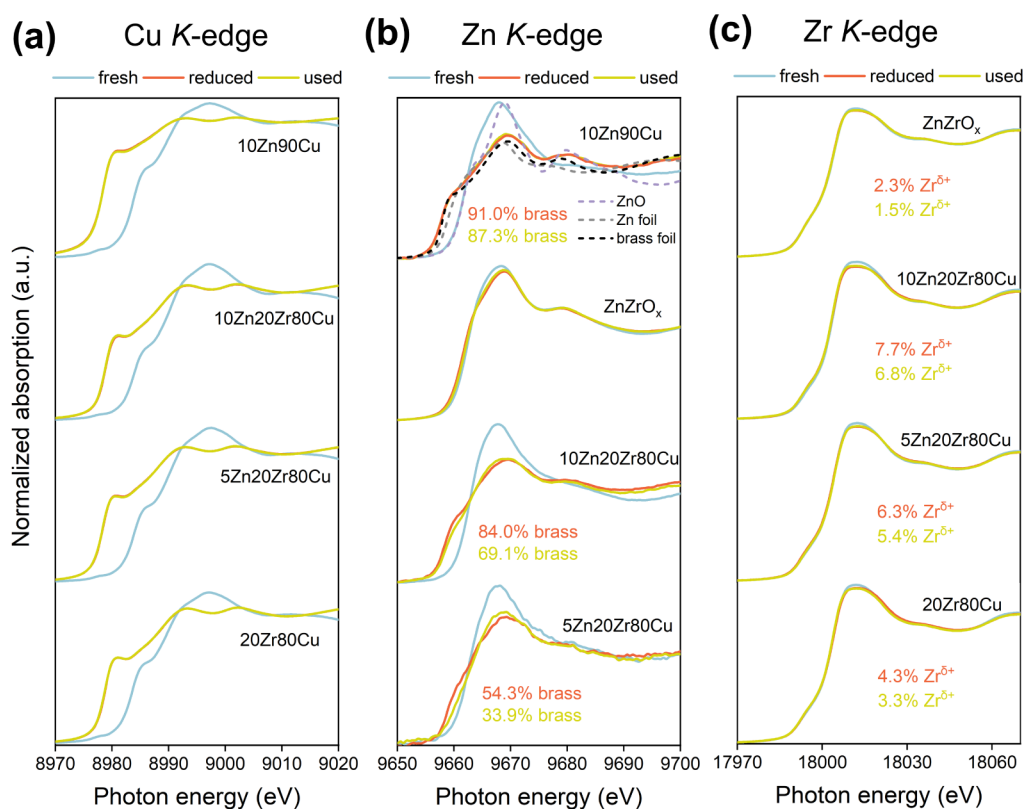


Figure 5. Operando (a) Cu K-edge; (b) Zn K-edge; and (c) Zr K-edge XANES spectra of the inverse catalysts. The H_2 reduction was performed at 300 °C with a feed of H_2/He (4/16 mL/min) for 30 min, and the CO_2 hydrogenation was performed at 250 °C and 4 bar with a feed of CO_2/H_2 (5/15 mL/min) for 20 min.

inverse ZnZrO_x/Cu is due to the high Cu surface area and strong Cu–Zn and Zn–Zr interactions.

Operando XAS investigations were conducted at the ROCK beamline (SOLEIL synchrotron, France),²⁸ where the Cu, Zn, and Zr K-edges XAS spectra were collected sequentially in the same experiment (Scheme S1 and Figure S24). 10Zn90Cu and ZnZrO_x were used as binary references. Cu K-edge X-ray absorption near-edge structure (XANES) confirmed that all inverse Cu catalysts contained fully metallic Cu after H_2 reduction at 300 °C for 30 min (Figure 5a and Figures S25 to S31), consistent with the H_2 -TPR results (Figure S13). The Cu species remained stable during subsequent CO_2 hydrogenation at 4 bar, as evidenced by the unchanged XANES features. Quasi-*in situ* XPS studies of the 10Zn90Cu catalyst also revealed the exclusive formation of metallic Cu species after both H_2 reduction and reaction in CO_2 hydrogenation at 6 bar for 20 h (Figure S33). Notably, 10Zn90Cu predominantly formed CuZn alloy (α -brass) upon H_2 reduction, as indicated by the Zn K-edge XANES (Figure 5b, Figures S26 and S34).^{29–33} Given its negligible N_2O consumption after H_2 reduction (Figure S4 and Table S1), it can be concluded that N_2O did not oxidize surface CuZn alloy at 50 °C. The CuZn alloy in 10Zn90Cu also remained stable during the subsequent CO_2 hydrogenation. Zn K-edge XANES and LCF results confirmed the formation of CuZn alloy in inverse ZnZrO_x/Cu catalysts upon H_2 reduction, followed by partial dealloying during CO_2 hydrogenation (Figure 5b, Figures S28–S31). The alloy fractions during CO_2 hydrogenation were determined to be 37.7%, 33.9%, 69.1%, and 54.8% for 2.5Zn20Zr80Cu, 5Zn20Zr80Cu, 10Zn20Zr80Cu, and 20Zn20Zr80Cu, respectively (Table S7). This trend was

further supported by our Zn K-edge k^2 -weighted Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) analysis, where 10Zn20Zr80Cu displayed the highest Zn–Cu/Zn–Zn coordination numbers (Figure S34 and Table S8). XPS analysis revealed a lower surface atomic Cu/Zn ratio of 1.6 in the reduced 10Zn20Zr80Cu catalyst compared to ratios of 2.8 in the fresh catalyst (from XPS) and 8.7 in the bulk (from ICP-OES), indicating that CuZn alloy formation occurred primarily on the surface region (Figure S35). This is further supported by *in situ* XRD patterns (Figure 4a),³¹ where the metallic Cu diffraction lines in reduced inverse ZnZrO_x/Cu catalysts show no shift relative to the 20Zr80Cu catalyst. In contrast, the ZnZrO_x catalyst retained predominantly unreduced Zn species after H_2 reduction (Figure 5b and Figure S32), suggesting that metallic Cu played a crucial role in facilitating Zn reduction.³⁴ The redox behavior of ZrO_2 species in inverse catalysts remains underexplored in the literature, particularly using XAS. Previous *in situ* XPS studies of inverse ZrO_2/Cu catalysts have reported only a minimal shift (~ 0.2 eV) to lower binding energy for Zr species during H_2 reduction, a change typically within the range of experimental uncertainty, thereby rendering the actual reducibility of ZrO_2 clusters unclear.^{14,35} Herein, detailed XAS investigation revealed that, compared to the ZnZrO_x containing 2.3% reduced Zr species after H_2 reduction, 20Zr80Cu exhibited a higher Zr reduction degree (4.3%) (Figure 5c, Figures S27, S32, S36 and Table S7). Notably, Zn incorporation further enhanced Zr reducibility, with 7.3%, 6.3%, 7.7%, and 5.1% reduced Zr species obtained in 2.5Zn20Zr80Cu, 5Zn20Zr80Cu, 10Zn20Zr80Cu, and 20Zn20Zr80Cu, respectively (Figure 5c and Figures S28–S31). A slight reoxidation of

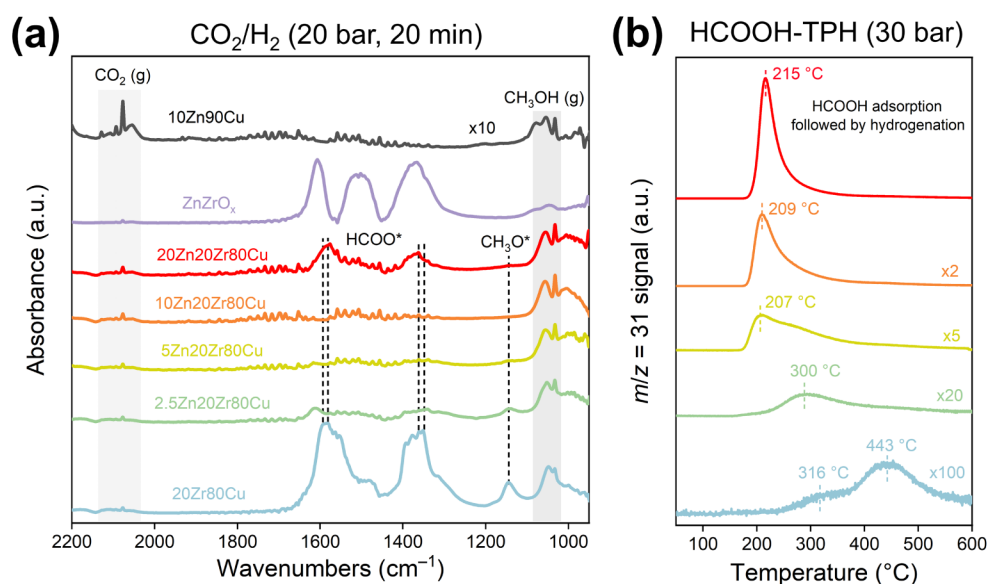


Figure 6. (a) *In situ* IR spectra of the catalysts after CO₂ hydrogenation (CO₂/H₂ = 1/3) at 250 °C and 20 bar for 20 min and (b) high-pressure HCOOH-TPH profiles of inverse Cu catalysts. Catalysts were exposed to 2 vol % HCOOH in He (50 mL/min), followed by flushing with He and then ramped from 50 to 600 °C at a rate of 5 °C/min in 20 vol % H₂ in He (50 mL/min) at 30 bar.

Zr species was observed during CO₂ hydrogenation across all Zr-containing samples, indicating the potential role of oxygen vacancies (O_v) for facilitating CO₂ adsorption and activation at the Cu–ZrO₂ interfacial sites (Figure S18).^{11,36–38} These findings highlight the synergistic redox behavior among the Cu, Zn, and Zr species. The dynamic changes in the electronic properties of Zr and Zn species under different atmospheres indicate their active roles in CO₂ hydrogenation to CH₃OH.

Reaction Mechanism

To further understand the reaction pathways underlying the Zn- and Zr-promoted CH₃OH synthesis, *in situ* IR spectroscopy was performed to investigate the CO₂ hydrogenation mechanisms over inverse Cu catalysts at 250 °C and 20 bar. Formate (HCOO*) species are widely considered as the key intermediates in CH₃OH synthesis. Previous studies have identified Cu–ZrO₂ and Cu–ZnO interfacial sites as active centers for HCOO* formation.^{15,39,40} As shown in Figure 6a and Figure S37, 20Zr80Cu exhibits distinct IR bands characteristic of HCOO* at 1351, 1362, 1576, and 1593 cm⁻¹,^{41,42} alongside signals attributed to methoxy species (CH₃O*, 1144 cm⁻¹) and gaseous CH₃OH (1030–1150 cm⁻¹).⁴³ Upon Zn promotion, the intensities of both HCOO* and CH₃O* features significantly decreased, becoming nearly undetectable in 2.5Zn20Zr80Cu and completely absent in 10Zn20Zr80Cu. A further increase in the Zn content in 20Zn20Zr80Cu led to a relatively small amount of HCOO*. These results suggest that Zn species accelerate the hydrogenation of HCOO* and CH₃O* species. While this effect has been observed previously in other Cu–Zn catalysts, the underlying mechanism remains poorly understood.^{15,44–46} Notably, fast HCOO* hydrogenation was also observed in 10Zn90Cu but not in ZnZrO_x. XAS analysis reveals that CuZn alloy formation is predominant in 10Zn90Cu and also abundant in inverse ZnZrO_x/Cu catalysts (Figure 5b). Moreover, quasi-*in situ* XPS spectra of 10Zn90Cu after 20 h of CO₂ hydrogenation show that the CuZn alloy was preserved during the reaction (Figure S38). Based on these findings, we propose that the CuZn alloy plays a primary role in

accelerating the hydrogenation of HCOO* and CH₃O*. Although CuZn alloys are frequently observed in reduced Cu–Zn catalysts, their role in CH₃OH synthesis remains debated.^{40,45,47} While some studies have reported that the CuZn alloy could enhance CH₃OH formation, potentially through Zn substitution at metallic Cu step sites,⁴⁸ they are generally not considered essential for CH₃OH formation.^{49–51} However, the present observation that the CuZn alloy significantly accelerates the hydrogenation of HCOO* intermediates re-emphasizes their potential importance in the reaction mechanism. This finding suggests that, although not strictly required, the CuZn alloy may play a more active and previously underappreciated role in facilitating key elementary steps in CH₃OH synthesis. Since the CuZn alloy did not promote H* spillover according to H₂–D₂ exchange results (Figure S19), it is most likely that HCOO* species formed on CuZn alloy or at CuZn alloy–ZrO₂ interfacial sites are intrinsically more active.⁴⁵ A study by Fujitani and coworkers also reported higher reactivity of HCOO* species on CuZn surfaces compared to pure Cu in model systems.⁴⁶ Nevertheless, the roles of CuZn alloy and Cu–ZnO interface in CH₃OH synthesis remain highly dependent on catalyst preparation, pretreatment, and reaction conditions.^{33,52} To further investigate the HCOO* hydrogenation promoted by the CuZn alloy, we performed high-pressure HCOOH temperature-programmed hydrogenation (HCOOH-TPH) experiments on the inverse Cu catalysts. HCOO*, formed via HCOOH decomposition on the catalyst surface, can be hydrogenated into CH₃OH, providing a direct measure of the hydrogenation activity. Following H₂ reduction, the catalysts were exposed to a flow of 2 vol % HCOOH in He, then flushed with pure He, and finally heated to 600 °C at 5 °C/min in a H₂-containing atmosphere at a total pressure of 30 bar. For 20Zr80Cu, CH₃OH formation initiated at ~250 °C, peaking at ~443 °C (Figure 6b). The inverse ZnZrO_x/Cu samples exhibited much lower CH₃OH formation temperatures, with maxima at ~300 °C for 2.5Zn20Zr80Cu, 207 °C for 5Zn20Zr80Cu, 209 °C for 10Zn20Zr80Cu, and 215 °C for 20Zn20Zr80Cu, indicating enhanced HCOOH hydrogenation

to CH₃OH upon Zn incorporation. Furthermore, the CH₃OH signal increased with Zn content, suggesting that more surface HCOOH species were converted to CH₃OH. This trend is corroborated by HCOOH temperature-programmed desorption (TPD) data, which show that more HCOOH desorbs from samples with a higher Zn content (Figure S39). Collectively, these findings demonstrate that Zn incorporation, most likely through CuZn alloy formation, substantially facilitates the hydrogenation of HCOO* intermediates. This mechanistic insight helps explain the enhanced CH₃OH formation rates observed in inverse ZnZrO_x/Cu during CO₂ hydrogenation.

The above discussion revealed the roles of reducible ZrO₂ clusters in stabilizing Cu nanoparticles and promoting CO₂ activation and CuZn alloy in facilitating the hydrogenation of HCOO* intermediates into CH₃OH. A schematic illustration summarizing the proposed component-specific functions of Cu, Zn, and Zr in the hydrogenation of CO₂ to CH₃OH is presented in Figure 7.

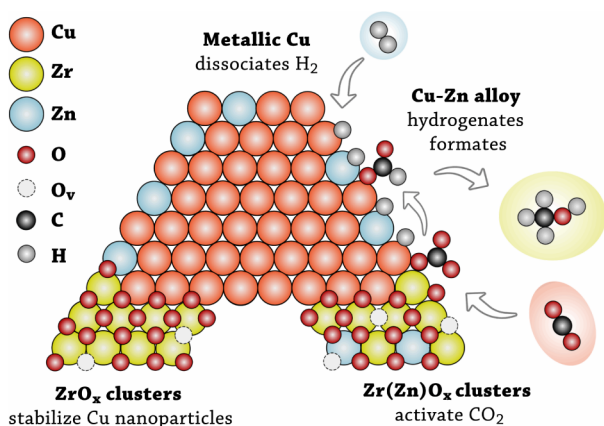


Figure 7. Schematic illustration of proposed component-specific roles of Cu, Zn, and Zr in CO₂ hydrogenation to CH₃OH.

CONCLUSION

Advanced *operando* characterization techniques are essential for uncovering complex physicochemical interactions in multicomponent catalysts under reaction conditions. In this work, we systematically elucidated the structure–performance relationships in FSP-prepared inverse ZnZrO_x/Cu catalysts for the hydrogenation of CO₂ to CH₃OH. *In situ* XRD revealed that ZrO₂ clusters effectively stabilize Cu nanoparticles, as evidenced by the unchanged Cu particle sizes following the H₂ reduction. *Operando* XAS at the Cu, Zn, and Zr K-edges demonstrated enhanced reducibility of Zr and Zn species in the inverse ZnZrO_x/Cu catalysts, which was attributed to synergistic interactions among Cu, Zn, and Zr. Reduced ZrO₂ species promote CO₂ adsorption and activation, assisted by H* spillover from metallic Cu, while the CuZn alloy significantly accelerates the hydrogenation of HCOO* intermediates to CH₃OH. These cooperative effects among Cu, Zn, and Zr result in superior CH₃OH synthesis rates in inverse ZnZrO_x/Cu catalysts compared to a commercial CuZnAl reference and all CuZnZr catalysts reported in the literature. The fundamental insights gained in this study provide a foundation for the rational design of next-generation catalysts for CO₂ hydrogenation and related sustainable chemical transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c19915>.

Experimental methods; TEM images; ICP-OES results; N₂O titration results; N₂ physisorption results; *in situ* XRD patterns; *in situ* XPS spectra; H₂-TPR profiles; catalytic performance; H₂–D₂ exchange profiles; *operando* XAS results; *in situ* IR spectra; and HCOOH-TPH profiles (PDF)

AUTHOR INFORMATION

Corresponding Authors

Nikolay Kosinov – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands; orcid.org/0000-0001-8520-4886; Email: n.a.kosinov@tue.nl

Emiel J. M. Hensen – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands; orcid.org/0000-0002-9754-2417; Email: e.j.m.hensen@tue.nl

Authors

Yu Gao – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Erfan Shahroudi – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Stefan Bouts – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Yonghui Fan – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Yin Li – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Peeranat Chaipornchalerms – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Junbu Wang – Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Konstantin Klementiev – MAX IV Laboratory, Lund University, Lund SE-221 00, Sweden

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.5c19915>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Yu Gao gratefully acknowledges the China Scholarship Council (CSC) for financial support. We thank Thijs Moerkens for facilitating the ICP-OES measurements and the technical assistance at the synchrotron. We also appreciate SOLEIL Synchrotron for granting proposal no. 20241129 to perform *operando* XAS experiments at the ROCK beamline, and we extend our thanks to Valérie Briois for her kind assistance. Additionally, we acknowledge the MAXIV synchrotron for proposal no. 20241189 for recording *in situ* XRD patterns at the Balder beamline, with valuable support from Mahesh Ramakrishnan, Damian Vico van Berkel, and Pietro De Angeli.

REFERENCES

- (1) Wang, W.; Wang, S.; Ma, X.; Gong, J. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. *Chem. Soc. Rev.* **2011**, *40*, 3703–3727.
- (2) Yarulina, I.; Chowdhury, A. D.; Meirer, F.; Weckhuysen, B. M.; Gascon, J. Recent Trends and Fundamental Insights in the Methanol-to-Hydrocarbons Process. *Nat. Catal.* **2018**, *1*, 398–411.
- (3) Xu, D.; Wu, P.; Yang, B. Origin of CO₂ as the Main Carbon Source in Syngas-to-Methanol Process over Cu: Theoretical Evidence from a Combined DFT and Microkinetic Modeling Study. *Catal. Sci. Technol.* **2020**, *10*, 3346–3352.
- (4) Shi, Y. F.; Kang, P. L.; Shang, C.; Liu, Z. P. Methanol Synthesis from CO₂/CO Mixture on Cu-Zn Catalysts from Microkinetics-Guided Machine Learning Pathway Search. *J. Am. Chem. Soc.* **2022**, *144*, 13401–13414.
- (5) Kurtz, M.; Wilmer, H.; Genger, T.; Hinrichsen, O.; Muhler, M.; Cu, B. Deactivation of Supported Copper Catalysts for Methanol Synthesis. *Catal. Lett.* **2003**, *86*, 77–80.
- (6) Liang, B.; Ma, J.; Su, X.; Yang, C.; Duan, H.; Zhou, H.; Deng, S.; Li, L.; Huang, Y. Investigation on Deactivation of Cu/ZnO/Al₂O₃ Catalyst for CO₂ Hydrogenation to Methanol. *Ind. Eng. Chem. Res.* **2019**, *58*, 9030–9037.
- (7) Pokrovski, K.; Jung, K. T.; Bell, A. T. Investigation of CO and CO₂ Adsorption on Tetragonal and Monoclinic Zirconia. *Langmuir* **2001**, *17*, 4297–4303.
- (8) Bisotti, F.; Moiola, E.; Manenti, F. Screening Kinetic Models for CO₂-to-Methanol over CuO–ZnO–ZrO₂–Al₂O₃ (CZZA) and CuO–ZnO–ZrO₂ (CZZ): Are They Consistent with the Experimental Evidence? A Critical Review of the Existing Kinetic Models and Relevant Literature on Experimental Characterization of Copper-Based Catalysts for CO₂-to-Methanol Process. *Chem. Eng. J.* **2025**, *503*, 158033.
- (9) Senanayake, S. D.; Ramirez, P. J.; Waluyo, I.; Kundu, S.; Mudiyansele, K.; Liu, Z.; Liu, Z.; Axnanda, S.; Stacchiola, D. J.; Evans, J.; Rodriguez, J. A. Hydrogenation of CO₂ to Methanol on CeO_x/Cu(111) and ZnO/Cu(111) Catalysts: Role of the Metal-Oxide Interface and Importance of Ce³⁺ Sites. *J. Phys. Chem. C* **2016**, *120*, 1778–1784.
- (10) Kattel, S.; Ramirez, P. J.; Chen, J. G.; Rodriguez, J. A.; Liu, P. Active Sites for CO₂ Hydrogenation to Methanol on Cu/ZnO Catalysts. *Science* **2017**, *355*, 1296–1299.
- (11) Chang, X.; Han, X.; Pan, Y.; Hao, Z.; Chen, J.; Li, M.; Lv, J.; Ma, X. Insight into the Role of Cu-ZrO₂ Interaction in Methanol Synthesis from CO₂ Hydrogenation. *Ind. Eng. Chem. Res.* **2022**, *61*, 6872–6883.
- (12) Schulte, M. L.; Truttman, V.; Doronkin, D. E.; Baumgarten, L.; Nicolai, A.; Beltran, D. A. M.; Summ, F. J.; Kiener, C.; Warmuth, L.; Pitter, S.; et al. Monitoring the Fate of Zn in the Cu/ZnO/ZrO₂ Catalyst during CO₂-to-Methanol Synthesis at High Conversions by Operando Spectroscopy. *Angew. Chem., Int. Ed.* **2025**, *64*, No. e202423281.
- (13) Zhang, J.; Medlin, J. W. Catalyst Design Using an Inverse Strategy: From Mechanistic Studies on Inverted Model Catalysts to Applications of Oxide-Coated Metal Nanoparticles. *Surf. Sci. Rep.* **2018**, *73*, 117–152.
- (14) Wu, C.; Lin, L.; Liu, J.; Zhang, J.; Zhang, F.; Zhou, T.; Rui, N.; Yao, S.; Deng, Y.; Yang, F.; et al. Inverse ZrO₂/Cu as a Highly Efficient Methanol Synthesis Catalyst from CO₂ Hydrogenation. *Nat. Commun.* **2020**, *11*, 5767.
- (15) Xu, Y.; Wang, M.; Xie, Z.; Tian, D.; Sheng, G.; Tang, X.; Li, H.; Wu, Y.; Song, C.; Gao, X.; Yao, S.; Ma, D.; Lin, L. Insights into the Interfacial Structure of Cu/ZrO₂ Catalysts for Methanol Synthesis from CO₂ Hydrogenation: Effects of Cu-Supported Nano-ZrO₂ Inverse Interface. *Chem. Eng. J.* **2023**, *470*, 144006.
- (16) Fujiwara, K.; Tada, S.; Honma, T.; Sasaki, H.; Nishijima, M.; Kikuchi, R. Influences of Particle Size and Crystallinity of Highly Loaded CuO/ZrO₂ on CO₂ Hydrogenation to Methanol. *AIChE J.* **2019**, *65*, No. e16717.
- (17) Tada, S.; Fujiwara, K.; Yamamura, T.; Nishijima, M.; Uchida, S.; Kikuchi, R. Flame Spray Pyrolysis Makes Highly Loaded Cu Nanoparticles on ZrO₂ for CO₂-to-Methanol Hydrogenation. *Chem. Eng. J.* **2020**, *381*, 122750.
- (18) Ortner, N.; Zhao, D.; Mena, H.; Weiß, J.; Lund, H.; Bartling, S.; Wohlrab, S.; Armbruster, U.; Kondratenko, E. V. Revealing Origins of Methanol Selectivity Loss in CO₂ Hydrogenation over CuZn-Containing Catalysts. *ACS Catal.* **2023**, *13*, 60–71.
- (19) Li, J.; Wang, D.; Xiong, W.; Ding, J.; Huang, W. Interfacial Site Density Engineering of ZnO/Cu Cube Inverse Catalysts for CO₂ Hydrogenation Reactions. *ACS Catal.* **2024**, *14*, 17413–17420.
- (20) Zhu, J.; Ciolca, D.; Liu, L.; Parastaev, A.; Kosinov, N.; Hensen, E. J. M. Flame Synthesis of Cu/ZnO-CeO₂ Catalysts: Synergistic Metal-Support Interactions Promote CH₃OH Selectivity in CO₂ Hydrogenation. *ACS Catal.* **2021**, *11*, 4880–4892.
- (21) Ge, Y.; Gao, Z.; Xu, Y.; Xu, M.; Qin, X.; Peng, M.; Wang, S.; Gao, R.; Zhou, W.; Ma, D. Inverting Methanol Dehydrogenation Selectivity by Crowding Atomic Ni Species over α -MoC Catalysts. *Angew. Chem., Int. Ed.* **2025**, *64*, No. e202423682.
- (22) Burch, R.; Golunski, S. E.; Spencer, M. S. The Role of Copper and Zinc Oxide in Methanol Synthesis Catalysts. *J. Chem. Soc., Faraday Trans.* **1990**, *1* (86), 2683–2691.
- (23) Burch, R.; Golunski, S. E.; Spencer, M. S. The Role of Hydrogen in Methanol Synthesis over Copper Catalysts. *Catal. Lett.* **1990**, *5*, 55–60.
- (24) Burch, R.; Chappell, R. J.; Golunski, S. E. Synergy between Copper and Zinc Oxide during Methanol Synthesis Transfer of Activating Species. *J. Chem. Soc., Faraday Trans.1* **1989**, *85*, 3569–3578.
- (25) Yu, J.; Liu, S.; Mu, X.; Yang, G.; Luo, X.; Lester, E.; Wu, T. Cu-ZrO₂ Catalysts with Highly Dispersed Cu Nanoclusters Derived from ZrO₂@HKUST-1 Composites for the Enhanced CO₂ Hydrogenation to Methanol. *Chem. Eng. J.* **2021**, *419*, 12966.
- (26) Witton, T.; Chalorngtham, J.; Dumrongbunditkul, P.; Chareonpanich, M.; Limtrakul, J. CO₂ Hydrogenation to Methanol over Cu/ZrO₂ Catalysts: Effects of Zirconia Phases. *Chem. Eng. J.* **2016**, *293*, 327–336.
- (27) Zou, T.; Araújo, T. P.; Krumeich, F.; Mondelli, C.; Pérez-Ramírez, J. ZnO-Promoted Inverse ZrO₂-Cu Catalysts for CO₂-Based Methanol Synthesis under Mild Conditions. *ACS Sustain. Chem. Eng.* **2022**, *10*, 81–90.
- (28) La Fontaine, C.; Belin, S.; Barthe, L.; Roudenko, O.; Briois, V. ROCK: A Beamline Tailored for Catalysis and Energy-Related Materials from ms Time Resolution to μ m Spatial Resolution. *Synchrotron Radiat. News* **2020**, *33*, 20–25.
- (29) Timoshenko, J.; Jeon, H. S.; Sinev, I.; Haase, F. T.; Herzog, A.; Roldan Cuenya, B. Linking the Evolution of Catalytic Properties and Structural Changes in Copper-Zinc Nanocatalysts Using Operando EXAFS and Neural-Networks. *Chem. Sci.* **2020**, *11*, 3727–3736.
- (30) Herzog, A.; Rüscher, M.; Jeon, H. S.; Timoshenko, J.; Rettenmaier, C.; Hejral, U.; Davis, E. M.; Haase, F. T.; Kordus, D.; Kühn, S.; Frandsen, W.; Bergmann, A.; Roldan Cuenya, B. Time-Resolved Operando Insights into the Tunable Selectivity of Cu-Zn

Nanocubes during Pulsed CO₂ Electroreduction. *Energy Environ. Sci.* **2024**, *17*, 7081–7096.

(31) Zabilskiy, M.; Sushkevich, V. L.; Palagin, D.; Newton, M. A.; Krumeich, F.; van Bokhoven, J. A. The Unique Interplay between Copper and Zinc during Catalytic Carbon Dioxide Hydrogenation to Methanol. *Nat. Commun.* **2020**, *11*, 2409.

(32) Spencer, M. S. α -Brass Formation in Copper/Zinc Oxide Catalysts: I. Bulk Equilibrium Concentrations of Zinc under Methanol Synthesis and Water-Gas Shift Reaction Conditions. *Surf. Sci.* **1987**, *192*, 323–328.

(33) Beck, A.; Zabilskiy, M.; Newton, M. A.; Safonova, O.; Willinger, M. G.; van Bokhoven, J. A. Following the Structure of Copper-Zinc-Alumina across the Pressure Gap in Carbon Dioxide Hydrogenation. *Nat. Catal.* **2021**, *4*, 488–497.

(34) King, D. S.; Nix, R. M. Thermal Stability and Reducibility of ZnO and Cu/ZnO Catalysts. *J. Catal.* **1996**, *160*, 76–83.

(35) Wang, M.; Xu, Y.; Tang, H.; Tian, S.; Zeng, L.; Li, H.; Wu, C.; Hu, Z.; Su, M.; Zheng, H.; Wang, M.; Ma, D. Optimizing Methanol Synthesis from CO₂ Hydrogenation over Inverse Zr-Cu Catalyst. *Chem. Catal.* **2024**, *4*, 100985.

(36) Ro, I.; Liu, Y.; Ball, M. R.; Jackson, D. H. K.; Chada, J. P.; Sener, C.; Kuech, T. F.; Madon, R. J.; Huber, G. W.; Dumesic, J. A. Role of the Cu-ZrO₂ Interfacial Sites for Conversion of Ethanol to Ethyl Acetate and Synthesis of Methanol from CO₂ and H₂. *ACS Catal.* **2016**, *6*, 7040–7050.

(37) Fisher, I. A.; Bell, A. T. In-Situ Infrared Study of Methanol Synthesis from H₂/CO₂ over Cu/SiO₂ and Cu/ZrO₂/SiO₂. *J. Catal.* **1997**, *172*, 222–237.

(38) Zhang, C.; Wang, L.; Chen, Y.; He, X.; Song, Y.; Gazit, O. M.; Zhong, Z. Shifting CO₂ Hydrogenation from Producing CO to CH₃OH by Engineering Defect Structures of Cu/ZrO₂ and Cu/ZnO Catalysts. *Chem. Eng. J.* **2023**, *475*, 146102.

(39) Li, K.; Chen, J. G. CO₂ Hydrogenation to Methanol over ZrO₂-Containing Catalysts: Insights into ZrO₂ Induced Synergy. *ACS Catal.* **2019**, *9*, 7840–7861.

(40) Gómez, D.; Collins, S.; Concepción, P.; Jiménez, R.; Karelovic, A. Elucidating the Promotional Effect of Ultra-Low Zn Content on Cu for CO₂ Hydrogenation to Methanol. *J. Catal.* **2023**, *427*, 115119.

(41) Li, N.; Wang, W.; Song, L.; Wang, H.; Fu, Q.; Qu, Z. CO₂ Hydrogenation to Methanol Promoted by Cu and Metastable Tetragonal Ce_xZr_{1-x}O₂ Interface. *J. Energy Chem.* **2022**, *68*, 771–779.

(42) Kim, Y.; Trung, T. S. B.; Yang, S.; Kim, S.; Lee, H. Mechanism of the Surface Hydrogen Induced Conversion of CO₂ to Methanol at Cu(111) Step Sites. *ACS Catal.* **2016**, *6*, 1037–1044.

(43) Xu, Y.; Gao, Z.; Xu, Y.; Qin, X.; Tang, X.; Xie, Z.; Zhang, J.; Song, C.; Yao, S.; Zhou, W.; Ma, D.; Lin, L. Cu-Supported Nano-ZrZnO_x as a Highly Active Inverse Catalyst for Low Temperature Methanol Synthesis from CO₂ Hydrogenation. *Appl. Catal., B* **2024**, *344*, 123656.

(44) Yang, M.; Yu, J.; Zimina, A.; Sarma, B. B.; Pandit, L.; Grunwaldt, J. D.; Zhang, L.; Xu, H.; Sun, J. Probing the Nature of Zinc in Copper-Zinc-Zirconium Catalysts by Operando Spectroscopies for CO₂ Hydrogenation to Methanol. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202216803.

(45) Lam, E.; Noh, G.; Larmier, K.; Safonova, O. V.; Copéret, C. CO₂ Hydrogenation on Cu-Catalysts Generated from Zn^{II} Single-Sites: Enhanced CH₃OH Selectivity Compared to Cu/ZnO/Al₂O₃. *J. Catal.* **2021**, *394*, 266–272.

(46) Nakamura, J.; Choi, Y.; Fujitani, T. On the Issue of the Active Site and the Role of ZnO in Cu/ZnO Methanol Synthesis Catalysts. *Top. Catal.* **2003**, *22*, 277–285.

(47) Li, M. M. J.; Zeng, Z.; Liao, F.; Hong, X.; Tsang, S. C. E. Enhanced CO₂ Hydrogenation to Methanol over CuZn Nanoalloy in Ga Modified Cu/ZnO Catalysts. *J. Catal.* **2016**, *343*, 157–167.

(48) Behrens, M.; Studt, F.; Kasatkin, I.; Kühn, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B.-L.; Tovar, M.; Fischer, R. W.; Nørskov, J. K.; Schlögl, R. The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts. *Science* **2012**, *336*, 893–897.

(49) Gao, Y.; Fan, Y.; Zhang, H.; Pornsetmetakul, P.; Mezari, B.; Wagemakers, J.; Ramakrishnan, M.; Klementiev, K.; Kosinov, N.; Hensen, E. J. M. Stable CO₂ Hydrogenation to Methanol by Cu Interacting with Isolated Zn Cations in Zincosilicate CIT-6. *ACS Catal.* **2025**, *15*, 1807–1818.

(50) Zabilskiy, M.; Sushkevich, V. L.; Newton, M. A.; Van Bokhoven, J. A. Copper-Zinc Alloy-Free Synthesis of Methanol from Carbon Dioxide over Cu/ZnO/Faujasite. *ACS Catal.* **2020**, *10*, 14240–14244.

(51) Kandemir, T.; Girgsdies, F.; Hansen, T. C.; Liss, K. D.; Kasatkin, I.; Kunkes, E. L.; Wowsnick, G.; Jacobsen, N.; Schlögl, R.; Behrens, M. InSitu Study of Catalytic Processes: Neutron Diffraction of a Methanol Synthesis Catalyst at Industrially Relevant Pressure. *Angew. Chem., Int. Ed.* **2013**, *52*, 5166–5170.

(52) Choi, Y.; Futagami, K.; Fujitani, T.; Nakamura, J. The Difference in the Active Sites for CO₂ and CO Hydrogenations on Cu/ZnO-Based Methanol Synthesis Catalysts. *Catal. Lett.* **2001**, *73*, 27–31.



CAS BIOFINDER DISCOVERY PLATFORM™

ELIMINATE DATA SILOS. FIND WHAT YOU NEED, WHEN YOU NEED IT.

A single platform for relevant, high-quality biological and toxicology research

Streamline your R&D

CAS
A Division of the American Chemical Society