Exploring the ternary interactions in Cu–ZnO–ZrO$_2$ catalysts for efficient CO$_2$ hydrogenation to methanol

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The synergistic interaction among different components in complex catalysts is one of the crucial factors in determining catalytic performance. Here we report the interactions among the three components in controlling the catalytic performance of Cu–ZnO–ZrO$_2$ (CZZ) catalyst for CO$_2$ hydrogenation to methanol. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements under the activity test pressure (3 MPa) reveal that the CO$_2$ hydrogenation to methanol on the CZZ catalysts follows the formate pathway. Density functional theory (DFT) calculations agree with the in situ DRIFTS measurements, showing that the ZnO–ZrO$_2$ interfaces are the active sites for CO$_2$ adsorption and conversion, while the presence of metallic Cu is also necessary to facilitate H$_2$ dissociation and to provide hydrogen resource. The combined experiment and DFT results reveal that tuning the interaction between ZnO and ZrO$_2$ can be considered as another important factor for designing high performance catalysts for methanol generation from CO$_2$. 

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Methanol is an important chemical and energy carrier. The catalytic synthesis of methanol from CO₂ (CO₂ + 3H₂ → CH₃OH + H₂O) has attracted considerable attention, because it is not only a potential way to mitigate CO₂ emission but also an alternative process for methanol synthesis in chemical industry³⁴. Cu/ZnO-based catalysts (e.g., Cu–ZnO–Al₂O₃ and Cu–ZnO–ZrO₂) are the most widely studied for this process due to the high activity, high product selectivity, and low cost³⁵–³⁷. As a promising support and promoter, ZrO₂ shows weak hydrophilic character in comparison to Al₂O₃, potentially inhibiting the poisoning effect of water on the active sites during methanol synthesis³⁶,³⁸–³⁹. The presence of ZrO₂ could also enhance the copper dispersion as well as the surface basicity, which should strongly affect the CO₂ adsorption and methanol selectivity¹¹,¹². As a result, the Cu–ZnO–ZrO₂ (CZZ) system has gained an increasing interest for its outstanding activity¹¹,¹³–¹⁷.

Despite great efforts, the reaction mechanism of CO₂ hydrogenation to methanol as well as the nature of the active sites on CZZ catalysts are still under debate and are not comprehensively understood due to the complexity of the ternary system²,³,⁷,¹⁶,¹⁸,¹⁹. In order to simplify the issues, binary catalyst models (e.g., Cu/ZnO and Cu/ZrO₂) have been widely used to discuss the reaction mechanism. A general conclusion is that methanol synthesis over Cu-based catalysts is a structure-sensitive reaction and the synergetic effect between Cu and oxides is responsible for the enhanced activity³,⁵,¹⁰,²⁰–²⁷. The Cu/ZnO synergy is proposed to create active sites for CO₂ and H₂ conversion via a combination of defective Cu nanoparticles with ZnO thin overlayer (including induced morphological changes of Cu)²²,二十四,₂⁸, junction effect at the Cu–ZnO interface (including enhanced electron transfer and increased generation of oxygen defects in the interface)³,⁵,²⁹–³¹, or formation of a specific Cu–Zn–ZrO₂ surface alloy (including migration of Zn atoms over the Cu surface and incorporation of Zn atoms into the Cu step-edge sites)¹⁹,²¹. The Cu/ZnO and Cu/ZrO₂ synergy is mainly attributed to the promotion of Cu–ZrO₂ interfacial sites, which may promote the adsorption of CO₂¹⁰,²⁶, enhance the dissociation of H₂ and spillover of atomic hydrogen³²,³³, bind the key reaction intermediates (e.g., *CO₂, *CO, *HCO, and *H₂CO) for further conversion²⁵, and increase the turnover frequency²⁶.

The role of ZnO–ZrO₂ interaction is an ongoing debate. Recently, it was reported that the binary ZnO–ZrO₂ oxide in the solid solution state also shows activity for CO₂ hydrogenation to methanol³⁴. The Zn-doped ZrO₂ without the presence of Cu could achieve high CO₂ conversion (10%) and methanol selectivity (86%) at high pressure (5 MPa) and high temperature (593 K). In comparison, CZZ catalysts with the presence of Cu usually could obtain high methanol yield at moderate conditions (3 MPa and 493–513 K, see the comparison in Supplementary Table 3). However, little is known about the atomic-level interaction among the three components in the Cu–ZnO–ZrO₂ complex system, in particular under in situ reaction conditions. Here, we report a mechanistic investigation of the ternary interactions of Cu/ZnO/ZrO₂ in CO₂ adsorption and activation for methanol synthesis by comparing the three-dimensional ordered macroporous (3DOM) catalysts with different particle size of ZnO. The 3DOM catalyst shows very high activity (18.2% CO₂ conversion and 80.2% methanol selectivity obtained at 493 K and 3.0 MPa). The results from the in situ DRIFTS measurements at an activity test pressure (3 MPa) and DFT calculations indicate that the synergy among Cu, ZnO, and ZrO₂ is essential to promote the CO₂ conversion and methanol selectivity. The presence of Cu is necessary to allow the formation of active *H at the Cu–ZnO or Cu–ZrO₂ interface for the final formation of methanol, while the ZnO–ZrO₂ interface strongly enhances the activation and transformation of CO₂ by promoting the hydrogenation of carbonate intermediate to more reactive species (e.g., formate and methoxy).

Results

Structural characterization. 3DOM catalysts with different particle sizes of ZnO were prepared. The full details for all samples are collected in the Supplementary Information (SI) including the (HR) TEM images, size distributions of ZnO and ZrO₂, XRD patterns, and specific surface areas of different samples. The specific surface area of the ZnO in the four 3DOM samples changes from 15 to 36 nm, and the ZrO₂ particles are much smaller (3–4 nm) for all the samples (Supplementary Fig. 1). The specific surface areas (Supplementary Table 1) for the 3DOM samples are in the range of 32–35 m²/g.

The EDS and TEM analyses (Fig. 1b–d) suggest that Cu makes up the 3DOM framework, and the ZnO particles are well dispersed on the wall of the macro pores. The HRTEM images (Fig. 1e–g) show that t-ZrO₂ nanoparticles (3.5 ± 1 nm, Supplementary Fig. 1), with a fringe spacing of 0.295 nm corresponding to the (011) plane, are highly dispersed on both the ZnO particles and Cu framework. The structural diagrammatic sketch of macroporous CZZ catalysts is shown in Fig. 1h. The XRD patterns, shown in Supplementary Fig. 2, reveal that the diffraction peak positions corresponding to Cu or ZrO₂ are very similar for all the four samples. However, the differences in the peak widths of ZnO suggest changes of ZnO crystallite size in different samples, supporting the observation by TEM (see Supplementary Fig. 1).

Catalytic performance and reaction intermediates. Figure 2a shows the CO₂ conversion, MeOH selectivity/yield and TOF value of methanol formation as a function of the ZnO particle size. The detailed data on the physicochemical and catalytic properties of different samples (e.g., diameter of Cu (dCu), specific surface area of Cu (SCu) and turnover frequency (TOF) values) are presented in Supplementary Tables 1, 2. As seen in Fig. 2a, the 3DOM catalyst with the smallest ZnO particles (M-CZZ(16) sample) possesses very high CO₂ conversion (18.2%), methanol selectivity (80.2%) and methanol yield (297 gMeOH·Kgₐₖₜ−¹·h−¹). To our knowledge, this catalyst is the most active for CO₂ hydrogenation to methanol among the CZZ catalysts under comparable conditions (Supplementary Table 3). It should be highlighted that the catalytic activity of the catalysts strongly relies on the ZnO particles. The CO₂ conversion, methanol selectivity and the TOF value decrease with increasing ZnO particle size, suggesting that ZnO particles play a significant role in determining the catalytic performance.

Figure 2b–d show the DRIFT spectra obtained during CO₂ hydrogenation at 493 K and 3 MPa over the M-CZZ(16) and M-CZZ(36) catalysts. For the M-CZZ(16) sample (Fig. 2b), strong bands at 1589, 1386, and 1362 cm⁻¹ are observed, which are assigned to the ν₅(OCO), δ(CH), and ν₃(OCO) modes of formate species²⁷, respectively. After the reaction proceeding for 10 min, vibrational bands at 1056, 1031, and 1005 cm⁻¹ corresponding to the C–O stretch of methanol are observed, and bands at 2975, 2943, 2920, 2871, 2840, and 2818 cm⁻¹, attributed to the C–H stretch of methanol, are also detected³⁵, indicating the formation of methanol. The comparison of the in situ DRIFT spectra of methanol and methoxy is shown in the SI (see the Supplementary Fig. 4 and the related discussion). On the other hand, peaks at 2175 and 2115 cm⁻¹, which are characteristic of gaseous CO, are also observed, indicating the occurrence of the reverse water-gas shift (RWGS) reaction. The weak and oscillating bands located in the range of 1400–1800 cm⁻¹ are attributed to water vapor, which originates from the RWGS and methanol synthesis reactions³⁶.

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Fig. 1 Morphological and compositional characterizations of a 3DOM CZZ catalyst (M-CZZ(16)). a) SEM image, indicating an average pore size of 120 nm. b, c) TEM images of the M-CZZ(16) sample, which shows the smallest ZnO particle size (15.8 nm) in the 3DOM catalyst series. d) EDS of different points in c. e-g) HRTEM images of M-CZZ(16). h) Structural diagrammatic sketch of the macroporous catalysts.

Fig. 2 Catalytic performance and in situ DRIFT spectra of the CO$_2$ + H$_2$ reaction over different catalysts. a) CO$_2$ conversion, MeOH selectivity, MeOH yield and TOF values as a function of the ZnO particle sizes in different catalysts. b) Evolution of the IR spectra over the M-CZZ(16) sample with time. c) DRIFT spectra over the M-CZZ(36) sample. d) Peak areas of generated intermediate species and methanol during the experiments: areas normalized to the values observed at the end of the transient. Reaction conditions for catalytic test: WHSV = 3 h$^{-1}$, $T = 493$ K, CO$_2$:H$_2$ = 1:3, $P = 3.0$ MPa; Reaction conditions for TOF calculation: WHSV = 10 h$^{-1}$, $T = 493$ K, CO$_2$:H$_2$ = 1:3, $P = 3.0$ MPa; Reaction conditions for in situ DRIFT spectra: gas flow rate = 40 mL/min, $T = 493$ K, CO$_2$:H$_2$ = 1:3, $P = 3.0$ MPa. Formate species (2870, 1589, 1386, and 1362 cm$^{-1}$) and methanol (2975, 2943, 2920, 2871, 2840, and 2818 cm$^{-1}$) can be observed over the two samples, especially for the M-CZZ(16) catalyst.
In Fig. 2c, the corresponding bands observed over M-CZZ(16) are also detected over the M-CZZ(36) sample, but the band intensities of formate species and methanol are much weaker. This indicates that the particle size of ZnO affects the formation and evolution of intermediate species, and smaller ZnO particles enhance the formation of formate and methanol.

The temporal evolution of the principal surface species (formate, methoxy, and methanol) on both samples during the CO2 hydrogenation process are presented in Fig. 2d. The concentration of formate increases sharply at the beginning of the reaction, which is followed by a slight increase of methanol. This indicates that the formation of formate is very fast, while the generation of methanol needs an induction period. It should be highlighted that the methoxy species, which is a common intermediate observed by in situ IR under atmospheric or lower pressures27,34, is almost absent over the present samples. To identify the relationship between formate and methoxy species, the in situ DRIFTS experiment under atmospheric pressure is also performed, and the results are shown in Supplementary Fig. 5.

After the catalysts were pre-treated in flowing pure CO2 for 10 min at 493 K, transient response spectra were recorded with switching H2 into the reactor chamber. As shown in Supplementary Figs. 5a and b, before the switching, only peaks at ca. 1522 and 1352 cm$^{-1}$ related to monodentate (m-CO3$^{2-}$) and bidentate (b-CO3$^{2-}$) carbonate species, as well as the peak at 1075 cm$^{-1}$ assigned to carbonate ion (CO3$^{2-}$), are detected.35,36 The bands for formate species located at ca. 2972, 2878, 1588, 1384, and 1367 cm$^{-1}$ appear as soon as H2 is introduced, while the peaks attributed to carbonate species almost disappear. This indicates that the carbonate could rapidly react with H to form formate.

It is also observed that the bands of formate slightly decrease in intensity with time, and the C–H (2930 and 2821 cm$^{-1}$) and C–O (1145 and 1045 cm$^{-1}$) stretching features attributed to the methoxy gradually increase in intensity. This suggests that methoxy should originate from the hydrogenation of formate species. After the reaction proceeds for 10 min, the bands related to water vapor (see the insert in Supplementary Figs. 5a and 5b) located in the range of 1400–1800 cm$^{-1}$ are observed, which is likely produced from the hydrogenation of formate. The evolution of surface species over catalysts during the onset of switching feed gas from CO2 to H2 after CO2 adsorption is presented in Supplementary Fig. 4c. It is clear that the intensity of methoxy slightly increases with the decrease in the formate intensity, evidencing the conversion of formate to methoxy. It is also noted that no CO intermediate is detected during the DRIFTS experiment under atmospheric pressure (see Supplementary Fig. 5), which is inconsistent with the formation of CO in the CO2 hydrogenation at 3.0 MPa (see Fig. 2). This reveals that the reaction pressure also affects the production of CO from CO2.

To eliminate the effect of 3DOM structure on the adsorption and catalytic activity, a series of conventional samples with various particle size of ZnO but comparable Cu and ZrO2 particle sizes were also prepared (which were labeled as nonporous samples, N-CZZ). All the characterization, catalytic tests and in situ DRIFTS experiments, which were performed on the 3DOM samples, were also performed on the N-CZZ. The results are shown in Supplementary Figs. 6–9 and Supplementary Tables 1 and 2. It is found that the catalytic performance and the evolution of the intermediate species during the reaction also strongly rely on the particle size of ZnO. This suggests that the size effect of ZnO is a common phenomenon for the CZZ catalyst system.

Comparison on Cu–ZnO, Cu–ZrO2, and ZnO–ZrO2 interactions. As observed above, the ZnO particle size strongly affects the CO2 adsorption, the formation of intermediate species and the methanol generation over the CZZ catalysts. On the other hand, the microstructures of Cu particles (e.g., Cu dispersion, Cu specific surface area and Cu particle size) in all the samples are similar (see Supplementary Table 1), and there is no direct correlation between the TOF values or methanol yields and the Cu surface area or Cu dispersion (see Supplementary Table 2). This suggests that the determining factor for the catalytic performance should be more complicated than the independent Cu related species. The size effect of ZnO may be related to the ZnO–ZrO2 interaction. To identify the roles of Cu–ZnO, Cu–ZrO2, and ZnO–ZrO2 interactions in CO2 adsorption and conversion, in situ DRIFT experiments were performed on all the three binary samples with switching the feed gas from CO2 to H2. The crystallite sizes of different phases in the three samples are controlled in a comparable range to ensure the comparability (see Supplementary Fig. 10).

Figure 3a shows the transient evolution of the principal surface species over the Cu–ZnO sample. In the CO2 atmosphere, the carbonate species (1522, 1329, and 1045 cm$^{-1}$) are observed. After switching gas to H2, the carbonate species disappear and very weak formate bands (1588, 1387, and 1365 cm$^{-1}$) are detected. Similar phenomena are also observed on the Cu–ZrO2 sample (Fig. 3b). This indicates that the conversion of carbonate species to formate species is very difficult on these two binary samples. In contrast, abundant formate species (2972, 2878, 1593, 1386, and 1362 cm$^{-1}$) are formed after switching CO2 to H2 on the ZnO–ZrO2 sample (Fig. 3c), concurrent with the decrease of carbonate species (Fig. 3d). The in situ DRIFT experiments at atmospheric or 3 MPa in the CO2/H2 mixture also reveal that only the ZnO–ZrO2 system shows relatively high intensity of formate bands among the three samples (Supplementary Figs. 11, 12). But it should be noted that no methanol is detected over the ZnO–ZrO2 sample at the activity test condition without the presence of Cu (see Supplementary Fig. 12c). These phenomena suggest that the ZnO–ZrO2 interface should be the active sites for CO2 adsorption to carbonate species and its subsequent conversion to formate and the Cu species may contribute to the further hydrogenation process.

To further study the effect of the ZnO–ZrO2 interaction on the CO2 adsorption and formate formation, a series of ZnO–ZrO2 samples with different particle sizes of ZnO and similar particle sizes (average sizes of 3–4 nm) of ZrO2 were prepared. The typical TEM images of different samples are shown in Supplementary Fig. 14. The average particle sizes for the three samples (ZnO(15)–ZrO2, ZnO (21)–ZrO2, and ZnO(42)–ZrO2) are 15.1, 21.4, and 42.2 nm, respectively.

Figure 4a–c represent the in situ DRIFT spectra over the samples when switching the feed gas from CO2 to H2. As shown in Fig. 4a, only carbonate species (1540, 1408, and 1084 cm$^{-1}$) are observed over the ZnO(15)–ZrO2 sample in CO2. After switching the feed gas from CO2 to H2, the formate bands (2972, 2878, 1590, 1386, and 1363 cm$^{-1}$) appear immediately with the decrease of carbonate, indicating the hydrogenation of carbonate to formate. Figures 4b, c show similar trend over the ZnO (21)–ZrO2 and ZnO(42)–ZrO2 samples. It is notable that the formation of carbonate and its further conversion to formate is inversely proportion to the ZnO particle size. Smaller ZnO particles promote the adsorption of CO2 and its further conversion to formate, which may be attributed to the more abundance of the ZnO–ZrO2 interface.

In order to further understand the interaction between ZnO and ZrO2, we have performed CO2-TPD experiments over the ZnO(15)–ZrO2 sample, pure ZnO particles with different average sizes (11, 19, and 37 nm) and pure ZrO2 with an average particle size of 10 nm. As shown in Fig. 4d, the CO2 adsorption capacity slightly decreases with increasing ZnO particle size.
In comparison, the ZnO(15)–ZrO2 sample shows much higher CO2 adsorption peak at low temperatures (373–473 K) than the pure ZrO2 or ZnO regardless of the particle size, indicating that the interaction between ZnO and ZrO2 strongly improves the CO2 adsorption capacity.

Oxygen vacancy also plays a very important role in the hydrogenation of CO or CO2 to methanol, which can adsorb and activate reactive gases and stabilize the reaction intermediates, elevating the catalytic activity. In the case of Cu–ZnO catalysts in CO2 hydrogenation, it is proposed that the activity is correlated to the number of oxygen defects between Cu and ZnO particles. In the case of Cu–ZrO2 catalysts, the oxygen vacancies created by the evolution of ZrO2 phase also strongly affect the reaction mechanisms. According to the literatures, catalysts with monoclinic ZrO2 (m-ZrO2) are nearly an order of magnitude more active for methanol synthesis from CO2 than catalysts with the same Cu surface density deposited on tetragonal ZrO2 (t-ZrO2) due to the relatively higher concentration of oxygen vacancies. The formation of oxygen vacancies resulting from the ZnO–ZrO2 interaction is evidenced by comparing the XPS spectra of ZnO/ZrO2 sample with that of pure ZnO or ZrO2 (see Supplementary Fig. 17 and the related discussions). Such oxygen vacancies can be the active sites for CO2 adsorption.

For CO2 hydrogenation to methanol over Cu-based catalysts, formate pathway (featured by formate as the main intermediate) and CO-Hydro pathway (featured by the CO intermediate produced via RWGS) are considered as two major reaction mechanisms. The formate pathway is defined by the following two conditions: (1) formate can be quickly generated and not easily decomposed into CO and (2) formate should not be excessively stable and can be hydrogenated to methoxy. In the present work, it can be seen from Supplementary Figs. 5 and 9 that the carbonate is rapidly converted to formate in the presence of H2 and no CO is detected in this process. Meanwhile, the DRIFTS intensity of *CH3O increases along with the decrease of the *HCOO signal. It is also found that the samples with more detectable formate in the DRIFTS experiments show higher activity for methanol formation (see Fig. 2), indicating that the formate (instead of being a spectator) should be an important intermediate for the formation of methanol. By contrast, no direct correlation is found between the formation of CO and the yield of methanol. These phenomena suggest that the CO2 hydrogenation over the present CZZ catalysts follows the formate pathway.

**Density functional theory studies.** DFT calculations were performed to understand the catalytic behavior of the ZrO2/ZnO interface during CO2 conversion to CH3OH. Herein, the ZrO2/ZnO interface is modeled by depositing a small ZrO2 cluster on the ZnO(1120) surface (for details see computational method section in the SI). The surface O atoms in our model were saturated with H atoms to account for the possible H spillover from Cu to oxide nanoparticles due to facile H2 dissociation on Cu, as predicted by DFT calculations and observed in our experiments.

Figure 5a and Supplementary Fig. 25 show the reaction intermediates that are involved in CO2 hydrogenation, and the structure of the intermediates with different views can be found in Supplementary Fig. 26. The binding energy (−2.32 eV) for CO2...
adsorption on ZrO$_2$-ZnO(1120) is much stronger than that for ZnO–Cu(111) ($-0.13$ eV), ZrO$_2$–Cu(111) ($-1.18$ eV), ZrO$_2$ cluster on ZnO(1120) ($-1.95$ eV), and ZnO(1120) ($-1.94$ eV), indicating that the activation and transformation of CO$_2$ prefer to occur at the ZrO$_2$/ZnO interface.

Previously, the role of ZnO for CO$_2$ hydrogenation has been debated and previous studies have suggested that ZnO acts as an active phase for CO$_2$/CO hydrogenation to CH$_3$OH$^{12,43}$. The CO$_2$ $\rightarrow$ CH$_3$OH conversion on ZnO(1120) is further investigated using DFT. The results suggest that the initial hydrogenation of CO$_2$ on ZnO(1120) likely proceeds via the formation of the *HOCO intermediate since *HOCO formation ($\Delta E = -0.16$ eV and $E_a = 0.15$ eV) is kinetically more favorable than *HCOO formation ($\Delta E = -1.42$ eV and $E_a = 0.32$ eV). The *HOCO dissociation produces a key reaction intermediate, *CO, along the RWGS + CO-Hydro pathway for CH$_3$OH synthesis$^{27,44}$. However, in consideration of the entropic contribution, *CO may not be stable on the ZnO(1120) surface under reaction conditions with a BE of $-1.33$ eV, preventing desorption rather than its further hydrogenation. Thus, CO is predicted to be the product of CO$_2$ hydrogenation on ZnO(1120), which agrees well with the corresponding experimental observation of CO but not CH$_3$OH as a product of CO$_2$ hydrogenation on ZnO(1120) (see Supplementary Figs. 18, 19).

The DFT optimized geometries at the ZrO$_2$/ZnO interface were then used to calculate the reaction energy ($\Delta E$) and activation energy ($E_a$) of each elementary step involved in CO$_2$ hydrogenation to CH$_3$OH via the formate pathway, which was identified as an active intermediate by in situ DRIFTS for the CZZ catalysts.

![Figure 4](https://example.com/figure4.png)

**Figure 4** Characterization of the surface species on the ZnO–ZrO$_2$ samples with different particle sizes of ZnO. In situ DRIFT spectra of a) ZnO(15)–ZrO$_2$, b) ZnO(20)–ZrO$_2$, and c) ZnO(42)–ZrO$_2$, at 493 K after switching the feed gas from CO$_2$ to H$_2$ with a flow rate of 40 mL/min under atmosphere pressure. d) CO$_2$-TPD patterns of ZnO(15)–ZrO$_2$, pure ZnO with different particle sizes and pure ZrO$_2$ with an average particle size of 10 nm.

5b shows the energy profile for the formation of CH$_3$OH from CO$_2$ and H$_2$ along the formate pathway. The initial step in CO$_2$ hydrogenation, i.e., the formation of the *HCOO intermediate is exothermic with $\Delta E$ of $-0.52$ eV and $E_a$ of 0.78 eV. Further hydrogenations of *HCOO leads to the formations of *H$_2$COOH ($\Delta E = -1.27$ eV; $E_a = 0.66$ eV) and *H$_2$COO (*HCOO to *HCOOH, the *H assisted dissociation to HCO (*HCOO + *H $\rightarrow$ *HCOOH, $\Delta E = -0.44$ eV; $E_a = 1.45$ eV) and subsequently to CO (*HCOO + *H $\rightarrow$ *HCOH, $\Delta E = 1.51$ eV; $E_a = 1.63$ eV) is kinetically more difficult at the ZnO/ZrO$_2$ interface. Thus, it suggests that the formation of *CO from *HCOO is highly unlikely, in agreement with the experimental results (Supplementary Figs. 5 and 9). The ZnO–ZrO$_2$ interface facilities not only the activation of *HCOO, the rate-limiting step for CO$_2$ hydrogenation at the ZnO–Cu interface$^3$ via lowering the barrier from 0.85 to 0.66 eV, but also the formation of *H$_2$COOH, a highly activated step via lowering the barrier from 0.90 to 0.52 eV. This agrees well with the in situ DRIFTS results (Supplementary Fig. 5), showing a fast conversion of *HCOO to *H$_2$CO over the CZZ catalyst. *H$_2$COOH is the precursor for C–O bond breaking as in the case of Cu/ZnO, however, the corresponding barrier ($\Delta E = -1.37$ eV; $E_a = 0.03$ eV) is much lower on ZnO–ZrO$_2$ than on Cu/ZnO ($E_a = 0.49$ eV)$^3$. The hydrogenation of dissociated *H$_2$CO results in the formation of *H$_2$CO ($\Delta E = -0.68$ eV; $E_a = 0.67$ eV) and eventually the production of *CH$_3$OH ($\Delta E = 0.59$ eV; $E_a = 0.67$ eV). Similar promotion is also observed when compared to Cu/ZrO$_2$, which shows more difficult activations of *HCOO to *HCOOH.
(ΔE = 0.70 eV, $E_a = 0.80$ eV) and *H$_2$COOH dissociation to *H$_2$CO and *OH (ΔE = 0.67 eV, $E_a = 1.32$ eV) than ZnO–ZrO$_2$.

For the reaction pathway at the ZnO–ZrO$_2$ interface, the dissociated *OH is removed from the surface by the formation of H$_2$O, which is an endothermic process (ΔE = 0.56 eV) and has to overcome the highest barrier of 0.96 eV along the pathway. In contrast, it is a facile step at the ZnO–Cu interface (ΔE = −0.43 eV; $E_a = 0.22$ eV)$^3$. Therefore, the potential synergy between the interfaces of ZnO–ZrO$_2$ and ZnO–Cu might also play an important role in promoting the removal of surface *OH to regenerate the active sites. According to the DFT calculated energy barriers, the formation of ZnO–ZrO$_2$ interface is able to promote the *HCOO activations, which have been identified to control the reaction rates at the Cu/ZnO and Cu/ZrO$_2$ interfaces during CO$_2$ hydrogenation; yet the removal of *OH from the surface to produce gas phase H$_2$O can be problematic at lower temperatures. Nevertheless, the barrier is <1 eV and is expected to be partially overcome at $T = 493$ K to maintain sufficient amount of active sites for hydrogenation of CO$_2$ to CH$_3$OH.

The Cu component was not specifically considered in the present DFT calculations. At the ZnO–ZrO$_2$ interface, the H$_2$ dissociative adsorption is an endothermic process (ΔE = 0.47 eV), which is less favorable than that at the Cu/oxide interface (ΔE = −0.33 eV)$^3$. On Cu(111), H$_2$ dissociation is thermodynamically and kinetically (ΔE = −0.39 eV; $E_a = 0.53$ eV) more favorable than that on the ZnO–ZrO$_2$ and Cu/oxide interfaces. Therefore, the presence of Cu is necessary to allow the facile formation of *H at the Cu/oxide interface under reaction conditions, which facilitates the subsequent hydrogenation processes by providing the surface *H species. This is consistent with the high pressure in situ DRIFTS (see Fig. 2 and Supplementary Fig. 12) results that CH$_3$OH is detected over the CZZ sample but not over the ZnO–ZrO$_2$ sample.

**Discussion**

For the Cu/ZnO system, the Cu–ZnO interface or the Cu–Zn surface alloy are considered as the active sites for CO$_2$ hydrogenation to methanol$^{3,5,7,24,28,29}$. In the case of Cu/ZrO$_2$, the Cu–ZrO$_2$ interface play a very important role for methanol formation$^{10,26,27,33}$. In both the binary catalysts, the catalytic activity is determined by the Cu–ZnO or Cu–ZrO$_2$ interaction that is closely related to the physicochemical features (e.g., Cu particle size and surface area of Cu) of Cu spices. As shown in the comparison of the catalytic activity of Cu/ZnO, Cu–ZrO$_2$, and Cu–ZnO–ZrO$_2$ in Supplementary Fig. 13, the Cu–ZnO–ZrO$_2$ ternary catalyst exhibits much higher methanol yield than either Cu–ZnO or Cu–ZrO$_2$ even though it shows a lower surface area of Cu (S$_{Cu}$) than the Cu/ZnO catalyst, suggesting that the ZnO–ZrO$_2$ interaction should also play an important role in the Cu–ZnO–ZrO$_2$ catalyst for CO$_2$ hydrogenation. Combining the results of XPS (Supplementary Fig. 17) and CO$_2$-TPD (Fig. 4d), it can be concluded that the ZnO–ZrO$_2$ interaction promotes the formation of oxygen vacancies, which should be the active sites for CO$_2$ adsorption. The in situ DRIFTS (Fig. 3 and Supplementary Fig. 12) experiments reveal that the
ZnO–ZrO2 interface is crucial for the transformation of carbonate to formate during CO2 hydrogenation. However, no surface methoxy, which is a crucial intermediate species for methanol synthesis, is detected on the ZnO–ZrO2 system. We identified several reaction intermediates for the CZZ catalyst during CO2 hydrogenation and highlights the importance of the strong interplay among Cu, ZnO, and ZrO2 in the ternary interaction and a full discussion is also provided.

Both the in situ DRIFTS experiments (Figs. 3 and 4) and DFT calculations (Fig. 5) suggest that CO2 adsorption and conversion to formate species (e.g., formate and methanol) strongly rely on the ZnO/ZrO2 interface, which promotes the HCOO activation, the rate-limiting step at the Cu/ZnO interface. Such promoting effect can be further enhanced by reducing the particle size of ZnO (Fig. 2 and Supplementary Fig. 8). The DFT results suggest that the presence of Cu at the ZnO–ZrO2 interface is necessary to promote the conversion of the carbonate species to formate, methoxy and eventually methanol, as observed by in situ DRIFT under the activity test condition (Fig. 2) or during the switching from CO2 to H2 (Supplementary Fig. 5). Overall, the combination of in situ characterization and DFT calculations enables the identification of active sites and reaction intermediates for the CZZ catalyst during CO2 hydrogenation and highlights the importance of the strong interplay among Cu, ZnO, and ZrO2 in promoting the CO2 conversion and methanol selectivity.

In summary, by designing different Cu–ZnO–ZrO2 (CZZ) catalysts and performing in situ experiments and DFT calculations, we identified the different functions of the ZnO–ZrO2 interface and Cu species in the catalytic CO2 hydrogenation to methanol. The obtained catalysts show very high activity (18.2% of conversion and 80.2% of selectivity obtained at 493 K and 3.0 MPa) for methanol generation. The formate pathway is identified for the CO2 hydrogenation process over the CZZ catalysts. ZnO–ZrO2 binary oxides show much higher ability for CO2 adsorption and the hydrogenation of carbonate species to reactive intermediates (formate and methoxy) than the Cu–ZnO or Cu–ZrO2 systems. DFT calculations show that the ZnO/ZrO2 interface is the active site for CO2 adsorption and conversion, in particular for *HCOO activation, which is the rate-limiting step at the Cu/ZnO interface during CO2 hydrogenation. The presence of Cu0 is also necessary to allow the presence of *H under reaction conditions, while tuning the interaction between ZnO and ZrO2 can affect the formation and evolution of the surface species, therefore controlling the catalytic performance. The findings proposed in this work would enrich the knowledge in understanding the fundamental features of the CZZ ternary CO2 hydrogenation catalysts and be helpful for designing complex catalysts with multiple active components.

Methods

3DOM catalyst preparation. 3DOM catalysts were prepared by a colloidal crystal template method. First, uniform monodisperse poly methyl methacrylate (PMMA) spheres were synthesized as template via an emulsifier-free emulsion polymerization route. After that, the required amounts of Cu(NO3)2·3H2O, Zn(NO3)2·6H2O, and Zr(NO3)4·5H2O were dissolved in 20 mL of deionized water to form a transparent solution (5 mol/L, Cu/Zn/Zr molar ratio = 5:2:3), and then 10 g of citric acid (C6H8O7·H2O) was added into the solution and dissolved at 333 K under stirring for 1 h. Then, 10 mL of ethylene glycol (EG) was added with the solution under stirring for 10 min. Subsequently, the dried PMMA templates were soaked in the precursor solutions for 6 h. After being filtered, the precursors were dried at 333 K for 12 h. Finally, the precursors were calcined at 723 K for 6 h with a ramp rate of 1, 2, 4, and 8 K/min under air, respectively. The obtained samples were labeled as M-CZZ(16), M-CZZ(19), M-CZZ(24), and M-CZZ(36), respectively.

Cu–ZnO (molar ratio of Cu/Zn = 5:2), Cu–ZrO2 (molar ratio of Cu/Zr = 7:3), and ZnO–ZrO2 (molar ratio of Zn/Zr = 7:3) samples were prepared by a co-precipitation method. The required amounts of Cu(NO3)2·3H2O, Zn(NO3)2·6H2O, and/or Zr(NO3)4·5H2O were dissolved in 20 mL of deionized water to form a transparent solution (5 mol/L). Then, the transparent solution and NH3·H2O (2.5 wt.%) was added dropwise into 200 mL of deionized water, simultaneously, controlling the pH at ~6.5. After aging for 1 h, the precursor was filtered and washed with deionized water. The precursors were then dried at 333 K for 12 h and further calcined at 723 K for 6 h with a ramp rate of 2 K/min.

Preparation of the nonporous samples. Conventional catalysts were prepared by a co-precipitation method. The required amounts of Cu(NO3)2·3H2O, Zn(NO3)2·6H2O, and Zr(NO3)4·5H2O were dissolved in 20 mL of deionized water and NH3·H2O (2.5 wt.%) was added dropwise to form a transparent solution (5 mol/L, Cu/Zn/Zr molar ratio = 5:2:3). Then, the transparent solution and NH3·H2O (2.5 wt.%) was added dropwise into 200 mL of deionized water, simultaneously, controlling the pH at ~6.5. After aging for 1 h, the precursor was filtered and washed with deionized water. The precursors was then dried at 333 K for 12 h and further calcined at 723 K for 6 h with a ramp rate of 2 K/min, and the obtained samples are labeled as N-CZZ(25) and N-CZZ(31), respectively. When the precipitating agent was changed from sodium carbonate (0.5 mol/L) to NH3·H2O (2.5 wt.%), and calcining the precursor at 723 K for 6 h with a ramp rate of 2 K/min, the obtained sample was labeled as N-CZZ(43).

Characterization. The specific surface area of the catalysts was calculated according to the BET method using the N2 adsorption isotherm at 77 K, obtained on a Quantachrome Autoabсорb-iQ instrument. The crystal phases of the prepared catalysts were identified using a powder X-ray diffractometer (Rigaku D/max-R) with Cu Ka radiation (λ = 0.15406 nm). The X-ray tube was operated at 40 kV and 40 mA. The XRD patterns were recorded for 20 values ranging from 20° to 80° at a scanning rate of 2°/min. The morphology of the catalysts was observed by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) technology. The SEM measurement was performed on a Nova NanoSEM 450 instrument using an accelerating voltage of 2000 V–30 kV. The SEM samples were dusted on an adhesive conductive carbon belt attached to a copper disk and coated with a conductive paint prior to the measurement. For TEM characterization, a Tecnai G2 T-F30 S-Twin microscope was used operating at 300 kV. The specimens were crushed into powder and immersed in a small volume of ethanol. After sonicating the mixture for 10 min, a droplet of the suspension was allowed to dry on a holey carbon/Formvar-coated copper TEM grid.

XPS dates were obtained with a PHI 5000 Versaprobe II system equipped with a monochromatic Al-Ka X-ray source. The reduced samples were placed on stainless steel sample-holders were transferred to the XPS pre-chamber under inert atmosphere and stayed there for 12 h in a vacuum atmosphere. The spectra were recorded after purging the samples at ambient temperature under vacuum (residual pressure <10−7 Pa). The C 1s signal at 284.8 eV was used as an internal standard for calibration of the XPS signals.

H2 temperature-programmed reduction (H2–TPR) was performed on a ChemBET Pulsar & TPR/TPD apparatus (Quantachrome Instruments) with a thermal conductivity detector (TCD). Prior to each experiment, the sample (50 mg) was pre-treated in flowing pure He (30 mL/min) at 573 K for 1 h and cooled to room temperature (RT). Thereafter, the temperature was increased at a rate of 10 K/min to 673 K in flowing 10% H2/Ar (30 mL/min). The metallic copper surface area (S Cu) was measured using N2O decomposition method. The catalyst (50 mg) was first reduced with 10% H2/Ar (30 mL/min) at 573 K for 1 h followed by purging with H2 (30 mL/min) for 1 h, and then cooled to 333 K. Then, a flow of 10% N2/He (30 mL/min) gas was fed into the reactor for 1 h. TPR measurement was subsequently performed under a 10% H2/Ar flow (30 mL/min) to 573 K with a ramp rate of 10 K/min. The copper surface area was calculated on base of Eq. (1) by assuming that the copper crystallites are spherical.

\[
S_{\text{Cu}} \text{ (m}^2/\text{nm}^3) = \frac{200 \times (\text{Vol} \times H_2)}{\left(5 \times N_{\text{Cu}} \times 1.25 \times \text{ Vol} \times H_2 \right)}
\]

\[
D_{\text{Cu}}(\%) = \frac{[\text{the amount of exposed copper}] \\ \text{[the total amount of copper atoms]}}
\]
Where \( \text{Mol } \text{H}_2 \) is the amount of \( \text{H}_2 \) consumed during the TPR step per unit mass of the catalyst (\( \text{mol } \text{H}_2/\text{gcat} \)), \( S \) is the stoichiometric factor (2.0), \( N_v \) is Avogadro’s number (6.022 x 10^23 atoms/mol), and \( \Delta S_{\text{HC}} \) is the copper surface density (1.47 x 10^{19} \text{atoms/m}^2).

**References**

1. Álvarez, A. et al. Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneously catalyzed CO2 hydrogenation processes. *Chem. Rev.* 117, 9804 (2017).
2. Graciani, J. et al. Highly active copper-terra and copper-terra-titania catalysts for methanol synthesis from \( \text{CO}_2 \). *Science* 345, 546–550 (2014).
3. Kattel, S., Ramirez, P. J., Chen, G. J., Rodriguez, J. A. & Liu, P. Active sites for \( \text{CO}_2 \) hydrogenation to methanol on Cu/ZnO catalysts. *Science* 357, 1296–1299 (2017).
4. Bernsoccou, W. & H. & H. H. Reversible hydrogenation of carbon dioxide to formic acid and methanol: Lewis acid enhancement of base metal catalysts. *Acc. Chem. Res.* 50, 1049–1058 (2017).
5. Kattel, S., Liu, P. & Chen, J. G. Tuning selectivity of \( \text{CO}_2 \) hydrogenation reactions at the metal/ozone interface. *J. Am. Chem. Soc.* 139, 7973 (2017).
6. Berg, R. V. D. et al. Structure sensitivity of Cu and CuZn catalysts relevant to industrial methanol synthesis. *Nat. Commun.* 7, 13057 (2016).
7. Behrens, M. et al. The active site of methanol synthesis over Cu/ZnO/Al\(_2\)O\(_3\) industrial catalysts. *Science* 336, 893 (2012).
8. Arena, F. et al. Synthesis, characterization and activity pattern of Cu-ZnO/ \( \text{ZrO}_2 \) catalysts in the hydrogenation of carbon dioxide to methanol. *J. Catal.* 249, 185–194 (2007).
9. Guo, X., Mao, D., Lu, G., Wang, S. & Wu, G. Glycine-nitrate combustion synthesis of CuO/\( \text{ZnO}/\text{ZrO}_2 \) catalysts for methanol synthesis from \( \text{CO}_2 \) hydrogenation. *J. Catal.* 271, 178–185 (2010).
10. Arena, F. et al. Solid-state interactions, adsorption sites and functionality of Cu-ZnO/ \( \text{ZrO}_2 \) catalysts in the CO\(_2\) hydrogenation to CH\(_3\)OH. *Appl. Catal. A* 350, 16–23 (2008).
11. Guo, P. et al. Influence of Zr on the performance of Cu/Zn/Al/\( \text{Zr} \) catalysts via hydrothermal-like precursors for \( \text{CO}_2 \) hydrogenation to methanol. *J. Catal.* 298, 51–60 (2013).
12. Bonura, G., Cordaro, M., Cannilla, C., Arena, F. & Frusteri, F. Changing the nature of the active site of Cu-Zn-Zr catalysts for the \( \text{CO}_2 \) hydrogenation reaction to methanol. *Appl. Catal. B* 152-153, 152–161 (2014).
13. Phongamwong, T. et al. \( \text{CO}_2 \) hydrogenation to methanol over CuO/\( \text{ZnO}/\text{ZrO}_2 \)-SiO\(_2\) catalysts: Effects of SiO\(_2\) contents. *Chem. Eng. J.* 316, 692–703 (2017).
14. Witton, T. et al. Tuning of catalytic \( \text{CO}_2 \) hydrogenation by changing composition of CuO/\( \text{ZnO}/\text{ZrO}_2 \) catalysts. *Energy Convers. & Manag.* 118, 21–31 (2016).
15. Frei, E., Schaad, A., Ludwig, T., Hillebrecht, H. & Krossing, I. The influence of the precipitation/ageing temperature on a Cu/ZnO/\( \text{ZrO}_2 \) catalyst for methanol synthesis from \( \text{H}_2 \) and \( \text{CO}_2 \). *ChemCatChem* 6, 1721–1730 (2014).
16. Li, L., Mao, D., Yu, J. & Guo, X. Highly selective hydrogenation of \( \text{CO}_2 \) to methanol over CuO/\( \text{ZnO}/\text{ZrO}_2 \) catalysts prepared by a surfactant-assisted co-precipitation method. *J. Power Sources* 279, 394–404 (2015).
17. Dong, X. et al. \( \text{CO}_2 \) hydrogenation to methanol over CuO/\( \text{ZnO}/\text{ZrO}_2 \) catalysts prepared by precipitation-reduction method. *Appl. Catal. B* 191, 8–17 (2016).
18. Wang, W., Wang, S., Ma, X. & Gong, J. Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.* 40, 5703 (2011).
19. Kuld, S. et al. Quantifying the promotion of Cu catalysts by \( \text{ZnO} \) for methanol synthesis. *Science* 352, 969 (2016).
20. Arena, F. et al. Effects of oxide carriers on surface functionality and process performance of the Cu/ZnO system in the synthesis of methanol via \( \text{CO}_2 \) hydrogenation. *J. Catal.* 300, 141–151 (2013).
21. Grunwaldt, J. D., Molenbroek, A. M., Topsoe, N. E., Topsoe, H. & Clausen, B. S. In Situ Investigations of Structural Changes in Cu/ZnO Catalysts. *J. Catal.* 194, 452–460 (2000).
22. Valant, A. L. et al. The Cu-ZnO synergy in methanol synthesis from \( \text{CO}_2 \). Part I: origin of active site explained by experimental studies and a sphere
contact quantification model on Cu-ZnO mechanical mixtures. J. Catal. 324, 41–49 (2015).

23. Bu, L. et al. Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. Science 354, 1410 (2016).

24. Vesborg, P. C. K. et al. Transient behavior of Cu/ZnO-based methanol synthesis catalysts. J. Catal. 262, 65–72 (2009).

25. Meunier, F. C. Mixing copper nanoparticles and ZnO nanocrystals: a route towards understanding the hydrogenation of CO2 to methanol? Angew. Chem. Int. Ed. 50, 4033–4054 (2011).

26. Ro, I. et al. The role of the Cu-ZrO2 interfacial sites for ethanol conversion to ethyl acetate and methanol synthesis from CO2 and H2. ACS Catal. 6, 7040–7050 (2016).

27. Kattel, S., Yan, B. H., Yang, Y. X., Chen, J. G. & Liu, P. Optimizing binding energies of key intermediates for CO2 hydrogenation to methanol over oxide-supported copper. J. Am. Chem. Soc. 138, 12440–12450 (2016).

28. Lunkenbein, T., Schumann, J., Behrens, M. & Willinger, M. G. Formation of a ZnO overlayer in industrial Cu/ZnO/Al2O3 catalysts induced by strong metal-support interaction. Angew. Chem. Int. Ed. 54, 4544–4548 (2015).

29. Liao, F. et al. Electronic modulation of a copper/zinc oxide catalyst by a heterojunction for selective hydrogenation of carbon dioxide to methanol. Angew. Chem. Int. Ed. 51, 5832–5836 (2012).

30. Liao, F. et al. Morphology-dependent interactions of ZnO with Cu nanoparticles at the materials’ interface in selective hydrogenation of CO2 to CH4/HER. Angew. Chem. Int. Ed. 123, 2210–2213 (2015).

31. Galván, C. Á. et al. Reverse water-gas shift reaction at the Cu/ZnO interface: influence of the Cu/Zn ratio on structure-activity correlations. Appl. Catal. B 195, 104–111 (2016).

32. Wang, Y. H. et al. Structure–activity relationships of Cu-ZrO2 catalysts for CO2 hydrogenation to methanol: interaction effects and reaction mechanism. RSC Adv. 7, 8709–8717 (2017).

33. Fisher, I. A., Bell, A. T., Fisher, I. A. & Bell, A. T. In situ infrared study of methanol synthesis from H2/CO over Cu/SiO2 and Cu/ZrO2/SiO2. J. Catal. 172, 222–237 (1998).

34. Wang, J. et al. A highly selective and stable ZnO-ZrO2 solid solution catalyst for CO2 hydrogenation to methanol. Sci. Adv. 3, e1701290 (2017).

35. Yang, R., Zhang, Y., Iwama, Y. & Tsubaki, N. Mechanistic study of a new low-temperature methanol synthesis on Cu/MgO catalysts. Appl. Catal. A 288, 126–133 (2005).

36. Qi, S., Liu, C. W., Wei, P., Zhu, Q. M. & Deng, J. F. In situ IR studies on the mechanism of methanol synthesis over an ultrathin Cu/ZnO/Al2O3 catalyst. Appl. Catal. A 171, 301–308 (1998).

37. Sato, A. G. et al. Effect of the ZrO2 phase on the structure and behavior of supported Cu catalysts for ethanol conversion. J. Catal. 307, 1–17 (2013).

38. Du, H., Williams, C. T., Ebner, A. D. & Ritter, J. A. In situ FTIR spectroscopic analysis of carbonate transformations during adsorption and desorption of CO2 in K-promoted HTiK. Chem. Mater. 22, 3519–3526 (2010).

39. Karch, M. et al. Active sites on oxide surfaces: ZnO-catalyzed synthesis of methanol from CO and H2. Angew. Chem. Int. Ed. 44, 2790–2794 (2005).

40. Rhodes, M. D. & Bell, A. T. The effects of zirconia morphology on methanol synthesis from CO and H2 over Cu/ZrO2 catalysts: Part I. Steady-state studies. J. Catal. 233, 198–209 (2005).

41. Rhodes, M. D., Pokrovski, K. A. & Bell, A. T. The effects of zirconia morphology on methanol synthesis from CO and H2 over Cu/ZrO2 catalysts: Part II. Transient-response infrared studies. J. Catal. 233, 210–220 (2005).

42. Kurtz, M. et al. Active sites on oxide surfaces: ZnO-catalyzed synthesis of methanol from CO and H2. Angew. Chem. Int. Ed. 44, 2790–2794 (2005).

43. French, S. A. et al. From CO2 to methanol by hybrid QM/MM embedding. Angew. Chem. Int. Ed. 40, 4437–4440 (2001).

44. Yang, Y. X., White, M. G. & Liu, P. Theoretical study of methanol synthesis from CO2 hydrogenation on metal-doped Cu(111) surfaces. J. Phys. Chem. C. 116, 248–256 (2012).

45. Xie, S. H. et al. Au@3DOM CO2: highly active nanocatalysts for the oxidation of carbon monoxide and toluene. Nanoscale 5, 11207–11219 (2013).

46. Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. Phys. Rev. B 136, B864–B871 (1964).

47. Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. Phys. Rev. 140, A1133–A1138 (1965).

48. Kresse, G. & Furthmüller, J. Efficiency of ab initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comp. Mater. Sci. 6, 15–50 (1996).

49. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

50. Bloch, P. F. Projected augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).

51. Perdew, J. P. & Wang, Y. Accurate and simple analytic representation of the electron-gas correlation-energy. Phys. Rev. B 45, 13244–13249 (1992).

52. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B 13, 5188–5192 (1976).

53. Tang, Q. L. & Luo, Q. H. Adsorption of CO2 at ZnO: a surface structure effect from DFT+U calculations. J. Phys. Chem. C. 117, 22954–22966 (2013).

54. Dudaere, S. L., Bottom, G. A., Savrasov, S. Y., Humphreys, C. J. & Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA+U study. Phys. Rev. B 57, 1505–1509 (1998).

55. Henkelman, G., Uberuaga, B. P. & Jonsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 113, 9901–9904 (2000).

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Author contributions

Y.W. and W.G. performed the catalyst preparation, catalytic tests, and high-pressure in situ DRIFTS measurement. K.L. designed the catalysts and contributed to the characterizations. S.K. and P.L. conducted the DFT calculations and wrote part of the paper (calculation). H.W., J.G.C., and K.L. designed the study, analyzed the data, and co-wrote the paper. All the authors discussed the results.

Additional information

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